ORGANOPHOSPHORUS PESTICIDE AIR MONITORING PROJECT

FINAL REPORT

Submitted to

Dr. Cynthia Lopez

Washington State Department of Health Pesticide Program
P.O. Box 47846
Olympia, WA 98504-7846

Prepared by

Dr. Richard Fenske, Principal Investigator
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Kit Galvin, CIH, Project Supervisor
Maria Tchong, MPH, Research Industrial Hygienist
Maria Negrete, Field Investigator
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Box 357234
Seattle, WA 98195

Date

June 30, 2009

(Updated September 15, 2009)

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Finally, we wish to acknowledge the extraordinary effort invested in the sample analysis component of the project by Dr. Jianbo Yu and Dr. Russell Dills at the University of Washington's Environmental Health Laboratory.

TABLE OF CONTENTS

LIST OF APPENDICES

EXECUTIVE SUMMARY

Agricultural pesticide applications represent a potential health concern for those living in nearby communities, particularly for children. The Washington State House of Representatives added funds to the budget of the Washington Department of Health (DOH) for air monitoring studies. DOH contracted with the Department of Environmental and Occupational Health Sciences at the University of Washington (UW) to measure air concentrations of organophosphorus (OP) pesticides used in Washington agriculture during 2008. The purpose of the monitoring was to examine whether off-target movement of OP pesticides during and following pesticide applications posed a potential risk to residents or bystanders.

Air monitoring was conducted in two phases. Phase 1 took place in March-April 2008 to capture chlorpyrifos orchard applications. Sampling occurred in two regions: North Central and the Yakima Valley. Phase 2 took place in June-July 2008 to capture azinphos-methyl orchard applications. Sampling for this phase occurred in the Yakima Valley. Twenty-four hour (24-hr) samples were collected at three sites near orchards and at one site distant from orchards for approximately 28 days in each case. Samples were also collected around the perimeter of an orchard block before, during and following an airblast application in the North Central and Yakima Valley regions for Phase 1 and in the Yakima Valley region for Phase 2. Samples were analyzed by the UW Environmental Health Laboratory. Phase 1 samples were analyzed for chlorpyrifos and its oxygen analog. Phase 2 samples were analyzed for azinphos-methyl, its oxygen analog, phosmet, and malathion.

Most samples collected in this study had measurable amounts of either chlorpyrifos-oxon or azinphos-methyl-oxon. Previous studies in California have indicated that these oxygen analogs can be produced artificially by the sampling process. For example, a chlorpyrifos molecule captured in the air sampling tube can be converted to chlorpyrifos-oxon during the sampling period. In these cases, we combined the concentration of the parent compound with the concentration of its oxygen analog to produce a total pesticide concentration for each sample. These were considered the final measured values for the samples.

Measured air concentrations were compared to screening levels developed by the California Department of Pesticide Regulation and the U.S. Environmental Protection Agency. None of the concentrations in 24-hour samples collected in this study exceeded the California or EPA screening levels. The highest 24-hour chlorpyrifos measurement was 607 ng/m^3 as compared to an acute screening level of 1,200 ng/m^3. The highest 24-hour azinphos-methyl measurement was 356 ng/m^3 as compared to California's acute screening level of 101,000 ng/m^3 and EPA's screening level of 5,000 ng/m^3. The highest azinphos-methyl concentration measured in the study was 9,658 ng/m^3. This 8-hour measurement took place on the perimeter of the orchard block during active spraying. The screening levels used for this study are based on 24-hour exposures, so this 8-hour measurement cannot be compared directly to the screening levels. Also, public exposure is not anticipated at the perimeter of an orchard for extended periods, so this measurement was not considered to represent a health risk. Phosmet and malathion levels were very low (most less than 1 ng/m^3) in Phase 2 receptor and ambient monitoring, several orders of magnitude lower than their screening levels. Results for both of these chemicals are not provided in the main report, but are included in Appendix I. If the screening levels cited in this study are used as the basis for

risk assessment, it appears that agricultural spraying in these regions did not pose a health risk to residents or bystanders by the inhalation route.

The presence of substantial amounts of oxygen analogs in our samples led us to conduct both a laboratory study and a field study to determine the extent to which the oxygen analog of chlorpyrifos could be formed artificially during sampling. We did so because the oxygen analogs of OP pesticides are generally considered to be much more toxic than their parent compounds. Thus, even a small amount of chlorpyrifos-oxon in ambient air could change our evaluation of health risk. Our preliminary analysis of these studies suggests that some of the chlorpyrifos-oxon measured in our 2008 air samples was present in the air sampled, and therefore presents a risk greater than the sum of chlorpyrifos and its oxygen analog. We recommend that additional research be conducted to fully characterize potential formation of oxygen analogs of OP pesticides in the air where OP pesticides are commonly applied.

INTRODUCTION

Agricultural pesticide applications represent a potential health concern for those living in nearby communities, particularly for children. Much attention has focused on the organophosphorus (OP) pesticides (Eskenazi et al. 1999). The health risks of one of the OP pesticides monitored in this study – chlorpyrifos – have been discussed recently by the U.S. Environmental Protection Agency's Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) Scientific Advisory Panel (SAP 2008). The panel's response to a series of questions posed by U.S. EPA, as well as all supporting documents, can be found at the panel's website (http://www.epa.gov/scipoly/sap/index.htm). The health risks of another OP pesticide monitored in this study – azinphos-methyl – have been discussed by the U.S. EPA in its Registration Eligibility Document (USEPA 2009a). This report presents the results of air monitoring conducted in Washington State in 2008 to characterize the potential non-occupational health risks of pesticide drift due to OP pesticides use in agriculture.
The U.S. EPA defines pesticide spray drift as follows (USEPA 2009b):

> The physical movement of a pesticide through air at the time of application or soon thereafter, to any site other than that intended for application (often referred to as off target). EPA does not include in its definition the movement of pesticides to off-target sites caused by erosion, migration, volatility, or contaminated soil particles that are windblown after application, unless specifically addressed on a pesticide product label with respect to drift-control requirements.

While this definition is appropriate as a basis for pesticide drift regulation, a broader definition that includes the movement of pesticides to off-target sites after application is more useful from a public health perspective. That is, the public's exposure to pesticides can be due to both primary pesticide drift (drift at the time of application or soon thereafter) and secondary drift (drift post-application). A number of studies have evaluated secondary drift from agricultural pesticide applications (Majewski et al. 1998; Carlsen et al. 2006). Drift due to volatilization is dependent on such factors as climatic conditions, which include temperature, plant surface and soil properties, and pesticide-specific physicochemical properties, which include vapor pressure (Mass et al. 1988; Leistra et al. 2006). Because of the high mobility of the resulting vapors and very small particles, pesticides have the potential to travel substantial distances (USGS 1995) and also disperse as they spread over a greater area than primary pesticide spray drift (RCEP 2005).

Several studies conducted outside Washington State have documented that agricultural pesticides are present in the ambient air of communities (USGS 1995; Baker et al. 1996; Majewski et al. 1998). Lee et al. (2002) conducted a probabilistic exposure assessment of the cancer and non-cancer effects of inhaling ambient air pesticide concentrations measured by the California Air Resources Board (CARB) between 1986 and 2000, and found that fumigants presented the highest inhalation risks, that risks to children were consistently higher than those to adults because of such factors as a higher inhalation rate to body weight ratio in children, and that pesticide vapor pressure was highly correlated with measures of ambient air concentration and risk. Leistra et al. (2006) estimated the extent of volatilization of two pesticides applied to a potato crop, and found that chlorpyrifos volatilization fluxes were higher than those for fenpropimorph and that the decline of chlorpyrifos following treatment of potato leaf surfaces was dominated by the volatilization process.

Illnesses due to OP pesticide drift in Washington State were first reported in 1965 (Quinby and Doornink 1965). Studies in Washington State over the past two decades have shown that residential proximity to pesticide-treated agricultural areas can increase the likelihood of exposure to pesticides (Simcox et al. 1995; Lowenherz et al. 1997; Lu et al 2000; Fenske et al 2002). Koch et al. (2002) found that OP pesticide metabolite levels in the urine of children from a Washington agricultural community rose coincident with agricultural pesticide spraying, and subsequently decreased as applications ended. Relevant exposure pathways could not be verified based upon the data collected, but the authors surmised that the children were exposed to pesticides directly via inhalation and/or indirectly via dermal contact with surfaces upon which the chemicals had settled. Weppner et al. (2006) also found elevated OP pesticide metabolite levels in children in a Washington agricultural community adjacent to agricultural fields both during and following pesticide spray events. Ramaprasad et al. (2004) used the data from this study to compare measured ambient air pesticide concentrations with fugitive dust gaussian dispersion model predictions for volatilization of pesticides from plant surfaces, and found that model estimates were correlated with field measurements. In addition, a fugitive dust model for estimating pesticide deposition indicated that pesticide drift would occur within the nearby community despite compliance with application guidelines for minimizing spray drift (Tsai et al. 2005). However, a recent analysis of these data indicated that potential risks from inhalation exposure for nearby residents were very low (Ramaprasad et al. 2008). Similarly, a study of ambient OP pesticide levels in the North Central region of Washington during the summer of 2007 found very low concentrations (Tolbert 2008).

At a hearing on January 11, 2007, the Select Committee on Environmental Health of the Washington State House of Representatives heard testimony regarding pesticide air monitoring. The House of Representatives subsequently added funds to the budget of the Washington State Department of Health (DOH) for two air monitoring projects, one to be focused on fumigants and one to be focused on the OP pesticides. DOH contracted with the University of Washington (UW) in December 2007 to measure air concentrations of OP pesticides used in Washington agriculture during the 2008 growing season. The purpose of the monitoring was to examine whether off-target movement of OP pesticides during and following pesticide applications posed a potential risk to residents or bystanders.

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METHODS

FIELD SAMPLING

Sampling Plan

UW developed a preliminary sampling plan in January 2008 (see Appendix A). The DOH Technical Review Panel (TRP) reviewed the sampling plan and called for a redesign of the community sampling component. The TRP recommended collection of 24-hr air samples every other day at multiple locations in agricultural communities for 28 days (referred here as "receptor" and "ambient" samples). The TRP recommendation for monitoring specific spray events was similar to the original UW sample plan: collection of samples around application sites before, during, and following a spray event, over a four-day period (referred to here as "perimeter" samples). Specifically, the TRP recommended that (a) four 24-hr samples be collected around an application site the day prior to application; (b) eight samples ringing the application site be collected at 8-hr intervals on the application day; and (c) samples continue to be collected at these eight locations for an additional two days. The UW study design and sample plan were revised in March 2008 to address the TRP recommendations (see Appendix A).

Selection of Regions for Air Sampling. Study regions within Washington State were selected based on the density of crops with typical OP pesticide use and the proximity of these crops to urban (residential) areas. Based on the 2005 and 2006 National Agricultural Statistical Survey (USDA 2005; 2006), tree fruit and potatoes were determined to be the crops with the most total pounds of OP pesticide use in Washington State agriculture. The survey also determined that chlorpyrifos and azinphos-methyl were the top two pesticides used based on total pounds and that these pesticides were predominately used on apples and other tree fruit.

Regions with the greatest density of these crops were identified using crop field-density maps provided by the Washington State Department of Agriculture (WSDA). Appendix B contains maps of estimated pesticide usage by census tract for the two compounds of primary interest in this study, chlorpyrifos, and azinphos-methyl. These maps were derived from 2005 National Agricultural Statistical Service data, U.S. census data, and WSDA crop maps. Three regions were identified: North Central District, Yakima Valley, and Columbia Basin. The North Central District and Yakima Valley were selected as the two study regions because of crop density and proximity to urban populations and residential areas.

Selection of Air Sampling Sites. Receptor and ambient sampling sites were identified through local cooperators in the North Central district and the Yakima Valley. Sites were then evaluated according to the criteria established for the study. The receptor site criteria were as follows: (a) within 100 meters from orchards likely to be treated with OP pesticides; (b) secured, fenced or locked; (c) daily access for staff; (d) low foot traffic; and (e) adequate sampling station distance from buildings, walls, or solid fences. The ambient sites followed the same site selection criteria as the receptor except for distance, as this site was required to be at least 500 meters from orchards.

