

## Appendix A:

### *Sampling Plans and Progress Reports*

#### **Documents:**

##### **Sampling Plans**

Preliminary Sampling Plan, January 28, 2009

Final Sampling Plan, March 31, 2009

##### **Progress Reports**

Progress Report, June 17, 2008

Progress Report: Task 4, August 1, 2008



## **Pilot Organophosphorus Pesticide Air Monitoring Project**

### **PRELIMINARY SAMPLING PLAN**

Richard Fenske, Michael Yost, Cole Fitzpatrick, Maria Tchong  
Department of Environmental and Occupational Health Sciences  
School of Public Health and Community Medicine  
University of Washington

**January 28, 2008**

Submitted to

Cynthia Lopez, Manager, Department of Health Pesticide Program  
P.O. Box 47845, Olympia, WA 98504-7845

### **Purpose**

In April 2007 the Washington State Legislature requested an “examination of airborne pesticide concentrations in agricultural areas of the state.” The University of Washington’s Department of Environmental and Occupational Health Sciences (UW-DEOHS) was assigned the task of monitoring organophosphorus (OP) pesticides in agricultural regions of Washington State. UW-DEOHS will measure air concentrations of OP pesticides used in Washington agriculture during the 2008 growing season. The purpose of this monitoring is to examine whether off-target movement of OP pesticides during and following pesticide applications poses a potential risk to residents or bystanders.

### **Phase 1 Sampling Strategy: Chlorpyrifos Applications**

Our sampling strategy for the measurement of chlorpyrifos air concentrations is outlined in Table 1.

#### ***Regions***

We propose to sample in two tree fruit regions of Washington State. These regions will differ in regard to the anticipated start date of Lorsban™ (chlorpyrifos) applications in each region; that is, the regions will be selected such that applications will start earlier in one region than in the other. The three possible sampling regions that have been identified are the Yakima valley, the lower Columbia valley, and the Wenatchee river basin. Appendix 1 provides a map of each of these regions, with chlorpyrifos use patterns indicated.

### ***Pesticide Use Areas***

We will use the pesticide-use-density maps (Appendix 1) developed by our research team to identify appropriate areas within each region for chlorpyrifos sampling. The sampling program targets airblast applications of chlorpyrifos in tree fruit orchards. These applications are believed to have the greatest potential for off-target movement of chlorpyrifos.

### ***Time Frame***

We intend to conduct sampling in four time periods. The first sampling period will coincide with the beginning of chlorpyrifos applications in Region 1. The second sampling period will coincide with the beginning of chlorpyrifos applications in Region 2. The third sampling period will occur in Region 1 near the end of chlorpyrifos applications. The fourth sampling period will occur in Region 2 near the end of chlorpyrifos applications. This approach will allow our field research team to work continuously for 4-6 weeks, moving back and forth between the two regions.

### ***Site Selection***

We intend to sample at four sites: two in each region: sites 1 and 2 will be located in Region 1; sites 3 and 4 will be located in Region 2.

***Site 1.*** The first site will be selected in cooperation with the grower community. In this situation we will ask the grower for information regarding the application rate, the duration of application, the total amount of active ingredient applied, and other information relevant to an emission rate estimate. We will also request permission to attach a global positioning system (GPS) unit to the spray tractor to document its movement. This information, in conjunction with on-site meteorological data, will allow us to construct a model of off-target pesticide movement. We will conduct near-field perimeter sampling similar to the approach used by the California Air Resources Board. That is, we will place samplers on the four sides of the application site. We will collect 24-hour samples for five consecutive days. We will also collect one ambient community sample over the same five days. The ambient sampler will be located in a nearby community to determine air concentrations distant from the application site. Prior experience and dispersion modeling results from other studies suggest that the ambient community monitoring locations should be located at least one-half kilometer from the nearest applied fields. Previous sampling in a Washington agricultural region (Tolbert et al. 2008) indicated that ambient community air can be considered reasonably well mixed on a scale of five to ten kilometers.

***Site 2.*** The second site will be selected in cooperation with the farm worker community. In this situation, we will ask farm workers to identify locations that they believe receive high chlorpyrifos exposures during airblast applications on tree fruit. We will then conduct near-field receptor sampling; that is, we will place two samplers in proximity to a residence or other inhabited structure (e.g., daycare, school) to capture the concentration of chlorpyrifos that might be

encountered by individuals living in or frequenting these locations. We will collect 24-hour samples for ten consecutive days to characterize potential bystander exposure. We will also collect one ambient community sample over five of the ten days. The ambient sampling will follow the procedures outlined above for Site 1.

**Sites 3 and 4.** These sites will be located in Region 2. The site selection criteria and the procedures described for Sites 1 and 2 will be followed at these sites.

## **Phase 2 Sampling Strategy: Multiple OP Pesticides**

The target compounds for Phase 2 sampling are expected to be azinphos methyl phosmet, and malathion. The temporal sampling frame is expected to be mid-May through early July. We intend to use the sampling strategy for Phase 2 that we have outlined for Phase 1. However, our experience in Phase 1 may lead to modifications in the Phase 2 sampling strategy. Any proposed modifications in the sampling plan for Phase 2 will be discussed with the Department of Health and the Technical Review Panel.

## **Sampling Methods**

### ***Meteorological Data***

A portable meteorological station will be deployed continuously throughout the sampling period at each sampling site to monitor local weather conditions such as temperature, pressure, rainfall, wind speed and wind direction.