Sampling Procedures

All air samples were collected with OSHA Versatile Sampler (OVS) tubes, containing two sections of XAD-2 sorbent material. The sampling train included a quartz filter to trap aerosols and a two-section (270/140 mg) XAD-2 sorbent to adsorb vapors. Flow rates for receptor and ambient samples were approximately 2 liters per minute. Flow rates for perimeter samples were approximately 6 liters per minute. The actual flow rate was calculated separately for each sample. Details related to the air monitoring are provided in Appendix B. Air sampling standard operating procedures are provided in Appendix C.

Phase 1. Phase 1 of the study took place in early spring, and focused on chlorpyrifos during airblast applications. Sampling took place in the North Central district from March 24 through May 3 (Region 1) and in the Yakima Valley from March 7 through April 11 (Region 2). Sample collection was conducted consistent with the revised sampling plan. In each region, staff collected samples at three receptor sites and one ambient site. At one of the receptor sites in each region, staff collected a co-located quality control air sample. Staff also carried out 4-day sampling on the perimeter of an orchard block before, during, and after an application event in each region.

Receptor/ambient sampling in the North Central region began on March 24 based on advice from local cooperators. However, the last week of March and the first week of April were unusually cold and included snowfall, so spraying was delayed. Staff therefore extended sampling for an additional 13 days (total sampling period of 41 days) to ensure that sampling occurred for 28 days when applications took place in this region. Receptor/ambient sampling in the Yakima Valley was carried out over a time period that was selected to include the peak application period for the region, according to our local cooperators.

Phase 2. Phase 2 of the study took place in the late spring and early summer and focused on airblast applications of OP pesticides for control of codling moths. Sampling was limited to one region (Yakima Valley). We collected receptor/ambient samples every third day rather than every other day, as spraying was estimated to take place over 60 days. Staff extended the sampling period for Phase 2 ambient/receptor samples to 70 days (May 21 – July 29) to ensure maximum coverage of the azinphos methyl applications. One 4-day perimeter sampling study conducted was consistent with the final sampling plan.

Selection of Samples for Analysis

For receptor and ambient samples, samples were analyzed from every other day for a 28-day period, as requested by the TRP (14 samples per site). For Phase 2 we analyzed samples from every third day (the sample collection interval) for a 60-day period (at least 20 samples per site).

For perimeter samples, one sample from each sampling location for each sampling period was analyzed. For the pre-spray day, samples from 4 locations plus the co-located QC sample for a single 24-hr period were analyzed. For the spray day, samples from 8 locations plus the co-located QC for three 8-hr time periods were analyzed. For the first day after spraying samples from 8 locations plus the co-located QC sample for two 12-hr time periods were analyzed. For the second day after spraying, samples from 8 locations plus the co-located QC sample for a single 24-hr period were analyzed.

All sampling sites or locations had a primary and a back-up sample. If the primary sample was lost due to pump failure, then its back-up sample was analyzed. However, if both the primary and back-up samples were lost, then the primary sample of a neighboring day was used for analysis.

Appendix B presents in detail the number of samples that were to be collected under the revised sampling plan, the number of primary samples collected by UW, the number of back-up samples collected, the number of samples analyzed, and the samples analyzed as a percent of the total number of samples.

DESCRIPTION OF FIELD SITES

The locations of the receptor and ambient monitoring stations were geo-coded using hand-held global positioning system instruments with data logging capacity (GPS-PAL, Enertech Consultants, Campbell, CA). Data were post-processed using GPS post-processing software (Version 2.0) provided with the instruments to ensure accuracy. The final measurement was determined to have at least 3-meter resolution. The distances to the closest buildings and fields were calculated using the geo-coded receptor or ambient monitoring station locations and high-resolution aerial photography in ESRI ArcGIS software (ESRI, Redlands, CA, Version 9.3). A map and layout for each field site is provided in Appendix B. Each site is described briefly below.

North Central Receptor and Ambient Sites (Phase 1)

The sampling for this region took place over 41 consecutive days starting on March 24, 2008. Only samples for the last 31 days were analyzed because there was snow off and on during the first two weeks. The sampling period was 24 hours with the exception of one sampling period that was 48 hours. Every receptor site was in close proximity to conventional apple orchards. All sites had access to outdoor AC power. The temperature during the Phase 1 sampling period was generally cold. The conditions ranged from dry to wet except for two days in late March when it snowed.

Ambient. There were no orchards within 1000 meters (3281 feet) of this site. The nearest building was located 85 meters (279 feet) away.

Receptor 1. This site was bordered by orchards on two sides. The south orchard was 17 meters (56 feet) away from the sampling station while the east orchard was 332 meters (1089 feet) away. The nearest building was located at 5 meters (16 feet).

Receptor 2. This site was bordered by apple orchards on all four sides. The sampling station was located at the corner of the site. From the sampling station, both the north and west orchard were 3 meters (9 feet) away, the south orchard was at 25 meters (82 feet), and the east orchard was at 431 meters (1414 feet). The nearest building was 90 meters (295 ft) away from the sampling station.

Receptor 3. This site served as a receptor site and a quality control site. It was bordered by orchards on all sides. From the sampling station, the north orchard was located 84 meters (276 feet), the south orchard was 38 meters (125 feet), the west orchard was 44 meters (144 feet), and the east orchard was 4 meters (13 feet) away. The quality control sampling station was located less than one meter from the receptor sampling station. The nearest building was located at 30 meters (98 feet).

Yakima Valley Receptor and Ambient Sites (Phase 1)

All sites were sampled over at least 28 days; however, not all sites started and stopped on the same day. One site had to be relocated after sampling had started at the other sites. The sampling for all of these sites took place starting on March 7, 2008 and ended on April 11, 2008. The sampling period was 24 hours with the exception of one sampling period that was 48 hours. All receptor sites were near conventional apple orchards. The weather temperature in this region was generally cold, but no snow was present during the sampling period.

Ambient. The nearest orchard was located more than 1000 meters (3281 feet) away from this site. The closest building was 100 meters (328 feet) away from the sampling station. This site operated for 37 consecutive days.

Receptor 1. This site was bordered by two orchard blocks. The south orchard was at 56 meters (184 feet) and the west orchard was at 99 meters (325 feet). The nearest building was 30 meters (98 feet). This site operated for 28 days.

Receptor 2. This site served as a receptor and quality control site. It was bordered by orchards on all sides. The north orchard was 22 meters (72 feet) away and the west orchard was 182 meters (597 feet) away. The nearest building to this site was located 28 meters (92 feet) away. The QC sampling station was located less than one meter from the receptor sampling station. Samples were collected for 31 consecutive days.

Receptor 3. This site was bordered by orchard blocks on three sides. From the sampling station, the north orchard was at 22 meters (72 feet), the south orchard was at 349 meters (1145 feet), and the west orchard was at 248 meters (813 feet). The nearest building to this site was located 8 meters (26 feet) away. This site had the latest start date but still operated for 28 consecutive days. Sampling began late at this site because it replaced a previously selected site that became unavailable just prior to the initiation of sampling.

Yakima Valley Receptor and Ambient Sites (Phase 2)

Phase 2 of the study took place in late spring and focused on azinphos-methyl airblast applications for the control of codling moths. Since azinphos-methyl spraying was estimated to take place over 60 days, staff collected the receptor/ambient samples every third day rather than every other day. The sampling was conducted in one region, the Yakima Valley, from May 21- July 29, 2008.

Ambient. This site was the same site as the ambient site in Phase 1 (Region 2). There were 23 sampling days for this site. The nearest orchard was located more than 1000 meters (3281 feet) away from this site. The closest building was 100 meters (328 feet) away from the sampling station.

Receptor 2. This site was the same site as the Receptor 2 site in Phase 1 (Region 2). In Phase 2 it served as a receptor and quality control site. The site was bordered by orchards on two sides. From the sampling station, the north orchard was 22 meters (72 feet) and the west orchard was 182 meters (597 feet) away. The nearest building to this site was located 28 meters (92 feet) away. The QC sampling station was located less than one meter from the receptor sampling station.

Receptor 4. This site was a new site identified for Phase 2. The site was bordered by orchards on all sides. From the sampling station, the north orchard was 75 meters (246 feet) away, west orchard was 13 meters (43 feet), south orchard was 43 meters (141 feet), and the east orchard was 92 meters (302 feet) away. The nearest building to this site was located 16 meters (53 feet) away.

Receptor 5. This was a new site identified for Phase 2. The site was bordered by orchards on three sides. From the sampling station, the north orchard was 52 meters (171 feet) away, and both the west and east orchard were 16 meters (53 feet) away from the sampling station. The nearest building to this site was located 95 meters (312 feet) away.

North Central Perimeter Site (Phase 1)

The region 1 site was a young vertical trellis apple orchard, situated amongst similar orchards. The study block was a 16,245 m^2 (4.02 acre) rectangular section at the end of a larger block. It had a perimeter of 614 m (2,014 ft) with rows spaced at 4.26 m (14 ft) apart and trees within rows 1.52 m (5 ft) apart. The study block was bordered by orchards, roads, a staging area, and a reservoir. Sampling stations were located 7.62 m (25 ft) out from the perimeter of the block (outside row of trees). This distance was selected because sampling stations 1, 2, 5, and 6 needed to be across access roads. We decided to place all sampling stations at the same distance from the block perimeter. Sampling took place over five days, beginning on April 6, 2008 and ending on April 10, 2008. The airblast application using an Accutech sprayer occurred between 8:40 and 9:37 am. The commercial product Govern 4E (EPA Registration No 62719-220-55467), with chlorpyrifos as the active ingredient was applied at a rate of 0.75 pints product per acre. A total of 1.5 pounds of the active ingredient chlorpyrifos was applied. The grower reported no use of chlorpyrifos in the surrounding area before or during the study period.

Yakima Valley Perimeter Site (Phase 1 and Phase 2)

This site was used for perimeter sampling in both Phase 1 and Phase 2. It was a mature traditional apple orchard situated near a mix of tree fruit blocks including apple, pear, and cherry. The north, east, and west sides were bordered by an orchard road that separated the block from other orchards. To the south, an irrigation ditch separated the block from orchards owned by a different grower. The study block was a 20,315 m^2 (5.02 acre) kidney-shaped block. There were 63 rows running east/west, and 13 rows running north/south. The rows were approximately 18 ft (5.5 m) apart. Sampling stations were located 6.01 m (20 ft) out from the perimeter of the block (outside row of trees).

For Phase 1, sampling took place over six days, as weather delayed the pesticide application one day after the background samples had been collected. Sampling began on March 31 and ended on April 5. The airblast application using a Rears sprayer took place between 2:00 and 4:30 pm on April 2, 2008. The commercial product Yuma 4E (EPA Registration No 62719-220-1381), with chlorpyrifos as the active ingredient, was applied at a rate of 2 quarts of product per acre. A total of 10 pounds of chlorpyrifos was applied.

For Phase 2, sampling took place over four days (June 19-22). During the pre-spray day sampling, airblast spraying was observed at the neighboring orchard located directly across from one of the sampling stations. The neighboring spray occurred when the sampling stations were being set-up. We were not able to confirm what was used during the spray. Azinphos-methyl spraying was delayed until the late afternoon/early evening of the spray day due to farm personnel issues, so only two sampling periods occurred instead of the three originally planned. The afternoon sampling period started at approximately 6:00 pm and the night sampling period started at approximately 1:00 am. The airblast application took place between 8:00 and 10:00 pm. Halfway through the application there was one break due to mechanical problems. The application resumed after switching to a different sprayer. The commercial product Azinphos-methyl (EPA Registration No 67545-AZ-001) was applied at a rate of 2 pounds product per acre. A total of 5 pounds active ingredient was applied.

LABORATORY ANALYSIS

Target Analytes

UW selected chlorpyrifos for analysis in Phase 1 and azinphos-methyl, phosmet, and malathion in Phase 2. The oxygen analogs of chlorpyrifos and azinphos-methyl were later added to the list of analytes.

NIOSH Method 5600

The initial analytical plan was based on use of NIOSH Method 5600 (GC-MS) for analysis of OP pesticides (NIOSH 1994). The UW laboratory had used this method successfully to analyze low levels of chlorpyrifos, azinphos-methyl, phosmet, and malathion in 2007. However, this earlier study did not include analysis of the oxygen analogs of the OP pesticides (Tolbert 2008).