### ***Chlorpyrifos Sampling***

Sampling for chlorpyrifos will be performed using methods similar to those presented in the National Institute for Occupational Safety and Health (NIOSH) Method 5600, OP Pesticides, and similar to those used by the California Air Resources Board, as summarized by Baker et al. (1996). Air will be sampled at six to ten liters per minute using glass Occupational Safety and Health Administration Versatile Sampler tubes. These tubes contain two sections of XAD®-2 sorbent material preceded by quartz particulate matter filters. Calibrated rotameters will be used to measure sample flow rates at the start and end of each sampling period. Sampling tubes will be placed one to two meters above ground level to avoid contamination from ground sources and at least one-half to one meter away from any obstructions. Tubes will be oriented vertically towards the ground and covers will be placed overhead to prevent contamination from precipitation, settling dust, and debris. Duplicate samples will be collected in tandem at each site and on every sampling day. Approximately ten field spikes and 10 field blanks (10% of total samples) will be collected during Phase 1 for quality assurance purposes.

### ***Sample Handling***

All sorbent tubes will be handled with latex gloves, capped, and stored individually in sealed plastic bags on ice in an insulated ice chest immediately

following sample collection and during transport from the site of collection to the University of Washington. Upon arrival at the University of Washington, samples will be removed from the ice chest and stored at approximately -10 °C pending transfer to the University of Washington's Environmental Health Laboratory and Trace Organics Analytical Center for pesticide analysis.

### **Sample Analysis**

In accordance with NIOSH Method 5600, samples will be extracted using a toluene/acetone solution and analyzed by gas chromatography using a flame photometric detector. To attain the low detection limits required for this study, exceptions to the procedures presented in NIOSH Method 5600 may include dilution of a 10-µg/mL versus 10-mg/mL OP pesticide stock solution, additional quality control spikes, preparation of quality control spikes, and modification of the sample preparation procedures.

### **Sampling Plan Rationale**

The proposed sampling plan seeks community stakeholder support from both growers and farm workers to achieve the study aims. Both community groups will be engaged to identify specific sample sites and ambient monitoring locations. The approach described above will sample a range of data sources and strikes a balance between a monitoring plan that closely follows a known spray and a monitoring plan that strictly samples receptor locations without regard to the conditions or timing of events at the applied fields. This sampling plan will provide data on the range of actual community exposures, and will also provide a basis for estimating the upper ranges of exposure that may occur near applied fields.

The near-field *perimeter* sample locations will provide air concentration data immediately adjacent to and downwind of an applied field. Valuable additional data such as the application rate, timing of the application, position and characteristics of the sprayer will be available by engaging grower cooperation. This will allow the study team to accurately measure and model the spray event and post-application emissions based on the source conditions and on-site meteorology. These measurements and modeling results together can provide an assessment of the upper range for potential pesticide exposures, and a modeling tool for estimating the range of exposures in nearby communities under a variety of application and weather scenarios. The monitoring will strive to capture the air concentrations near a sprayed field on a typical day and for several days post spray. We recognize that prior knowledge of the monitoring potentially could affect measurements during applications, but obtaining accurate spray information during the application removes a large uncertainty in the data collection. We believe that post-application volatilization is unlikely to be affected by prior notification, since this largely depends on the local meteorology, which is beyond the grower's control.

The near-field *receptor* sample locations will provide air concentration data at community receptor locations near applied fields. Ideally the near-field receptor locations will be within 200 meters of applied fields, but we will not have specific information on the application timing or locations. These receptor positions will be sampled without prior notification, and at locations noted by community members to be of special concern. This sampling also will be conducted so as to respect the privacy and wishes of community members to remain anonymous. The near-field receptor locations will allow the study team to establish a range of exposures that occur in community areas near applied fields when multiple sources are present. In addition, when coupled with ambient community monitoring data, this monitoring should capture data representing the distribution of community air exposures during the sampling periods.

We have considered monitoring aerial applications of methamidophos on potatoes, but our previous work has indicated that the off-target concentrations following such applications do not represent a significant health risk for nearby communities (Ramaprasad et al., 2008).

## References

Baker LW, Fitzell DL, Seiber JN, Parker TR, Shibamoto T, Poore MW, Longley KE, Tomlin RP, Propper R, Duncan DW. 1996. Ambient air concentrations of pesticides in California. *Environ Sci Technol* 30:1365-1368.

Ramaprasad J, Yost MG, Fenske RA et al. 2008. Children's Inhalation Exposure to Methamidophos from Sprayed Potato Fields in Washington State: Exploring the Use of Probabilistic Modeling of Meteorological Data in Exposure Assessment. *J Exp Sci Environ Epid* (Manuscript ID JESEE-07-0526; accepted for publication)

Tolbert LA, Yost MG, Kissel JC, Galvin K, Fenske RA. 2008. Ambient air concentrations of organophosphorus pesticides due to volatilization during seasonal pesticide applications. Manuscript in preparation. (See also Master of Science Thesis by Lisa A. Tolbert, University of Washington Department of Environmental and Occupational Health Sciences, 2007.)