For chlorpyrifos-oxon, initial validation studies with a limited number of spiked samples showed a relatively high limit of quantification (LOQ = 100 ppb) and a high standard deviation. However, the average recovery was within the analytical goal for accuracy, and the relative standard deviation was about 20%, the upper limit of our analytical goal for precision. A principal difficulty in the analysis of chlorpyrifos-oxon was the lack of a suitable internal standard. Given the time-sensitive nature of this project, UW proceeded with analysis of Phase 1 samples in the summer of 2008.

The UW laboratory found highly variable chlorpyrifos-oxon recoveries across sample batches (40-200%) and sample extracts run in duplicate showed variability of greater than 20%, concluded that the chlorpyrifos-oxon values produced with this method were not reliable, and discontinued analysis with the GC-MS method.

Liquid Chromatography Method

The UW laboratory then turned to a liquid chromatography method. The extraction method used was adapted from NIOSH Method 5600, with substitution of a solvent compatible with aqueous chromatography (acetonitrile was used instead of toluene/acetone). Instrumental analysis was based on published liquid chromatography/mass spectrometry (LC-MS-MS) methods (Sancho et al. 2004; Agilent 2008). This method used a stable isotope internal standard for both chlorpyrifos and chlorpyrifos-oxon, and later for azinphos-methyl, azinphos-methyl-oxon, phosmet, and malathion. A complete description of the method and its performance for this project is provided in Appendix D.

Table 1 presents the quality control results for this method. Method validation consisted of samples at three fortification levels (nanograms): 5 ng/sample, 50 ng/sample, and 1000 ng/sample. Four replicate samples were run at each level. The limits of detection, limits of quantification, mean percent recoveries, and coefficients of variation are presented in Table 2 below. The R-squared value for all calibration curves was >0.999.

The XAD-2 tubes contain two sections, permitting a quality control check on potential breakthrough. This meant that each sample required two separate analyses. NIOSH Method 5600 procedures were followed to determine potential breakthrough: i.e., if the back portion of the tube contains 10% or more of the analyte that is contained in the front portion, then breakthrough has occurred. One sample met this criterion, and in this case sorbent loss from

the front portion of the tube was noted, so the back-up sample was analyzed. Reported analyte values are the front/back mass sum for each tube. Additional details are provided in the Results section of this report.

Table 1. Quality control results for the EH Laboratory LC-MS-MS method

Fortification level	Limit of detection[a,b,c]		Limit of quantification[a,b,c]		Mean Recovery	Coefficient of variation
	(ng/sample)	(ng/m^3)	(ng/sample)	(ng/m^3)	(%)	(%)
Chlorpyrifos	1	0.35	2	0.69		
5 ng					94.6	5.2
50 ng					92.3	2.1
1000 ng					86.1	3.4
Chlorpyrifos-oxon	1	0.35	2	0.69		
5 ng					97.6	3.3
50 ng					93.9	3.6
1000 ng					85.8	7.7
Azinphos methyl	0.5	0.17	1.8	0.62		
5 ng					109	4.8
50 ng					103	1.9
1000 ng					89.7	1.6
Azinphos methyl-oxon	0.5	0.17	1.5	0.52		
5 ng					111	2.0
50 ng					104	3.0
1000 ng					94.7	1.5
Phosmet	0.5	0.17	1.5	0.52		
5 ng					111	2.1
50 ng					105	3.1
1000 ng					91.0	1.6
Malathion	0.4	0.14	1.2	0.42		
5 ng					122	2.2
50 ng					114	2.8
1000 ng					99.1	3.0

a -- The limit of detection (LOD) and the limit of quantification (LOQ) were determined as follows: a series of spiked samples at or near the LOD were analyzed, and the standard deviation calculated; the LOD was defined as three times this standard deviation; the LOQ was defined as ten times this standard deviation.

b -- Nanograms per sample (ng/sample) LOD and LOQ values were reported by the EH Laboratory

c -- Nanograms per cubic meter of air (ng/m^3) LOD and LOQ values were calculated based on the air volume resulting from the protocol for the receptor and ambient sampling: 2 L/min * 1 m3/1000 L * 60 min/hr * 24 hr/sample = 2.88 m^3. LOD and LOQ air concentrations varied for each sample based on specific air volume sampled.

Quality Control Samples

The final sampling plan included collection of quality control (QC) samples through co-location of an additional sampler at one of the receptor sites, and co-location of an additional sampler at one of the sampling locations at the perimeter site. In addition, blank and spiked sampling tubes (trip spikes) were taken into the field and treated in a similar manner to samples collected in the field with regard to handling, storage, and shipment, but no air was drawn through the field blank or trip spike samples. This QC approach did not include fortified field spikes, as defined by the California Department of Pesticide Regulation in several of its air monitoring studies; i.e., an air sampling tube is spiked with a pesticide and then attached to an air sampling pump for a period equivalent to the sampling period. We addressed this issue in subsequent laboratory and field studies, as discussed below.

Approximately 10% of blank samples and 10% of spiked samples were submitted for analysis for each component of the study. If results from these blank and spiked samples did not conform to QC expectations, then additional spikes and blanks were analyzed.

Additional Field Quality Control Samples

The final UW sampling plan had two important additional quality control features. First, 24-hr air samples were collected every day rather than every other day at receptor/ambient sites, since our field team would need to visit each sampling site every day to begin and end a sampling session, which was not cost-effective. Second, a back-up sample was collected at each sampling location in case of sample loss in the field (e.g., pump failure) or in the laboratory (e.g., broken sample tube). Additional information regarding field quality control samples is provided in Appendix E.

Storage Stability Samples

Sample tubes were spiked with known amounts of our analytes at the time of field sampling and placed in the freezer at the UW Environmental Health Laboratory. The original analytical plan did not include chlorpyrifos-oxon, so staff generated an additional set of storage stability samples in November 2008 that included both chlorpyrifos and its oxon. Additional information regarding storage stability is provided in Appendix F.

Inter-Laboratory Comparison Sub-Study

At the request of DOH, we developed an inter-laboratory comparison study with the California Department of Pesticide Regulation laboratory to test our laboratory's liquid chromatography with the more traditional gas chromatography method recommended in NIOSH Method 5600. UW sent CDPR a set of spiked OVS tubes and a set of sample extracts, while retaining duplicates, and both laboratories analyzed the samples in parallel. Details of this study are provided in the Results section and in Appendix G.

Potential Chlorpyrifos-oxon Generation Sub-Study

UW also conducted a laboratory study and a field study to determine if chlorpyrifos could be transformed to chlorpyrifos-oxon in the OVS tubes during air sampling. In both studies, air was drawn for 24 hours through OVS tubes that had been spiked with chlorpyrifos, and

samples were analyzed for both chlorpyrifos and chlorpyrifos-oxon. Details of this study are provided in the Results section and in Appendix H.

METEOROLOGICAL DATA COLLECTION

Meteorological data were collected from two sources. For the receptor/ambient monitoring sites, data were drawn from seven Washington State Agricultural Weather Network stations (Network Version 2.0: AgWeatherNet). Data for each receptor and ambient site were taken from the nearest AgWeatherNet station. For the perimeter studies, a temporary meteorological station was set up adjacent to the site for the duration of the air monitoring.

Washington State Agricultural Network

The meteorological data were obtained online through *The Washington Agricultural Weather Network Version 2.0: AgWeatherNet* at http://weather.wsu.edu/. AgWeatherNet provides current and historical meteorological data from a number of observation points within Washington State, with the majority of observation points east of the Cascades. From this network we downloaded data for air temperature precipitation, wind speed, and wind direction every 15 minutes at seven locations, covering both Phase 1 and 2 and Region 1 and Region 2. Precipitation data were the 24-hr total accumulation for each sample period at each location.

Perimeter Study On-Site Meteorological Station

UW staff set up a meteorological station at each perimeter site for the duration of sampling. The station was located in proximity to the treated block and in an open area away from trees, at a distance that avoided having the instruments come into contact with the application spray. The station was set up and run prior to the pre-spray sampling day and taken down at the end of the post-spray day 2. The meteorological station used at the perimeter sites was purchased from Campbell Scientific Instrumentation (Logan, Utah). Instruments were mounted on a 10-meter mast (Force-12 Inc, Bridgeport, TX). The instruments and mounting heights were as follows: Vaisala HMP45AC Temperature and Relative Humidity probe (2.0 m); Campbell Temperature 109 Sensor (10.0 m); Met One 034b Wind Cup Anemometer (3.0 m); RM Young 81000V Ultrasonic Anemometer (10.5 m); Campbell Scientific CR1000 Datalogger. All data except for the ultrasonic anemometer were collected at 1-minute intervals. The Ultrasonic anemometer was 2-hertz data during the spray event, and 10-second data outside of the spray times. Data were downloaded daily during the study period.

<><><><>

RESULTS

CALIFORNIA SCREENING LEVELS FOR AIRBORNE PESTICIDES

The Technical Review Panel for this project recommended that air concentrations be compared with screening levels developed by the California Department of Pesticide Regulation and the U.S. Environmental Protection Agency (CDPR 2006). Two types of screening levels were used in this project: acute and subchronic.

Derivation of Screening Levels

The method for deriving these screening levels was as follows:

> The screening levels are based on identified critical toxicology values or exposure levels taken from existing documents that have already been subject to peer review . . . Acute toxicity can be defined as the toxicity manifested within a relatively short time interval, generally not longer than one day. In this document, unless specifically noted, acute screening levels are for 24 hours. Subchronic toxicity can be defined as the toxicity manifested within a more extended interval, but not one that constitutes a significant portion of the lifespan of the species in question. In subchronic toxicity testing using mammalian species, the period of exposure is generally 30 to 90 days (CDPR 2006)
>
> The Reference Concentration (RfC) . . . is an estimate of the daily air concentration of a chemical that is likely to be without adverse effects to the exposed human population. . . . Children have the highest inhalation rate relative to body weight; therefore, they would inhale the highest amount of airborne material relative to their body weight. Since the screening levels are being used to evaluate ambient air levels, it is appropriate that health protective values are used, and the screening levels will be based on children less than one year of age. Unless otherwise stated, this document uses a default inhalation rate for a child less than one year of age of 4.5 m^3/day [cubic meters per day] and a default body weight of 7.6 kg [kilograms] (CDPR 2006).

Since most toxicology data are generated from rodent studies, CDPR uses a factor of 1.6 to convert from rodent to human inhalation (rodent inhalation rate * 1.6 = human equivalent). If an inhalation study in rodents is not available, then CDPR uses the oral Reference Dose (RfD) with the following equation:

RfC (or screening level) = RfD * body weight/inhalation rate

The acute and subchronic screening levels for chlorpyrifos are based on a subchronic rat inhalation study, resulting in an acute screening level of 1,200 ng/m^3 and a subchronic screening level of 850 ng/m^3. These values are consistent with those used by U.S. EPA.

In the case of azinphos-methyl, the method used to determine the Reference Concentration differed between U.S. EPA and CDPR. U.S EPA relied on a 90-day rat inhalation study, producing an acute screening level of 5,000 ng/m^3 and a subchronic screening level of 3,500 ng/m^3. CDPR chose to base its calculation on a 28-day human dosing study, producing an acute screening level of 101,000 ng/m^3 and a subchronic screening level of 11,000 ng/m^3. The use of the human dosing study removed a 10-fold uncertainty factor from the calculation of the Reference Dose, thereby raising the azinphos-methyl screening level. The intentional human dosing study used by CDPR was rejected by the U.S. EPA Human Studies Review Board in 2006, so U.S. EPA is prohibited from using the study as a basis for regulations (USEPA 2006).

Screening Levels for Oxygen Analogs of OP Pesticides

Most samples collected in this study had measurable amounts of either chlorpyrifos-oxon or azinphos-methyl-oxon. It seems likely that a significant fraction of the oxygen analogs found in our samples were an artifact of sampling; that is, the parent OP pesticide was transformed to its oxygen analog in the sampling tube as air was drawn through the tube during the sampling period. However, it appears that for at least some of our samples, oxygen analogs were present as air contaminants distinct from the parent compounds. This issue is explored further in the Results section.

Regulatory agencies currently provide no guidance regarding appropriate screening levels for oxygen analogs in air, or they provide screening levels identical to the parent compounds, despite the fact that most toxicology texts indicate that the oxygen analogs of OP pesticides are more toxic than their parent compounds (Ecobichon 1996; Chambers et al. 2001).