**Table 1.** Phase 1 sampling strategy for measurement of chlorpyrifos air concentrations associated with orchard spraying

<b>Location</b>	Region 1 – high chlorpyrifos use areas			Region 2 -- high chlorpyrifos use areas		
	Early Spray Period	Late Spray		Early Spray Period	Late Spray	
<b>Site</b>	1	2	1 & 2	3	4	3 & 4
<b>Site Selection</b>	Grower cooperation	Farm worker cooperation	*	Grower cooperation	Farm worker cooperation	*
<b>Sample type 1</b>	Near-field perimeter	Near-field receptor	*	Near-field perimeter	Near-field receptor	*
<b>Sampling points</b>	4	2	*	4	2	*
<b>Sampling days</b>	5	10	*	5	10	*
<b>Sample type 2</b>	Ambient community	Ambient community	*	Ambient community	Ambient community	*
<b>Sampling points</b>	1	1	*	1	1	*
<b>Sampling days</b>	5	5	*	5	5	*
<b>Total samples</b>	<b>25</b>	<b>25</b>	<b>50</b>	<b>25</b>	<b>25</b>	<b>50</b>

\* Sampling procedures during the later part of the chlorpyrifos spray period will replicate those used in the early spray period for Sites 1, 2, 3 and 4.



## **Pilot Organophosphorus Pesticide Air Monitoring Project**

### **FINAL SAMPLING PLAN**

Richard Fenske, Michael Yost, Kit Galvin, Cole Fitzpatrick, Maria Tchong  
Department of Environmental and Occupational Health Sciences  
School of Public Health and Community Medicine  
University of Washington

**February 29, 2008**  
**(revised March 31, 2008)**

Submitted to

Cynthia Lopez, Manager, Department of Health Pesticide Program  
P.O. Box 47845, Olympia, WA 98504-7845

#### **1. PURPOSE**

In April 2007 the Washington State Legislature requested an “examination of airborne pesticide concentrations in agricultural areas of the state.” The University of Washington’s Department of Environmental and Occupational Health Sciences (UW-DEOHS) was assigned the task of monitoring organophosphorus (OP) pesticides in agricultural regions of Washington State. UW-DEOHS will measure air concentrations of OP pesticides used in Washington agriculture during the 2008 growing season. The purpose of this monitoring is to examine whether off-target movement of OP pesticides during and following pesticide applications poses a potential risk to residents or bystanders.

##### **1.1 Budget**

The University of Washington submitted a fiscal note in February 2007 at the request of the state legislature. The UW fiscal note requested \$289,000 in direct costs to conduct this project. UW also agreed to waive all indirect costs for the project. The Department of Health awarded the University of Washington a contract of \$250,000, resulting in a 13.5% reduction in available resources for the project. Further budget information is available upon request.

##### **1.2 Target Chemical Selection**

We plan to use the limited resources available to focus on OP pesticide applications that have relatively high toxicity, are in common use, and for which there has been little or no previous community air monitoring in Washington. We consulted U.S. Environmental Protection Agency information on acute and chronic toxicity; the Pesticide Incident Report and Tracking Panel reports for information on OP pesticide-related illnesses in the state; data from the National Agricultural Statistical Service to determine the most commonly used OP pesticides in the state; and a review of the existing literature to determine prior air monitoring of OP pesticides in the state. We also considered the physical characteristics of the compounds and the manner of their application. We concluded that orchard power blast applications of chlorpyrifos, (the active ingredient of Lorsban™) and azinphos-methyl (the active ingredient of Guthion™) were of highest priority. We did not prioritize malathion due its relatively low mammalian toxicity; we did not prioritize phosmet due to its low toxicity relative to azinphos-methyl; we did not prioritize aerial applications of methamidophos on potatoes, since an earlier study suggests that off-target

concentrations following such applications are probably not a significant health risk for nearby communities (Ramaprasad et al., 2008).

### **1.3 General Design**

We plan to conduct sampling in two phases. Phase 1 will focus on the late winter or early spring dormant airblast applications of OP pesticides on tree fruit. The target compound for Phase 1 will be the OP pesticide, chlorpyrifos. Phase 2 will focus on the late spring and early summer orchard spraying for codling moth control. The target compound for Phase 2 will be the OP pesticide, azinphos-methyl. The sampling strategy outlined below for Phase 1 will be duplicated for Phase 2.

## **2. PHASE 1 SAMPLING STRATEGY: CHLORPYRIFOS APPLICATIONS**

Our sampling strategy for the measurement of chlorpyrifos air concentrations is outlined in Table 1.

### **2.1 Regions**

We plan to sample in two tree fruit regions of Washington State where chlorpyrifos applications typically occur: the Yakima Valley and the greater Wenatchee area. The lower Columbia River valley was considered, but this was not possible logistically, since spraying in that region usually begins earlier than in the other regions. The appendix provides a chlorpyrifos and azinphos-methyl use-density maps for the Yakima and Wenatchee regions. The maps were developed by our research team using data from the WA Department of Agriculture, the National Agricultural Statistical Service, and the U.S. census. A description of the method used to develop the maps is included in the appendix.

### **2.2 Sample Types**

We intend to collect three types of samples: near-field receptor; ambient community; and near-field perimeter. Collection of each of these types of samples requires a different sampling strategy, as outlined below.

#### **2.2.1 Near-Field Receptor Sampling**

The purpose of near-field receptor sampling is to determine chlorpyrifos air concentrations at locations where people live or spend significant amounts of time, and to produce data sufficient to evaluate the risk for sub-acute exposures.

Sampling sites will be selected in cooperation with farm worker and other residential community members. We will identify locations that are believed to receive relatively high chlorpyrifos exposures during airblast applications on tree fruit. We will then place samplers in that location to capture the concentration of chlorpyrifos that might be encountered by individuals living at or frequenting these locations. We will collect two 24-hour samples each day for 28 days at each of three sampling sites in each region to characterize potential bystander exposure. Two quality assurance air samples will be collected at one site in each region concurrent with the other samples.