In this report, the measured air concentrations of both the parent compound and its oxygen analog are presented. These are then combined by transforming the concentration of the oxygen analog to its equivalent parent compound concentration using the molar ratio of the two compounds. In this report, this sum is referred to as “chlorpyrifos total” or ”azinphos-methyl total”. It is these “total” values that are compared to the relevant screening levels. To the extent that the oxygen analog measured in a sample was an actual air contaminant, the toxic potential of that sample will be underestimated by this approach.

Complete air monitoring results are provided in Appendix I. Reports from the UW Environmental Health Laboratory are provided in Appendix J.

Phase 1: Receptor and Ambient Sampling Results

Data for receptor and ambient sampling in Phase 1 are presented in Table 2. The highest chlorpyrifos total air concentration measured at receptor and ambient sites was 607 ng/m^3, approximately one-half the acute screening level of 1,200 ng/m^3. The highest 28-day average was 59 ng/m^3, substantially lower than the sub-chronic screening level of 850 ng/m^3.

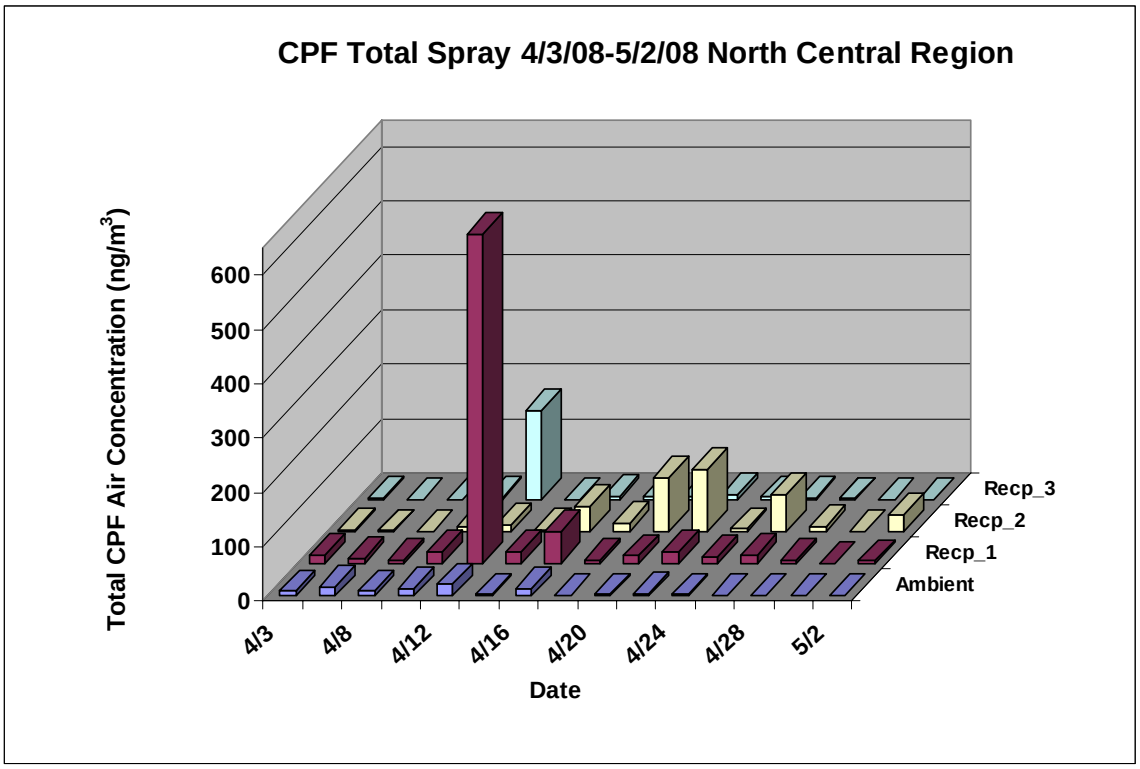
These data are also provided as time-series graphs for both the North Central and Yakima Valley regions (Figure 1). In the North Central region (upper graph), sampling on April 12 captured the peak concentration from receptor sites 1 and 3, whereas the peak concentration occurred later in the month at the receptor 2 site. In the Yakima Valley region (lower graph), peak concentrations were measured at the end of March and in early April. These findings are consistent with differences in the time bloom occurs across these regions.

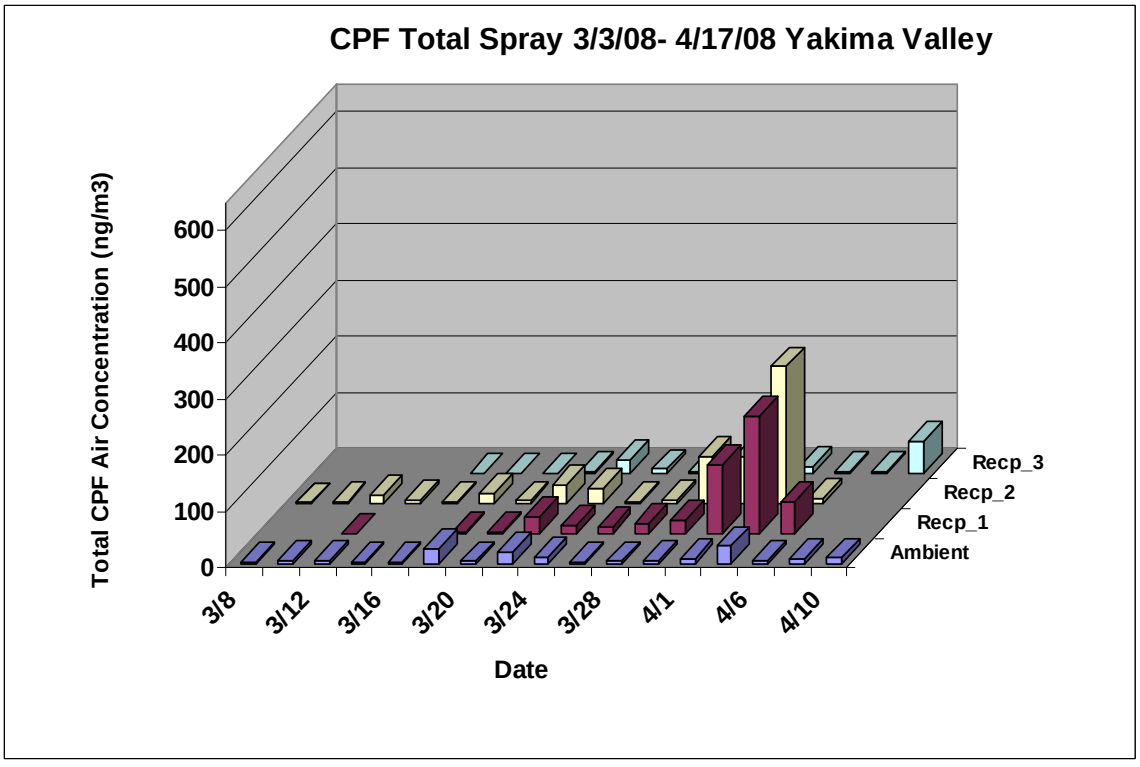
Table 2. Phase 1 receptor and ambient (community) chlorpyrifos, chlorpyrifos-oxon (CPF-oxon), and chlorpyrifos total (CPF total) air concentrations (ng/m^3). Values presented in the left three columns are the maximum concentrations measured in a 24-hr period at each site. These are compared to the CDPR acute screening level (ASL, 1,200 ng/m^3). Values presented in right three columns are the average concentrations over 28 days at each site. These are compared to the CDPR sub-chronic screening level (SCSL, 850 ng/m^3).[1]

	Average Temp. (Celsius) [2]	CDPR Acute = 1,200 ng/m^3 24-hr Maximum concentration			CDPR Sub-chronic = 850 ng/m^3 28-day Average concentration		
		Chlorpyrifos	CPF-oxon	CPF total[3]	Chlorpyrifos	CPF-oxon	CPF total[3]
North Central							
Receptor 1	10.0	493.9	107.7	606.8	47.3	11.2	59.1
Receptor 2	10.0	102.9	11.3	114.7	22.5	7.3	30.2
Receptor 3	9.3	128.5	33.6	163.7	10.9	4.1	15.2
QC (at receptor 3)	9.3	9.1	2.7	11.9	2.9	1.7	4.7
Ambient	10.3	15.8	5.0	21.1	4.7	2.4	7.2
Yakima Valley							
Receptor 1	10.9	186.5	20.7	208.2	37.9	6.2	44.3
Receptor 2	11.5	222.4	19.9	243.2	37.6	3.5	41.2
Receptor 3	11.5	45.3	10.4	56.2	7.2	3.1	10.5
QC (at receptor 2)	11.5	190.6	26.1	218.0	33.2	4.2	37.6
Ambient	11.6	19.9	9.9	30.2	5.6	3.6	9.3

1. Air concentration values have not been adjusted for possible losses during field sampling, storage, or laboratory analysis. See the following section on Quality Control for details.
2. Average ambient temperature for the entire sampling period at each site.
3. CPF-total was calculated by adding the chlorpyrifos air concentration to the CPF-oxon chlorpyrifos concentration equivalent (CPF-oxon * CPF molecular weight/CPF-oxon molecular weight; molecular weight ratio = 350.5879/334.5219)

Figure 1. Chlorpyrifos total air concentrations (ng/m^3) at North Central (above) and Yakima Valley (below) receptor and ambient sites over time. Chlorpyrifos concentration is expressed as total chlorpyrifos; i.e., the sum of measured chlorpyrifos and the measured chlorpyrifos-oxon's chlorpyrifos equivalent concentration. See Table 2 for details. The bars represent sample values at each site.





Phase 1: Perimeter Sampling Results

Data for perimeter sampling in Phase 1 are presented in Table 3 and Figure 2. Sampling before, during and after two airblast applications resulted in a peak concentration in the North Central region of 1,145 ng/m^3, and a peak concentration in the Yakima Valley region of 1,002 ng/m^3, both below but very close to the acute screening level of 1,200 ng/m^3. These peak concentrations occurred during the sampling period that included active spraying in both regions. Concentrations measured in the morning following the spray day were higher than the prior overnight concentrations at both sites, suggesting that post-application volatilization occurred during this period as temperatures increased. Chlorpyrifos concentrations two days after the applications remained substantially higher than pre-spraying concentrations.

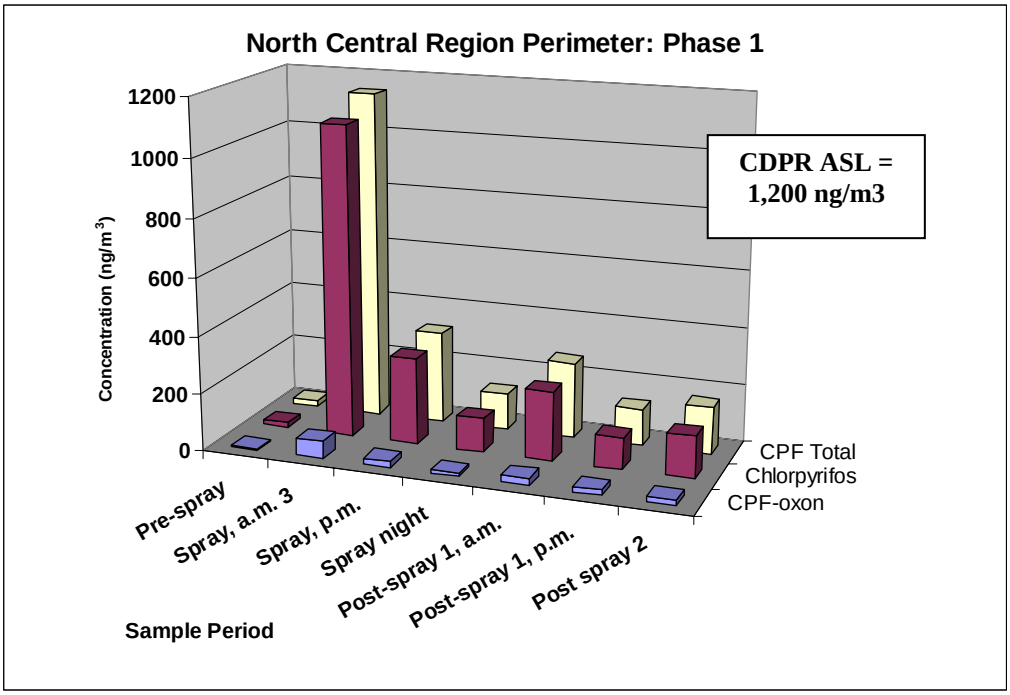
Table 3. Phase 1 perimeter (field boundary) chlorpyrifos, chlorpyrifos-oxon (CPF-oxon) and chlorpyrifos total (CPF total) air concentrations (ng/m^3). Values presented in the left three columns are the maximum concentrations measured at any location around the perimeter of the orchard block for each time period. These are compared to the CDPR acute screening level (ASL, 1,200 ng/m^3). Values presented in right three columns are the average of concentrations at all eight sampling locations around the perimeter of the orchard block for each time period.[1]

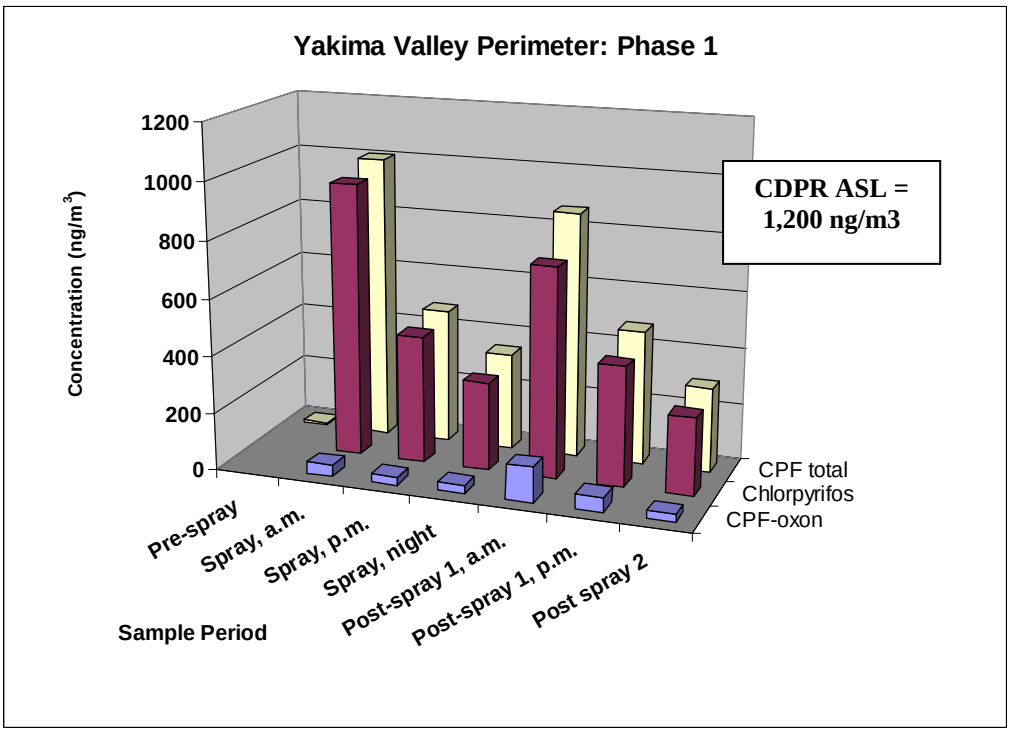
Region, Day, Sample Period	Average Temp. (Celsius) [2]	CDPR ASL = 1,200 ng/m^3 Maximum value			Average of all 8 samples (ng/m^3)		
		Chlorpyrifos	CPF-oxon	CPF total[3]	Chlorpyrifos	CPF-oxon	CPF total[3]
North Central							
Pre-spray	5.10	17.3	4.2	21.8	9.3	2.8	12.2
Spray, am [4]	7.55	1080.6	61.3	1144.9	367.0	21.9	389.9
Spray, pm	7.75	298.6	20.5	320.1	154.6	12.2	167.3
Spray night	3.37	117.6	10.2	128.3	57.9	6.0	64.1
Post-spray1 am	7.02	238.5	24.7	264.4	83.5	11.2	95.2
Post-spray1 pm	3.64	109.9	18.1	128.9	78.6	13.0	92.2
Post spray2	7.40	145.3	18.2	164.4	76.9	13.0	92.2
Yakima Valley							
Pre-spray	4.18			8.8			5.1
Spray, am[4]	10.66	958.9	40.8	1001.7	523.4	26.8	551.5
Spray, pm [5]	8.20	448.2	26.9	476.4	249.8	15.6	266.1
Spray, night	4.47	310.6	29.8	341.8	144.5	16.7	162.0
Post-spray, am	14.38	734.5	123.6	864.0	443.2	57.8	503.7
Post-spray1 pm	8.83	419.2	51.8	473.5	181.5	30.6	213.6
Post spray2	6.80	270.4	25.8	297.5	149.8	25.7	176.7

1. Air concentration values have not been adjusted for possible losses during field sampling, storage or laboratory analysis. See the following section on Quality Control for details.
2. Average ambient temperature for each sample period.
3. CPF-total was calculated by adding the chlorpyrifos air concentration to the CPF-oxon chlorpyrifos concentration equivalent (CPF-oxon * CPF molecular weight/CPF-oxon molecular weight; molecular weight ratio = 350.5879/334.5219).
4. Airblast orchard application occurred during this time period.

5. Normally the ambient temperature increases in the afternoon; however, for the Spray, pm sample period, the temperature decreased since the sampling period started at 18:28-00:46 (past midnight).

Figure 2. Phase 1 perimeter (field boundary) chlorpyrifos, chlorpyrifos-oxon (CPF-oxon), and chlorpyrifos total (CPF total) air concentrations (ng/m^3). Values presented are the maximum concentrations measured at any location around the perimeter of the orchard block for each time period. These are compared to the CDPR acute screening level (ASL, 1,200 ng/m^3).





Phase 2: Receptor and Ambient Sampling Results

Data for receptor and ambient sampling in Phase 2 are presented in Table 4. The highest azinphos-methyl total air concentration measured at receptor and ambient sites was 356 ng/m^3, much lower than either the CDPR acute screening level of 101,000 ng/m^3, or the EPA acute screening level of 5,000 ng/m^3. The highest 28-day average of 35 ng/m^3 was much lower than either the CDPR sub-chronic screening level of 11,000 ng/m^3, or the EPA sub-chronic screening level of 3,500 ng/m^3. The screening levels differ since CDPR in its risk assessment used an intentional human dosing study that was rejected by the EPA's Human Studies Review Board in 2006.

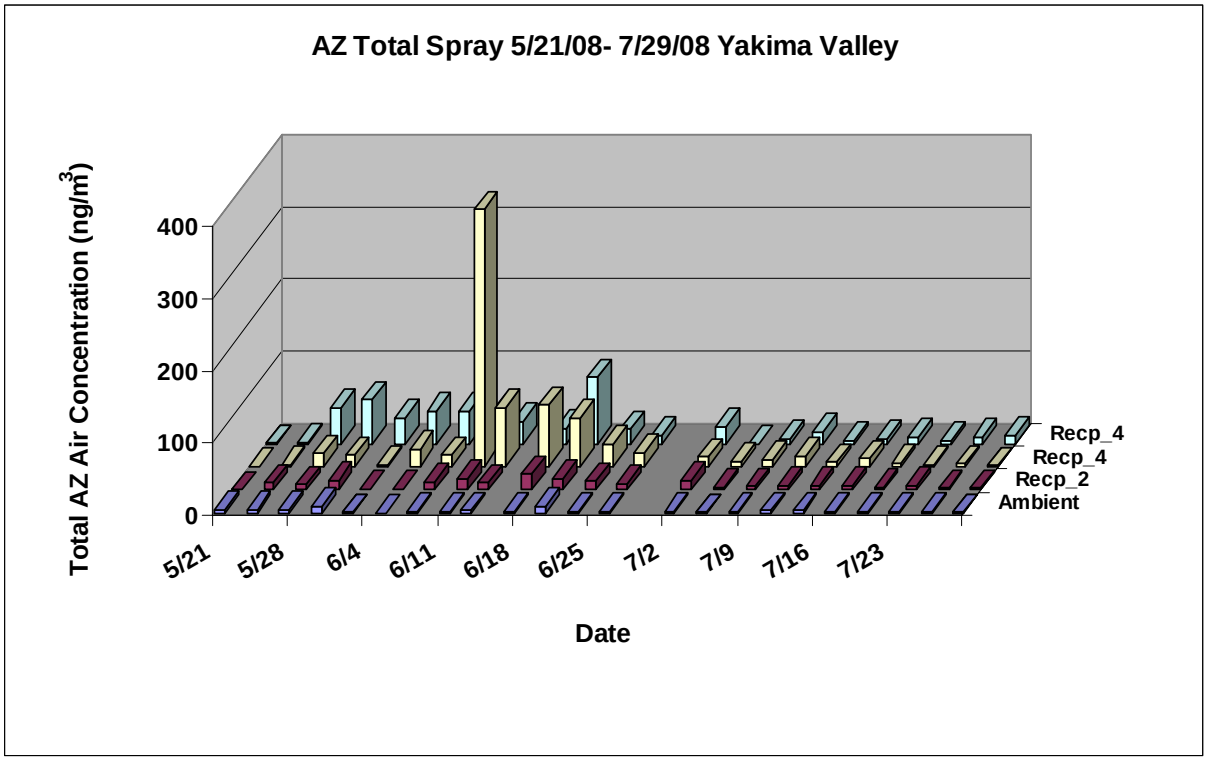
These data are also provided as a time-series graph for the Yakima Valley region (Figure 3). Elevated azinphos-methyl total concentrations occurred early in the sampling period for the Receptor 5 site. Elevated concentrations were notable for much of June at the Receptor 4 site, with a high value recorded on June 11. Azinphos-methyl total air concentrations at the Receptor 2 site were elevated relative to the ambient site, but the peak concentration was only 22 ng/m^3.

Table 4. Phase 2 receptor and ambient (community) azinphos-methyl, azinphos-methyl-oxon (AZ-oxon), and azinphos-methyl total (AZ total) air concentrations (ng/m^3). Values presented in the left three columns are the maximum concentrations measured in a 24-hr period at each site. These are compared to the CDPR acute screening level (ASL, 101,000 ng/m^3) and the EPA acute screening level (ASL, 5000 ng/m^3). Values presented in the right three columns are the average concentrations over 28 days at each site. These are compared to the CDPR sub-chronic screening level (SCSL, 11,000 ng/m^3) and the EPA acute screening level (SCSL, 3,500 ng/m^3).[1]

	Average Temp. (Celsius) [2]	**CDPR ASL = 101,000 ng/m^3 EPA ASL = 5,000 ng/m^3 24-hr Maximum concentration**			**CDPR SCSL = 11,000 ng/m^3 EPA SCSL = 3,500 ng/m^3 28-day Average concentration**		
		Azinphos -methyl	**AZ-oxon**	**AZ Total**[3]	**Azinphos -methyl**	**AZ-oxon**	**AZ Total**[3]
Yakima Valley							
Receptor 2	20.4	21.4	0.5	21.9	7.7	0.3	8.0
Receptor 4	20.4	351.7	4.5	356.5	34.0	0.9	35.0
Receptor 5	20.9	89.4	2.7	92.3	24.2	0.9	25.2
QC (at receptor 2)	20.4	18.1	1.3	19.5	6.8	0.4	7.2
Ambient	20.9	8.2	0.6	8.9	2.9	0.2	3.0

1. Air concentration values have not been adjusted for possible losses during field sampling, storage or laboratory analysis. See the following section on Quality Control for details.
2. Average ambient temperature for the entire sampling period at each sampling site.
3. AZ-total was calculated by adding the azinphos-methyl air concentration to the AZ-oxon azinphos-methyl concentration equivalent (AZ-oxon * AZ molecular weight/AZ-oxon molecular weight; molecular weight ratio = 317.3268/301.2608)

Figure 3. Azinphos-methyl total air concentrations (ng/m^3) at Yakima Valley receptor and ambient sites over time. Azinphos-methyl concentration is expressed as total azinphos-methyl; i.e., the sum of measured azinphos-methyl and the measured azinphos-methyl-oxon equivalent concentration. See Table 4 for details. The bars represent sample values at each site.