The near-field receptor site criteria are as follows: less than 100 meters from a crop associated with chlorpyrifos power blast applications; secure (fenced and locked or not readily accessible to the public); access seven days per week for 28 days; outdoor AC 110 power outlet; low foot traffic; not a pet area or play area; no vehicle traffic; samplers located 1-2 meters from the ground; sampler distance from buildings, walls or solid fences at least one-half the height of structure.

### **2.2.2 Ambient Community Sampling**

The purpose of ambient community sampling is to determine the exposure potential for the general population in the study area, and to provide a reference value for the other data collected in the study.

We will collect one 24-hour ambient community sample each day in each region over the 28-day study period. The ambient sampler will be located in a nearby community to determine air concentrations distant from the application site. Prior experience and dispersion modeling results from other studies suggest that the ambient community monitoring locations should be located at least one-half kilometer from the nearest applied fields. Previous sampling in a Washington agricultural region (Tolbert et al. 2008) indicated that ambient community air can be considered reasonably well mixed on a scale of five to ten kilometers.

The ambient community site criteria are as follows: at least one-half kilometer (500 meters) from from a crop associated with chlorpyrifos power blast applications; secure (fenced and locked or not readily accessible to the public); access 24 hours per day and 7 days per week for 28 days; outdoor AC 110 power source.

### **2.2.3 Near-Field Perimeter Sampling**

The purpose of near-field perimeter sampling is to determine chlorpyrifos air concentrations at the edge of an application site, and to produce data sufficient to evaluate the risk for acute exposures.

We will conduct near-field perimeter sampling at two sites. These sites will be selected in cooperation with the grower community. The grower will provide information regarding the application rate, the duration of application, the total amount of active ingredient applied, and other information relevant to an emission rate estimate. We plan to attach a global positioning system (GPS) unit to the spray tractor to document its movement. We will also collect on-site meteorological information throughout the sampling period. The combination of this information will allow us to construct a model of off-target pesticide movement.

We will conduct near-field perimeter sampling following the approach used by the California Air Resources Board. A four day sampling schedule will be used for each region: pre-spray day; spray day; post-spray day 1; post-spray day 2.

On the pre-spray day 12 to 24-hour samples will be collected at four locations around the perimeter of the orchard block to be sprayed. On the spray day and on the first post-spray day three consecutive approximate 8-hour samples (for a total of 24 hours) will be collected at eight locations. On the second post-spray day, 12 to 24-hour hour samples will be collected at the eight locations. The eight-hour samples will take place at approximately 6:00-14:00, 14:00-22:00, and 22:00-6:00). Each day two quality assurance samples will be collected at each site as per the sample schedule for that day.

The near-field perimeter site criteria are as follows: well-defined orchard block that can be treated in one day by a single applicator; access 24 hours per day for the 4-day study period; use of power blast application equipment; no drift retardant used during applications; secure; use of generators 24 hours per day acceptable to property owners and neighbors; at least 100 meters from other orchards that will be treated with chlorpyrifos during the study period.

### **3. PHASE 2 SAMPLING STRATEGY: AZINPHOS-METHYL APPLICATIONS**

The target compound for Phase 2 sampling will be azinphos-methyl and phosmet.. The temporal sampling frame is expected to be mid-May through early July. We intend to use the sampling strategy for Phase 2 that we have outlined for Phase 1. Any proposed modifications in the sampling plan for Phase 2 will be discussed with the Department of Health and its Technical Review Panel.

### **4. SAMPLING METHODS**

#### ***4.1 Meteorological Data***

A portable meteorological station will be run continuously throughout the sampling period at each of the near-field perimeter sampling sites to monitor local weather conditions such as temperature, pressure, rainfall, wind speed and wind direction. Local weather data will be collected in association with the near-field receptor and ambient community sampling.

#### ***4.2 OP Pesticide Sampling***

Sampling for chlorpyrifos will be performed according to methods presented in the National Institute for Occupational Safety and Health (NIOSH) Method 5600, OP Pesticides, and similar to those used by the California Air Resources Board, as summarized by Baker et al. (1996). Near-field perimeter samples will be collected at 6 liters per minute using glass Occupational Safety and Health Administration Versatile Sampler (OVS) tubes. Near-field receptor and ambient community sampling will use the same tubes and a flow-rate of 2 liters per minute. The sampling tubes contain two sections of XAD®-2 sorbent material preceded by quartz particulate matter filters. Calibrated rotameters will be used to measure sample flow rates at the start and end of each sampling period. Sampling tubes will be placed one to two meters above ground level to avoid contamination from ground sources and will be covered to shield from sunlight and rain. Samplers will be placed at a distance from obstructions according to the following formula used by the California Air Resources Board: place the sampler at a distance from the obstruction that is at least one-half the height of the obstruction. Duplicate samples will be collected at each sample location and on every sampling day. Field spikes and blanks representing the equivalent of 10% of the samples collected will be prepared and analyzed for quality assurance purposes. Standard operating procedures (SOPs) for the field sampling and QA/QC sampling are available upon request.

#### ***4.3 Sample Handling***

All sorbent tubes will be handled with nitrile gloves, capped, and stored individually in sealed plastic bags on ice in an insulated ice chest immediately following sample collection and during transport from the site of collection to a field transfer station. Upon arrival samples will be removed from the ice chest and stored at approximately -20 °C pending transfer to the University of Washington's Environmental Health Laboratory and Trace Organics Analytical Center for pesticide analysis.

#### ***4.4 Sample Analysis***

Samples will be analyzed at the University of Washington Environmental Health Laboratory. This laboratory is AIHA certified, and has many years of experience in the analysis of environmental samples containing pesticides. We expect the laboratory to follow NIOSH Method 5600: i.e., samples will be extracted using a toluene/acetone solution and analyzed by gas chromatography using a flame photometric detector. To attain lower detection limits the laboratory may modify NIOSH Method 5600 procedures. A full report providing the laboratory

procedures will be submitted to the Department of Health as part of the University of Washington's Analytical Plan.