Phase 2: Perimeter Sampling Results

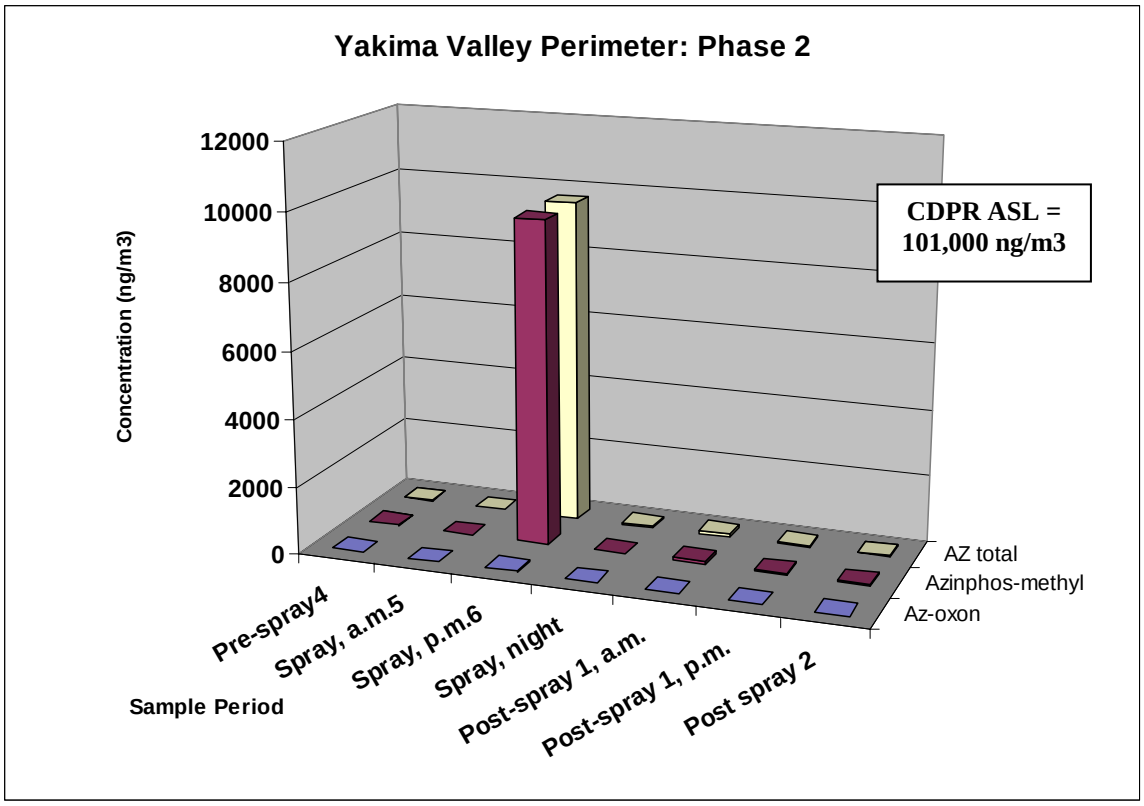
Data for perimeter sampling in Phase 2 are presented in Table 5 and Figure 4.. Sampling before, during, and after airblast application resulted in a peak azinphos-methyl total concentration 9,683 ng/m^3, exceeding the EPA acute screening level of 5,000 ng/m^3, but well below the CDPR acute screening level of 101,000 ng/m^3. This peak concentration occurred during the sampling period that included active spraying. Concentrations in the other sampling periods did not exceed 100 ng/m^3. As was seen in Phase 1, the concentration measured in the morning following the spray day was higher than the overnight concentration and the concentration on the following afternoon, suggesting that post-application volatilization occurred during this period.

Table 5. Phase 2 perimeter (field boundary) azinphos-methyl, azinphos-methyl-oxon (AZ-oxon), and azinphos-methyl total (AZ-total) air concentrations (ng/m^3). Values presented in the three left columns are the maximum concentrations measured at any location around the perimeter of the orchard block for each time period. These are compared to the CDPR acute screening level (ASL, 101,000 ng/m^3) and the EPA acute screening level (ASL, 5000 ng/m^3). Values presented in right three columns are the average of concentrations at all eight sampling locations around the perimeter of the orchard block for each time period.[1]

Day, sample period	Average Temp. (Celsius) [2]	CDPR ASL = 101,000 ng/m^3 EPA ASL = 5,000 ng/m^3 Maximum concentration			Average for all samples ng/m^3		
		Azinphos -methyl	AZ-oxon	AZ total[3]	Azinphos -methyl	AZ-oxon	AZ total[3]
Yakima Valley							
Pre-spray[4]	20.71	22.1	1.2	23.3	16.8	0.9	17.8
Spray, am[5]	--	--	--	--	--	--	--
Spray, pm[6]	26.00	9648	33.1	9683	2646	11.5	2658
Spray, night	19.66	40.5	1.4	42.0	18.1	1.5	19.7
Post-spray1 am	25.77	86.7	3.0	89.9	54.8	1.9	56.8
Post-spray1 pm	16.77	43.8	1.0	44.8	21.0	0.7	21.7
Post spray 2	19.20	27.4	1.3	28.7	16.5	0.8	17.4

1. Air concentration values have not been adjusted for possible losses during field sampling, storage, or laboratory analysis. See the following section on Quality Control for details.
2. Average ambient temperature for the sample period.
3. AZ-total was calculated by adding the azinphos-methyl air concentration to the AZ-oxon azinphos-methyl concentration equivalent (AZ-oxon * AZ molecular weight/AZ-oxon molecular weight; molecular weight ratio = 317.3268/301.2608)
4. A pre-spray sample was found to be invalid and removed from the results. The total sample size for the pre-spray sampling period is 6, excluding the QC sample.
5. Application was planned for the morning, but was delayed until the evening due to equipment problems; the evening (pm) spray day sample began at 6:00 p.m.
6. Airblast orchard application occurred during this time period.

Figure 4. Phase 2 perimeter (field boundary) azinphos-methyl, azinphos-methyl oxon (AZ-oxon), and azinphos-methyl (AZ total) air concentrations (ng/m^3). Values presented are the maximum concentrations measured at any location around the perimeter of the orchard block for each time period. These are compared to the CDPR acute screening level (ASL, 101,000 ng/m^3).



Complete field quality control results are provided in Appendix E. Key findings are summarized below.

Field Blanks

Blank sampling tubes were carried into the field and were treated as if they were field samples in terms of handling, labeling, storage, and transport. These samples did not have air drawn through them. Field blanks representing the equivalent of 10% of the samples collected were analyzed for parent compound (chlorpyrifos or azinphos-methyl) and its oxygen analog.

None of the 28 field blanks in Phase 1 had measurable chlorpyrifos or chlorpyrifos-oxon in either the front section or the back section of the sampling tube (all values less than the 2 nanograms per sample limit of quantitation). The same was true for the 15 field blanks analyzed for Phase 2. Table 6 indicates the number of field blanks analyzed for each phase, each region, and each type of sampling.

Table 6. Field blank sample analysis

Region	Sample Type	Number of samples	Number >LOQ
Phase 1			
North Central	Receptor	8	0
	Perimeter	6	0
Yakima Valley	Receptor	8	0
	Perimeter	6	0
	Subtotal	28	0
Phase 2			
Yakima Valley	Receptor	11	0
	Perimeter	4	0
	Subtotal	15	0
	Total	**43**	**0**

Field (Trip) Spikes

Spiked sampling tubes were carried into the field and were treated as if they were field samples in terms of handling, labeling, storage, and transport. These samples did not have air drawn through them. Field (trip) spikes representing the equivalent of 10% of the samples collected in Phase 1 were analyzed for chlorpyrifos. These samples were spiked before the decision had been taken to include chlorpyrifos-oxon as an analyte in the study, so they were not spiked with the oxygen analog. Field (trip) spikes representing the equivalent of 10% of the samples collected in Phase 2 were analyzed for both azinphos-methyl and its oxygen analog.

Phase 1 field (trip) spike samples were spiked during the Phase 1 sampling period (late February through mid-April), but were not analyzed until mid-October. The time between spiking and analysis ranged from 185 to 234 days. This compares to a range of sample analysis from 126-236 days post-collection. Samples were spiked at three different levels: 12.5, 50, and 250 nanograms per sample. One sample spiked at 12.5 ng/sample appeared to

have been inadvertently spiked twice, since the amount recovered from the sample was approximately twice the spiking level. This sample was considered an outlier and was removed from the data set.

Phase 2 field (trip) spike samples were spiked with azinphos-methyl and its oxygen analog between mid-May and mid-June, but were not analyzed until early December. The time between spiking and analysis ranged from 169 to 197 days. Samples were spiked at 50 nanograms per sample.

Results are presented below in Table 7. For Phase 1, recoveries from samples spiked at 12.5 ng/sample were near 100% (average of 94% with a coefficient of variation of 9.8%), while recoveries from samples spiked at either 50 ng/sample or 250 ng/sample were approximately 70%. The difference in recoveries between the low spike samples and higher spike samples was not associated with time between spiking and analysis. A reason for this difference is not apparent. For Phase 2, recoveries were from 90-93% for azinphos-methyl, and about 80% for its oxygen analog.

Table 7. Field (trip) spike sample analysis

Spike level (ng/sample)	Sample type	Number of samples	Average recovery (%)		Coefficient of variation (%)	
Phase 1: chlorpyrifos						
12.5[1]	Receptor	16	94.4		9.8	
50	Receptor	6	70.1		10.9	
250	Perimeter	6	70.6		9.5	
50 + 250	Perimeter	12	70.3		9.8	
Phase 2: azinphos-methyl						
			AZ	AZ-oxon	AZ	AZ-oxon
50	Receptor	11	90	78	2.0	8.0
50	Perimeter	4	93	80	2.0	2.0

1. One sample contained 2x the spike quantity including oxon, so was excluded from the data set.

OVS Sampling Tube Breakthrough Analysis

Sampling was conducted using Occupational Safety and Health Administration Versatile Sampler (OVS) tubes containing XAD-2 resin. Each tube has a front section and a back section of XAD-2™ sorbent material to permit evaluation of potential breakthrough. Breakthrough means that some sample loss may have occurred. We used the criterion presented in NIOSH Method 5600 to evaluate breakthrough:

$$\text{Breakthrough} = M_b/M_f * 10 > 1$$

Where M_b is the mass of chemical measured in the back section and M_f is the mass of chemical measured in the front section. In other words, the amount measured in the back section should be less than 10% of the amount measured in the front section.

A total of 265 air samples were analyzed in Phase 1 for chlorpyrifos and chlorpyrifos-oxon. For one sample the mass of chlorpyrifos and its oxon was substantially higher in the back section than in the front section. Prior to analysis, this sample tube was noted to have sorbent

missing from the front section. We therefore analyzed the back-up sample for this sample tube. The back-up sample had normal amounts of sorbent in the front and back sections. The results for this tube did not show significant breakthrough, so the measurement for this back-up have been substituted for the original measurements.

Results, presented below in Table 8, indicate that no breakthrough occurred in the study. Chlorpyrifos was detected in 45% of the back sections of samples, but the amount of chlorpyrifos in the back sections of these tubes was a small fraction of the chlorpyrifos in the front section, well below the NIOSH Method 5600 criterion for breakthrough. Azinphos-methyl was detected in 43% of the back section of the samples. During the initial analysis, five samples had back sections greater than the NIOSH criterion. Back-up samples for three of the samples were analyzed and updated in Appendix I. The remaining samples were below the NIOSH criterion for breakthrough. Chlorpyrifos-oxon and azinphos-methyl-oxon were detected at very low levels in the back sections of samples, well below the NIOSH Method 5600 criterion for breakthrough.

Table 8. OVS tube breakthrough analysis[1]

Chemical	Section	Number ≥LOD	% ≥LOD	Breakthrough calculation Average	Maximum	Number with breakthrough >1
Chlorpyrifos	Front	258	97.4	0.12	0.60	0
	Back	120	45.3			
CPF-oxon	Front	260	98.1	0.094	0.33	0
	Back	29	10.9			
Azinphos-methyl	Front	163	95.9	0.350	4.001	2[2]
	Back	73	42.9			
AZ-oxon	Front	134	78.8	0.350	0.395	0
	Back	2	1.2			

1 Back section needed to be above the LOQ to be considered for the breakthrough analysis.

2 Breakthrough calculation is the mass measured in the back section divided by the mass measured in the front section; ratios over 1.0 exceed the NIOSH criterion for breakthrough. When the back section of a sample was greater than the LOD, then it is added to the front section. Two samples still have ratios over 1.0 and are included in the results found in Appendix I. One sample with a ratio of 1.62 did not have a back-up sample. Another sample with a ratio of 1.32 had low azinphos-methyl concentrations (AZ= 1.9 ng/m^3, AZO= 0.1 ng/m^3) in which breakthrough was unlikely.