## 5. SAMPLING PLAN RATIONALE

The proposed sampling plan seeks community stakeholder support from both growers and farm workers to achieve the study aims. Both community groups will be engaged to identify specific sample sites. The approach described above will sample a range of data sources and strikes a balance between a monitoring plan that closely follows a known spray and a monitoring plan that strictly samples receptor locations without regard to the conditions or timing of events at the applied fields. This sampling plan will provide measurements of actual community exposures, and will also provide a basis for estimating the upper range of exposure that may occur near applied fields.

The near-field receptor sample locations will provide air concentration data near crops that are likely to be sprayed with chlorpyrifos. Washington State does not require pesticide use reporting, so we may be unable to confirm specific information on applications to nearby crops. This sampling will be conducted so as to respect the privacy and/or wishes of community members to remain anonymous. The near-field receptor locations will allow the study team to establish a range of exposures that occur in community areas near commonly treated crops during the peak spraying time when multiple orchards may be sprayed concurrently or consecutively.

The near-field perimeter sample locations will provide air concentration data immediately adjacent to known chlorpyrifos-treated orchards. Additional data such as the application rate, timing of the application, position and characteristics of the sprayer will be available by engaging grower cooperation. This information will allow the study team to accurately measure and model the spray event and post-application emissions based on the source conditions and on-site meteorology. These measurements can provide an assessment of the upper range for potential pesticide exposures, and will serve as the basis of a modeling tool for estimating the range of exposures in nearby communities under a variety of application and weather scenarios. The monitoring will strive to capture the air concentrations near a sprayed field on a typical day and for several days post spray. We recognize that prior knowledge of the monitoring potentially could affect measurements during applications, but obtaining accurate spray information during the application removes a large uncertainty in the data collection. We believe that post-application volatilization is unlikely to be affected by prior notification, since this largely depends on the local meteorology, which is beyond the grower's control.

## 6. REFERENCES

- Baker LW, Fitzell DL, Seiber JN, Parker TR, Shibamoto T, Poore MW, Longley KE, Tomlin RP, Propper R, Duncan DW. 1996. Ambient air concentrations of pesticides in California. *Environ Sci Technol* 30:1365-1368.
- Ramaprasad J, Yost MG, Fenske RA et al. 2008. Children's Inhalation Exposure to Methamidophos from Sprayed Potato Fields in Washington State: Exploring the Use of Probabilistic Modeling of Meteorological Data in Exposure Assessment. Submitted to the *Journal of Exposure Science and Environmental Epidemiology*.
- Tolbert LA, Yost MG, Kissel JC, Galvin K, Fenske RA. 2008. Ambient air concentrations of organophosphorus pesticides due to volatilization during seasonal pesticide applications. Manuscript in preparation. (See also M.S. Thesis by Lisa A. Tolbert, University of Washington Department of Environmental and Occupational Health Sciences, 2007)

**Table 1.** Phase 1 sampling strategy for measurement of chlorpyrifos air concentrations associated with orchard spraying in Yakima and Wenatchee regions

<b>Receptor Samples</b>	Within 100 meters of orchard land
Time frame	28 days to capture chlorpyrifos spray
Number of sites per region	3
Number of air samples per site	2 per day
Sample duration	24-hour
Sample flow rate	2 liters per minute
Quality assurance air samples	2 per day at one site in each region
Total air samples	336 (168 per region)
QA air samples	112 (56 per region)
Field spikes and blanks	45 (additional 10%)
<b>Total Receptor Samples</b>	<b>493</b>
<b>Ambient Samples</b>	At least 500 meters from orchard land
Time frame	28 days to capture chlorpyrifos spray
Number of sites per region	1
Number of air samples per site	2 per day
Sample duration	24-hour
Sample flow rate	2 liters per minute
Quality assurance air samples	none
Total air samples	112 (56 per region)
Field spikes and blanks	11 (10% additional)
<b>Total Ambient Samples</b>	<b>123</b>
<b>Perimeter Samples</b>	Within 15 meters of sprayed orchard
Time frame	4 days to capture chlorpyrifos spray
Number of sites per region	1
<i>Pre-spray day samples</i>	
Number of air samples per site	8
Sample duration	12 to 24-hour
Sample flow rate	6 liters per minute
Quality assurance air samples	2 at each site
<i>Spray day samples</i>	
Number of air samples per site	16
Sample duration	3 8-hour time periods
Sample flow rate	6 liters per minute
Quality assurance air samples	2 at each site for each time period
<i>Post-spray: day 1 samples</i>	
Number of air samples per site	16
Sample duration	3 8-hour time periods
Sample flow rate	6 liters per minute
Quality assurance air samples	2 at each site for each time period
<i>Post-spray: day 2 samples</i>	
Number of air samples per site	16
Sample duration	12 to 24-hour
Sample flow rate	6 liters per minute
Quality assurance air samples	2 at each site
Total air samples	272 (136 per site)
Field spikes and blanks	27 (10% additional)
<b>Total Perimeter Samples</b>	<b>297</b>
<b>Total Phase 1 Air Samples</b>	<b>913</b>



## Pilot Organophosphorus Pesticide Air Monitoring Project

### PROGRESS REPORT

June 17, 2008

Richard A. Fenske and Michael G. Yost  
 Kit Galvin, Maria Tchong-French, Pablo Palmández, Maria Negrete, Cole  
 Fitzpatrick, Ming Tsai, Robert Crampton

Department of Environmental and Occupational Health Sciences  
 School of Public Health and Community Medicine  
 University of Washington

Submitted to

Cynthia Lopez, Manager, Department of Health Pesticide Program  
 P.O. Box 47845, Olympia, WA 98504-7845

#### 1. PERIMETER AIR SAMPLING AND ANALYSIS

Perimeter samples at one application site (orchard) in each of two regions were collected in accordance with the Phase 1 sampling plan presented in Table 1.1 below. For each sample period, duplicate samples were collected at each sample site at each location. Details regarding field blank and spike quality control (QC) samples are included in Appendix 1, SOP #3.