Duplicate (Co-located) Samples

Duplicate samples were collected at one receptor site in each region each day during the sampling period. Duplicate samples were also collected at one location at the perimeter sites in each region throughout the sampling period (four days). The duplicate sample data are provided in Appendix E.

A total of 50 comparisons were made using duplicate samples collected at receptor and perimeter sites. For this comparison we excluded samples pairs in which both samples had very low concentrations (<3 times the LOQ, or about 5 ng/m^3). We considered that the variability inherent in measurements near the LOQ would make comparisons across samples unreliable. The exclusion of low concentration pairs resulted in a total of 31 receptor comparisons and 19 perimeter comparisons.

We calculated the percent difference between the primary and the co-located sample to evaluate sampling precision, using total chlorpyrifos or total azinphos-methyl (i.e., the sum of the parent compound and its oxygen analog). Percent difference was defined as follows:

$$\text{Percent difference} = [(\text{sample}_p - \text{sample}_c)/(\text{sample}_p + \text{sample}_c)/2]*100$$

where sample_p is the primary sample and sample_c is the co-located sample.

We used the criteria of <40% difference described in the California Air Resources Board report on chlorpyrifos monitoring in Tulare County (CARB 1998):

> There are no established acceptance criteria for collocated samples for this program. Generally, though, relative difference results of up to 40% (i.e., the average +/- 20%) are reasonable. (p.9)

Table 9 provides the number of comparisons for each study phase and sample type, the number of samples within the quality control goal of <40% difference, and the percent of sample pairs within the quality control goal. The receptor and perimeter values were pooled to produce an overall measure of 90% of samples meeting the QC goal.

Table 9. Duplicate (co-located) samples: average percent difference for each region and each sample type.

Phase	Compound	Sample type	Number of comparisons	Number within QC goal of <40%	Percent within QC goal
1	Chlorpyrifos	Receptor	16	14	88%
1	Chlorpyrifos	Perimeter	14	13	93%
2	Azinphos-methyl	Receptor	15	14	93%
2	Azinphos-methyl	Perimeter	5	4	80%
1+2		Receptor	31	28	90%
1+2		Perimeter	19	17	89%
All			50	45	90%

Storage Stability

The complete results from storage stability studies are provided in Appendix F. Air samples analyzed for chlorpyrifos and its oxygen analog were stored from 171-236 days, as indicated in Table 10. An initial set of storage stability samples was prepared on May 9, 2008, but these samples contained chlorpyrifos only. Chlorpyrifos recoveries from these samples were 81% +/- 1.8% after 221 days of storage and 86% +/- 4.9% after 249 days of storage. A second set of storage stability samples that included chlorpyrifos-oxon was prepared on November 13, 2008. These have been analyzed after storage times of up to 242 days, and show similar chlorpyrifos recovery when compared to the initial set; that is, chlorpyrifos recovery was 82% after 242 days. Chlorpyrifos-oxon recovery was somewhat lower (63% after 242 days).

Air samples analyzed for azinphos-methyl and its oxygen analog, as well as for phosmet and malathion were stored for 126-202 days, as indicated in Table 10. Recoveries from storage stability samples that had been stored for 209-294 days were 86-103% for azinphos-methyl, 76-90% for azinphos-methyl-oxon, 75-95% for phosmet, and 87-101% for malathion.

Table 10. Storage time of field air samples

			Range		Collected		Analyzed		Duration (days)	
Sample Type	**Phase**	**Region**	**Sample Collection**	**Samples Analyzed**	**First date**	**Last date**	**First date**	**Last date**	**Min**	**Max**
Receptor & Ambient	1	2	3/8/08 - 4/1/08	10/20/08 - 10/30/08	3/8	4/1	10/20	10/30	202	236
Receptor & Ambient	1	1	4/3/08 - 5/2/08	10/20/08 - 10/30/08	4/3	5/2	10/20	10/30	171	210
Perimeter	1	2	3/31/08 - 3/31/08	10/20/08 - 10/31/08	3/31	3/31	10/20	10/31	203	214
Perimeter	1	1	4/6/2008 - 4/9/08	10/20/08 - 10/31/08	4/6	4/9	10/20	10/31	194	208
Receptor & Ambient	2	2	5/21/08 - 7/29/08	12/2/08 - 12/9/08	5/21	7/29	12/2	12/9	126	202
Perimeter	2	2	6/19/08 - 6/22/08	12/2/08 - 12/9/08	6/19	6/22	12/2	12/9	163	173

Inter-Laboratory Comparison Sub-Study

The study protocol and full results are presented in Appendix G. The key findings of the study are summarized here.

The CDPR laboratory compared the UW analytical standards with its own analytical standards and found less than one percent difference between the two standards when measured by gas chromatography (0.97% for chlorpyrifos; 0.45% for chlorpyrifos-oxon).

The two laboratories measured chlorpyrifos and chlorpyrifos-oxon in six spiked OVS tubes. Results are presented in Table 11. One blank tube was provided to each lab for quality control, and each lab reported this sample as non-detectable.

Table 11. Percent recoveries of chlorpyrifos (CPF) and chlorpyrifos-oxon (CPF-oxon) from spiked OVS tubes

CPF spike (ng)	**N**	**UW (mean %)**	**Coefficient of variation**	**CA (mean %)**	**Coefficient of variation**
400	3	93	2.3	81	3.8
800	3	96	1.8	80	5.9
CPF-oxon spike (ng)					
400	3	77	2.4	71	10.2
800	3	79	1.9	72	1.5

The accuracy and precision for both laboratories was very good. Recoveries were similar for the two spiking levels in each case. Recoveries for chlorpyrifos were higher than for chlorpyrifos-oxon for both laboratories. The UW lab mean recoveries tended to be higher than the CA lab recoveries. These data indicate that both laboratories performed well with spiked samples, and the results they produced were comparable.

Five extracts from field samples that had been collected in 2008 were also sent to the CDPR laboratory for analysis. In this case, the sample volumes supplied to the California lab proved to be too small for complete analysis, and the results were deemed unreliable. CDPR results for chlorpyrifos for all five samples were outside the range of the laboratory's calibration curve (>1,000 ng/sample). Insufficient extract volume remained to perform dilution and reanalysis.

Potential Chlorpyrifos-oxon Generation Sub-Study

The study protocol and full results are presented in Appendix H. The key findings of the study are summarized here.

The study consisted of two parts: a laboratory study and a field study. The laboratory study was conducted in the winter of 2009 at UW. The field study was conducted in the early spring of 2009 in the Yakima Valley. The time period for the field study was selected to coincide with chlorpyrifos applications in the region. The field sampling site was the same site used for ambient sampling in 2008.

All sampling was conducted for 24 hours. In the laboratory study, two spiking levels were evaluated at a flow rate of two liters per minute to correspond to the receptor/ambient sampling conducted in 2008, and one spiking level was evaluated at six liters per minute to correspond to the 2008 perimeter. Similarly, in the field study, five spiking levels were evaluated at two liters per minute and four spiking levels were evaluated at six liters per minute. Spiking levels were selected based on the distribution of air concentrations measured in the 2008 field study for the receptor/ambient and perimeter samples, respectively.

Results from these studies are presented in Table 12. For the laboratory study the percent of chlorpyrifos converted to its oxygen analog decreased as the spiking level increased, with mean percent oxon values ranging from a high of 32% to a low of 16%. The findings were similar for the field study. Chlorpyrifos conversion to oxon at two liters per minute was 25% at the lowest spiking level but only 12% at the highest spiking level. Conversion to oxon at six liters per minute followed the same pattern: 19% at the highest spiking level and 7% at the lowest spiking level.

Table 12. Percent chlorpyrifos-oxon generated during 24 hours by drawing air through OVS tubes spiked with chlorpyrifos.

CPF spike (ng)	Flow rate (liter/min)	N	Percent oxon (mean)	Coefficient of variation
Laboratory				
42	2	3	31.6	18
210	2	3	23.5	14
2100	6	3	16.2	40
Field				
0	2	2	30.5	35
15	2	3	24.6	31
30	2	2	20.2	23
60	2	3	13.7	6
200	2	3	11.7	25
0	6	3	29.5	2
200	6	3	18.9	10
592	6	3	12.8	33
2628	6	3	8.6	23

A preliminary analysis was conducted to determine the plausible range of percent oxon values. The pattern of chlorpyrifos conversion to oxon in the field study is illustrated in Figure 5. The lower line in the figure is the best-fit curve, and the upper line is the 95% confidence interval for these data. This graph demonstrates that percent oxon conversion decreases rapidly as total chlorpyrifos concentration increases. At 25 ng/m^3, for example, the upper confidence interval is 25-30%, whereas at 250 ng/m^3, the upper confidence interval is about 4%.

As a first step, we examined those samples that contained greater than 40% chlorpyrifos-oxon as a fraction of total chlorpyrifos. This percentage exceeds the 95% confidence interval in Figure 5 for all but the very lowest sample concentrations. Of the 142 receptor and ambient air samples collected in Phase 1, 52 samples (37%) chlorpyrifos-oxon represented greater than 40% of the total chlorpyrifos. When we examined samples with total chlorpyrifos concentrations between 5 and 25 ng/m^3, we found that for 17 of 55 samples (31%) chlorpryifos-oxon represented more than 40% of the total chlorpyrifos. And for samples with concentrations between 25 and 50 ng/m^3, chlorpyrifos-oxon represented more than 30% of total chlorpyrifos in 4 of 9 cases (44%).

We also found that the distribution of samples with a high contribution of chlorpyrifos-oxon to total chlorpyrifos (>40%) was variable across sampling sites, as indicated in Table 13: in the North Central region (Region 1), the Receptor 3 site was relatively high (11 of 15), while Receptor 1 was relatively low; in the Yakima Valley (Region 2), the

ambient site was relatively high (11 of 15), while the Receptor 2 site had no samples with 40% chlorpyrifos-oxon. The reason for these differences is not known. But if we assume that all chlorpyrifos-oxon is produced artificially during sampling, then it is hard to explain why high fractional oxon generation occurred in some regions and sampling locations but not others. It therefore seems plausible to assume that at least some of the chlorpyrifos-oxon measured in these samples was formed in the environment.

Figure 5. Total chlorpyrifos mass per cubic meter of air drawn through the sampling tube ("concentration") vs. log percent oxon conversion. Lower line in the graph is the best-fit curve; upper line is the upper 95% confidence interval. (Graph includes all field samples; total chlorpyrifos mass recovered has been divided by total air volume for each sample to produce the "concentration" values.)