**Table 1.1** Perimeter Sampling Plan – Phase 1

	Sample Day			
	Pre-spray	Spray	Post-spray 1	Post-spray 2
<b># Sample periods</b>	1	3	3	1
<b>Perimeter air samples</b>				
# sample locations	4	8	8	8
# samples per location <sup>a</sup>	2	2	2	2
# <i>perimeter samples</i>	8	48	48	16
<b>QC air samples</b>				
# sample location <sup>b</sup>	1	1	1	1
# samples per location <sup>a</sup>	2	2	2	2
# <i>QC air samples</i>	2	6	6	2
<b># Air samples/day</b>	10	54	54	18
# air samples/region			136	
# air samples/ two regions			272	
# field blanks and spikes (10%) estimate			27	
<b>Total number of sample tubes</b>			<b>299</b>	

<sup>a</sup> At each sample location two samples 'side-by-side' were collected during each sample period.

<sup>b</sup> The QC samples were co-located at one of the perimeter sampling locations.

**NOTE:** In the original sampling plan, the number of sampling periods for Post-spray day 1 was three (8-hr) sampling periods. For both regions, the number of sampling periods for Post-spray day 1 was changed to two (12-hr) sampling periods. For Region 1, the sample period durations for the Spray day were two 6-hr periods followed by one 12-hr period. For Region 2, Spray day had three 8-hour sample periods.

The total number of samples collected is indicated in Table 1.2 below.

**Table 1.2** Perimeter sample collection

<b>Sample Type</b>	<b>Region 1</b>	<b>Region 2</b>	<b>Total</b>
# air samples	118	118	<b>236</b>
# field blanks	14	14	<b>28</b>
# field spikes	14	14	<b>28</b>
<b>Total</b>	<b>146</b>	<b>146</b>	<b>292</b>

We plan to submit an initial batch of samples for analysis that will include one air sample for every sample period, for each location within each region (site) and one QC air sample for each sample period within each region. We will also submit one field blank and two (one high and one low) field spikes per day. If field blanks show levels of concern, then the remaining field blanks will be analyzed. All remaining samples will be kept in storage (-20°C).

**Table 1.3** Perimeter sample analysis

<b>Sample Type</b>	<b>Region 1</b>	<b>Region 2</b>	<b>Total</b>
# air samples	59	59	<b>118</b>
# field blanks	4	4	<b>8</b>
# field spikes	8	8	<b>16</b>
<b>Total</b>	<b>71</b>	<b>71</b>	<b>142</b>

## **2. RECEPTOR AND AMBIENT SAMPLE COLLECTION AND ANALYSIS**

We collected air samples at three receptor locations and one ambient location in each of two regions, in accordance with the Phase 1 sampling plan (see Tables 2.1a and 2.1b). Two samples were collected side-by-side at each location during each sampling period. QC air samples were collected at one of the receptor locations in each region. Details regarding field blank and spike QC samples are included in Appendix 1, SOP #4.

**Table 2.1a** Receptor sampling plan – Phase 1

<b>Receptor air samples</b>	
# sampling periods	28
# sites	3
# samples per site <sup>a</sup>	2
# receptor air samples/region	168
<b># receptor air samples/2 regions</b>	<b>336</b>
<b>QC air samples</b>	
# sampling periods	28
# sites <sup>b</sup>	1
# samples per site <sup>a</sup>	2
# QC air samples	56
<b># QC air samples/2 regions</b>	<b>112</b>
<b>Total Air Samples</b>	<b>448</b>
<b>Field blanks and spikes</b>	
# estimate (10%)	45
<b>Total number of sample tubes</b>	<b>493</b>

<sup>a</sup> At each sample site two samples 'side-by-side' were collected during each sample period.

<sup>b</sup> The QC samples were co-located at one of the sampling locations.

**Table 2.1b** Ambient Sampling Plan – Phase 1

<b>Ambient air samples</b>	
# sampling periods	28
# sites	1
# samples per site <sup>a</sup>	2
# receptor air samples/region	56
<b># receptor air samples/2 regions</b>	<b>112</b>
<b>QC air samples</b>	
# sampling periods	0
<b># QC air samples/2 regions</b>	<b>0</b>
<b>Total Air Samples</b>	<b>112</b>
<b>Field blanks and spikes</b>	
# estimate (10%)	11
<b>Total number of sample tubes</b>	<b>123</b>

<sup>a</sup> At each sample site two samples 'side-by-side' were collected during each sample period.

<sup>b</sup> The QC samples were co-located at one of the sampling.

**NOTES:** There were 40 sampling periods for Region 1 and 35 sampling periods in Region 2. The duration of all sampling periods were 24 hours, except for one 48 hr period in both regions. In Region 1, the sampling period was extended from 28 to 40 days because

weather conditions delayed the onset of chlorpyrifos application in the region. In Region 2, all sites were sampled over at least 28 days. However, not all sites started and stopped on the same day. Site 1 (ambient) started on day 1 had 35 sampling periods with valid samples; Site 2 (receptor) started on day 5 and had 21 sampling periods with valid samples; Site 3 (receptor and QC) was started on day 2 and had 30 sampling periods with valid samples; and Site 4 started on day 9 and had 26 sampling periods with valid samples. The staggered start days and invalid samples were due to a combination of un-anticipated restricted access to the samplers and power supply failures. In addition, one site had to be relocated after starting the study.

**Table 2.2** Receptor and ambient air sample collection

<b>Sample Type</b>	<b>Region 1</b>	<b>Region 2</b>	<b>Total</b>
# sample periods	40	35	n/a
# air samples	392	280	<b>672</b>
# field blanks	40	35	<b>75</b>
# field spikes	40	37	<b>77</b>
<b>Total</b>	<b>472</b>	<b>352</b>	<b>824</b>

We plan to submit an initial batch of samples for analysis that will include one side-by-side sample from each receptor site, the ambient site, and the QC site for every other sampling period (Table 2.3). Also for each region we will submit one field blank and one field spike from half of the submitted air sampling periods. For Region 1, we will submit samples from every other sample period for the last 30 sample periods. The remaining samples will be kept in storage (-20C).

**Table 2.3** Receptor and ambient air sample analysis

<b>Sample Type</b>	<b>Region 1</b>	<b>Region 2</b>	<b>Total</b>
# air samples	75	70	<b>145</b>
# field blanks	8	9	<b>17</b>
# field spikes	8	9	<b>17</b>
<b>Total</b>	<b>91</b>	<b>88</b>	<b>179</b>

### 3. STANDARD OPERATING PROCEDURES

Standard Operating Procedures for the study are attached as Appendix 1.

### 4. SAMPLE ANALYSIS

Samples will be analyzed by the UW Environmental Health Laboratory following the NIOSH 5600 method for organophosphorus pesticides. This method will be used for both chlorpyrifos and chlorpyrifos-oxon.

## **5. PHASE 2 SAMPLING**

Sampling in Phase 2 will focus on azinphosmethyl and phosmet applications for codling moth. Due to budget constraints sampling in this phase will be limited to one region. Due to the longer spraying period (60-90 days), receptor and ambient sampling will take place every third day.

## **6. ANALYSIS FOR AZINPHOSMETHYL AND PHOSMET DURING PHASE 2**

Samples will be analyzed by the UW Environmental Health Laboratory following the NIOSH 5600 method for organophosphorus pesticides. This method will be used for both azinphosmethyl and phosmet in Phase 2.

## **7. PROJECT BUDGET**

See Appendix 2.



## **Pilot Organophosphorus Pesticide Air Monitoring Project**

### **Progress Report: Task 4**

**August 1, 2008**

Richard A. Fenske and Michael G. Yost  
Kit Galvin, Maria Tchong-French, Pablo Palmández, Maria Negrete, Cole Fitzpatrick,  
Ming Tsai, Robert Crampton

Department of Environmental and Occupational Health Sciences  
School of Public Health and Community Medicine  
University of Washington

Submitted to

Cynthia Lopez, Manager, Department of Health Pesticide Program  
P.O. Box 47845, Olympia, WA 98504-7845

This report provides the study protocols used to collect air samples, meteorological and other data for the Pilot Organophosphorus Pesticide Air Monitoring Project. The protocols include siting, scheduling, handling and chain of custody documentation, as well as a description of analytical methods, data gathering, and reporting procedures in fulfillment of Task #4 from the Statement of Work, contract number N162243. Standard Operating Procedures referenced in this report are included in the Appendices. This report does not contain study results.

## Table of Contents

<b>1.0 Introduction</b>	<b>1</b>
<b>2.0 Site Selection</b>	<b>1</b>
2.1 Regions	1
2.2 Near-field perimeter sites	2
2.3 Near-field receptor sites	2
2.4 Ambient community sites	3
<b>3.0 Air Sample Collection</b>	<b>3</b>
3.1 Sampling apparatus	3
3.2 Near-field perimeter site layout and sampling plan	4
3.3 Near-field receptor and ambient community air samples sampling plan	5
3.4 Sample storage and transport	6
3.5 Chain of custody	6
<b>4.0 Air Sample Analysis</b>	<b>6</b>
4.1 Sample analysis plan	6
4.2 Analytical methods	7
<b>5.0 Meteorological Data Collection</b>	<b>7</b>
5.1 Meteorological station site selection	8
5.2 Meteorological data collection methods	8
<b>6.0 Data Management and Analysis</b>	<b>9</b>
6.1 Data entry and storage	9
6.2 Air sample data analysis	9
6.3 Meteorological data summary	9
<b>7.0 References</b>	<b>9</b>
<b>Appendices</b>	
<b>Appendix A: Chlorpyrifos and Azinphosmethyl Use-Density Maps for     Selected Regions in Washington State</b>	
<b>Appendix B: Standard Operating Procedures (SOPs)</b>	
SOP 1: Sample Apparatus Set-Up	
SOP 2: This calibration procedure was not used	
SOP 3: Perimeter Air Sample Collection	
SOP 3A: Perimeter Air Sample Collection – Addendum	
SOP 4: Receptor & Ambient Air Sample Collection	
SOP 4A: Receptor & Ambient Air Sample Collection – Addendum	
SOP 5: Labeling	
SOP 6: DryCal Calibration in Laboratory	
SOP 7: Rotameter Calibration in Laboratory	
SOP 8: Chain of Custody	



## **1.0 Introduction**

In accordance with the revised Sampling Plan submitted on March 31, 2008, air sampling took place over two phases. Phase 1 occurred during the early spring and captured dormant power blast applications of the organophosphorus (OP) pesticide, chlorpyrifos, on tree fruit. Phase 2 took place during late spring and early summer during power blast applications of azinphosmethyl. Two other organophosphorus pesticides, phosmet and malathion, were also used on tree fruit during Phase 2 and were included in laboratory analyses. Malathion was not necessarily applied with a power blast sprayer but may be found in the air.