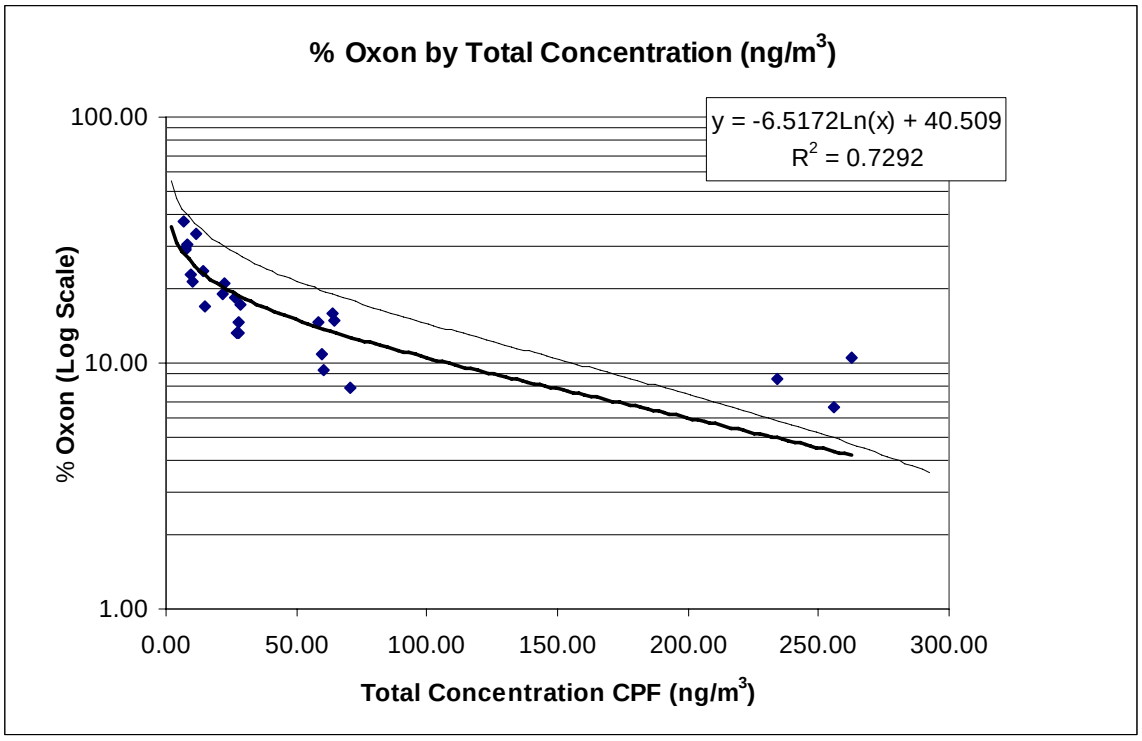


Table 13. Distribution of Phase 1 receptor and ambient air concentrations that contained greater than 40% chlorpyrifos-oxon as a fraction of the total chlorpyrifos concentration

Region	Sampling location	N	# of samples >40% oxon	Percent of samples >40% oxon
1	Ambient	15	7	47
1	Receptor 1	15	3	20
1	Receptor 2	15	7	47
1	Receptor 3	15	11	73
1	Receptor QC	15	7	47
		Sum = 75	**Sum = 35**	**Mean = 47%**
2	Ambient	15	11	73
2	Receptor 1	11	1	9
2	Receptor 2	15	0	0
2	Receptor 3	12	5	42
2	Receptor QC	15	0	0
		Sum = 68	**Sum = 17**	**Mean = 25%**

A complete report of the meteorological data is provided in Appendix K (wind) and Appendix L (temperature, precipitation, and weather observations). A summary of these data is presented below.

Wind Speed and Direction

Wind speed was reported in meters per second (m/s). Wind direction was reported in terms of the wind source (e.g., a wind blowing from the southwest to the northeast would be referred to as "southwest" or SW). For the receptor and ambient sites, wind data were collected from the nearest Washington State University (WSU) Agricultural Network monitoring station. The wind roses for receptor and ambient sites in Appendix K include all days from the first to last sampling day started and ending at 12 pm (noon), including days when air samples were not collected. Appendix K also has wind roses on peak days at receptor sites in each phase. A peak day for each site was defined as having an air concentration in the 90^{th} percentile of all receptor air concentrations for that phase. If a receptor site had no days in the 90^{th} percentile, than a wind rose was provided for the day with the highest air concentration for that site.

For the perimeter sites we used the average of one-minute wind data from the on-site meteorological station. The perimeter site wind roses in Appendix K are based on this one-minute data and are for each sample period. In general, there was a slight trend towards higher air concentrations on the samplers located downwind from the predominant wind direction. For example, in the evening of post-spray day 1 at the North Central perimeter site, the predominant wind was from NW and the highest air concentration came from sampler #4 located SE of the orchard block.

Temperature

Temperatures were reported in degrees Celsius for all sites. The minimum, maximum, and mean temperatures were determined for each sample period at each site. For the receptor and ambient sites, data from the nearest WSU Agricultural Weather Network monitoring station were collected at 15-minute interval data for each 24 hours, with the period starting at 12:00 pm (noon). For the perimeter sites, data from the on-site temporary meteorological stations were collected at one-minute intervals and averaged over 24 hours for each sampling day.

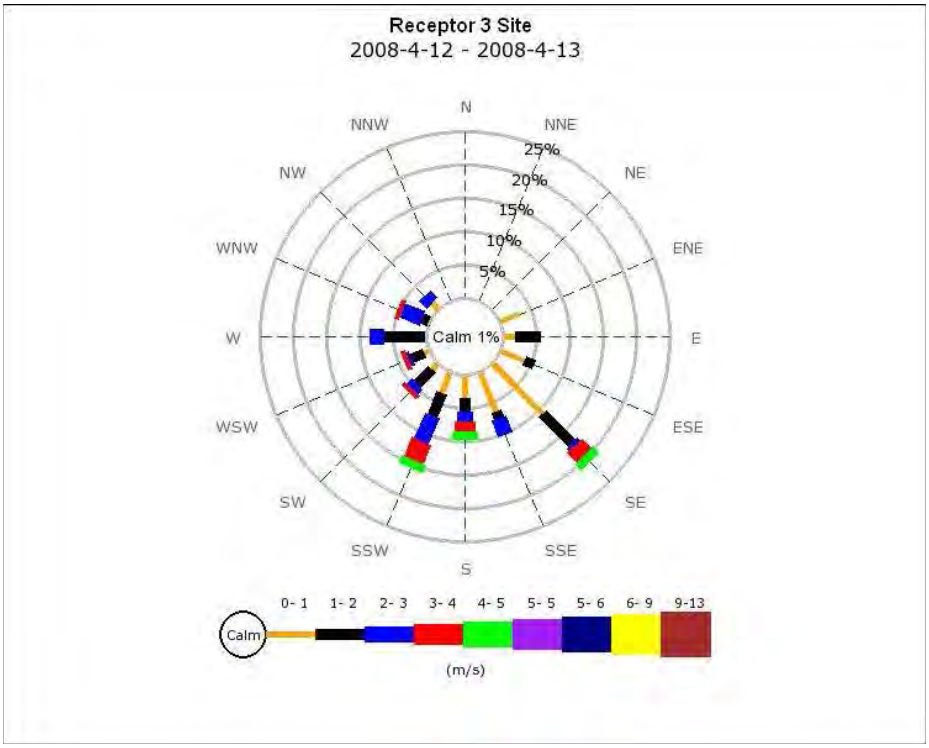
At the Yakima Valley perimeter site, air concentrations increased as temperature increased for both Phase 1 and Phase 2. However, this was not observed at the North Central perimeter site.

Precipitation

Precipitation was reported in millimeters for all sites. Data from the nearest WSU Agricultural Weather Network monitoring station were used for each sampling site. For the receptor and ambient sites we used 24-hour accumulated precipitation data, with periods starting at 12:00 pm (noon).

We were not able to find associations between the air concentrations and temperature, wind, or proximity for our receptor sampling sites. Spraying observations for each receptor site were only recorded if a staff member was at the site and observed the spray. However, we did find one case in which temperature, wind speed and proximity likely affected the air concentration. In the North Central Region, receptor sampling site 3 had a chlorpyrifos total air concentration of 163 ng/m^3 on its peak day of April 12, 2008. A staff member observed spraying occurring near this site for three days around this peak day. The weather data lists sunny weather with a mean temperature of 10°C for this peak day. The wind rose showed the wind coming mostly from the SE and SSW directions with speed in the 3-4 m/s range. Since the site is surrounded by apple orchards on four sides, it would be in the pathway of the pesticide spray, especially with the wind moving the spray downwind (or NW and NNE). Below is the wind rose for the peak day in the North Central Region (Figure 6).

Figure 6. Wind rose for April 12, 2008, receptor sampling site #3, North Central region.



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DISCUSSION

The purpose of this air monitoring project was to examine whether off-target movement of organophosphorus pesticides during and following pesticide applications posed a potential risk to residents or bystanders. Information gathered from our cooperators indicated that our sampling periods coincided with the peak application periods in both regions and for both phases of the study. The data collected in this study support the conclusion that peak air concentrations at our sampling sites were probably captured in our data set. The quality control data collected in the study were sufficient to conclude that the air sampling results were reliable measurements of airborne pesticides. Total pesticide air concentrations reported in this study were the sum of the parent compound and its oxygen analog for chlorpyrifos and azinphos-methyl. This calculation was made based on the assumption that the oxygen analog represented parent compound molecules that been transformed in the OVS sampling tubes. If the oxygen analogs had not been included in the analysis, then the concentrations of these pesticides would have been underestimated.

Screening Level Comparisons

Comparison of the air measurements with screening levels developed by the California Department of Pesticide Regulation or the U.S. Environmental Protection Agency indicated that none of the pesticide air concentrations measured at receptor or ambient sites exceeded the screening levels. Samples collected around the perimeter of orchard blocks during and after applications showed higher pesticide concentrations than those found in the community sampling. Those sample concentrations that approached the California screening levels were found only during active spraying and over relatively short sampling periods (approximately 8 hours). These measurements cannot be compared to the screening levels, since the screening levels are based on a 24-hr exposure period. If the screening levels cited in this study are used as the basis for a first tier risk assessment, then it appears that agricultural spraying in these regions does not pose a health risk to residents or bystanders.

Oxygen Analogs

Substantial levels of the oxygen analogs of chlorpyrifos and azinphos-methyl were measured in this study. Several earlier air monitoring studies in California also found oxygen analogs in their samples. Studies in the 1970s demonstrated that parathion residues on dusts in agricultural fields could undergo environmental transformation to paraoxon (Spear et al. 1977; 1978). A 1993 study of diazinon air concentrations found measurable diazoxon (CDPR 1993). The authors speculated that diazoxon "could have been caused by artificial conversion of the parent product to the oxygen analog during sample collection." They also noted that conversion of OP pesticides to their oxygen analogs can "occur in air due to the presence of hydroxy (OH) radicals." A 1996 study of chlorpyrifos in Tulare County found chlorpyrifos-oxon in samples (CARB 1998). The authors stated that "the method development results indicate that conversion of chlorpyrifos to the oxon may take place on the trapping media during sampling." Similarly, Segawa et al. (1990) reported what appeared to be conversion of malathion to malaoxon, and speculated that this conversion might be correlated with ambient ozone concentrations. Malaoxon was also found on deposition samplers placed in the spraying area to collected residues. The authors were not able to determine if these residues were environmental transformation products or if the malaoxon was present in the malathion/bait mixture being used for control of the Mediterranean fruit fly. Later studies in

Lompoc and Parlier, California also found oxon residues in air samples, but were not able to determine their source (Segawa et al. 2003; CDPR 2006).

Relative Potency of OP Pesticides and Oxygen Analogs

The high toxicity of paraoxon relative to its parent compound, parathion, has been well documented in studies of field worker poisonings (e.g., Spear et al. 1977), but similar studies have not been conducted for chlorpyrifos or azinphos-methyl. Since our follow-up studies focused on chlorpyrifos, we conducted a literature search to identify studies with a direct comparison between chlorpyrifos and chlorpyrifos-oxon toxicity. Huff et al. (1994) exposed rat striatum to either chlorpyrifos or chlorpyrifos-oxon. They found that the oxon phosphorylated acetyl cholinesterase (AChE) three times as rapidly as did chlorpyrifos, and that the dissociation constant was almost three orders of magnitude smaller for chlorpyrifos-oxon. Monnet-Tschudi et al. (2000) found that chlorpyrifos-oxon was several orders of magnitude more potent than chlorpyrifos in inhibiting AChE in cultured brain cell aggregates. However, these *in vitro* studies are limited in that they do not examine relative potency in whole animals.

Chambers and Carr (1993) compared brain AChE inhibition in rats for chlorpyrifos and its oxon, and found at least a 3-fold difference in potency (chlorpyrifos-oxon toxicity greater than chlorpyrifos toxicity). Cole et al. (2005) conducted dermal dosing of mice with both chlorpyrifos and chlorpyrifos-oxon. Six hours after the initial exposure, the mice were sacrificed, and AChE inhibition was measured in the brain and diaphragm. This study found that chlorpyrifos-oxon was 50 times more potent than chlorpyrifos for these two mice types.

It is also important to note that we are evaluating inhalation exposures for this study. Nearly all of the work in animal bioassays and in human studies has focused on either the oral or dermal exposure route. Timbrell (2000) points out that “absorption from the lungs . . . is generally rapid and exposes major organs very quickly.” Inhaled chlorpyrifos-oxon can move from the lungs to the heart and to the brain without passing through the liver.

The toxicological evidence of a difference in potency led to us conduct the laboratory and field studies discussed earlier in the report, since even a small amount of chlorpyrifos-oxon in ambient air would likely change our evaluation of health risk. Our preliminary analysis of these studies suggests that some of the chlorpyrifos-oxon measured in our 2008 air samples was present in the air sampled, and therefore presents a risk greater than the sum of chlorpyrifos and its oxygen analog. We recommend that additional research be conducted to fully characterize potential formation of oxygen analogs of OP pesticides in the air where OP pesticides are commonly applied.

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