Three types of samples were collected: near-field perimeter, near-field receptor, and ambient community air samples. The following describes the purposes of each sample type:

### *Near-field Receptor*

- Determine OP air concentrations at locations where people live or spend significant amounts of time.
- Produce data sufficient to evaluate the risk for sub-acute exposures.

### *Ambient Community*

- Determine the exposure potential for the general population in the study area.
- Provide a reference value for the other data collected in the study.

### *Near-field Perimeter*

- Determine OP air concentrations at the edge of an application site.
- Produce data sufficient to evaluate the risk for acute exposures.

Two tree fruit growing regions in Washington State were selected for the study. During Phase 1 air sampling was conducted in both regions: at three near-field receptors sites, one ambient community site, and one near-field perimeter site. During Phase 2 air sampling was conducted in only one of the two regions.

## **2.0 Site Selection**

The site selection process first identified two regions. Within each region we contacted potential cooperators as described below. A key aspect to obtaining cooperation from each site was to assure the grower or occupant that participation in the study was confidential, and we would not identify the cooperator or disclose the site location. For every site in the study, study team members conducted a pre-selection visit to determine site suitability and verify that the site met study requirements. We also confirmed that the cooperator understood the study requirements and was comfortable with the placement of equipment on the property.

### **2.1 Regions**

The site selection process started with identifying two tree fruit regions of Washington State where OP pesticide applications typically occur: the greater

Wenatchee area (Region 1) and the Yakima Valley (Region 2). Appendix A provides the chlorpyrifos and azinphos-methyl use-density maps for the Yakima and Wenatchee regions. The maps were developed by our research team using data from the WA Department of Agriculture, the National Agricultural Statistical Service, and the U.S. census. A description of the method used to develop the maps is also included in Appendix A. Prior to selecting specific sites we spoke with Agricultural Extension Service scientists and specialists, crop advisors (field men), and growers. We compared their reports of 2008 practices and pesticide usage to data from the maps. We also used the 2008 information to select appropriate areas within a region from which we recruited specific sites.

### **2.2 Near-field perimeter sites**

The near-field perimeter sampling sites were selected in cooperation with the grower community. The following criteria were used to select these sites:

- Well-defined orchard block that can be treated in one day by a single applicator
- Research staff access to the site 24 hours per day for the 4 day study period
- Application with power blast application equipment
- No drift retardant used during applications
- Secure; based on discussions with the owner
- Use of generators 24 hours per day acceptable to property owners and neighbors
- Treated block at least 100 meters from other orchards that will be treated with chlorpyrifos (Phase 1) or azinphosmethyl (Phase 2) during the study period
- Access to information on the amount of pesticide used during the application

One near-field perimeter site was selected for each region. The same Region 2 site was used for both Phase 1 and Phase 2. The grower provided information regarding the application rate, the duration of application, the total amount of active ingredient applied, and other information relevant to an emission rate estimate.

### **2.3 Near-field receptor sites**

Potential sampling sites were identified in cooperation with farm workers, residential and school community members, and community organizations. We selected three sites in each region that had the potential to receive relatively high OP pesticide exposures during power blast applications on tree fruit. When possible, we selected sites in proximity to multiple orchards. While we were not able to pre-determine if nearby orchards were being treated with conventional pesticides, staff observed posted signs such as those for re-entry and those posted along road right-of-ways indicating organic orchards. The following were the near-field receptor site requirements:

- Within 100 meters of orchards to be treated with chlorpyrifos (Lorsban®), azinphosmethyl (Guthion®), or phosmet (Imidan®) during the study period
- Secure; fenced and locked or not readily accessible to the public
- Access for staff 7 days per week for 28 days
- Outdoor AC 110 power outlet, if possible
- Low foot traffic
- Not a pet or play area
- No vehicle traffic

- Visitor-friendly pets only
- Sampler located 1-2 meters from the ground
- Sampler distance from buildings, walls, or solid fences at least one-half the height of structure (for buildings use the roof peak as the structure height)

Three sites in each region were selected for the near-field receptor sampling. Each sample location was documented with GPS coordinates using an EnerTech Global Positioning System Recording Meter (Campbell, CA). The quality control air samples were co-located at one of the three near-field receptor sites in each region.

*Note: Replacement sites were recruited as needed following the same protocol as for the original site selection. During Phase 1 one site in Region 2 was replaced before sampling started. Before Phase 2 began, two sites in Region 2 were replaced.*

### **2.4 Ambient community sites**

The ambient community sites were situated in a community nearby the near-field receptor sites. The ambient community site criteria were as follows:

- At least 500 meters from orchards to be treated with chlorpyrifos (Lorsban®), azinphosmethyl (Guthion®), or phosmet (Imidan®) during the study period
- Secure; fenced and locked or not readily accessible to the public
- Access for staff 7 days per week for 28 days
- Outdoor AC 110 power source, if possible

One ambient community site was selected for each of the two regions.

## **3.0 Air Sample Collection**

Sampling and analysis for volatilized OP pesticides were conducted following the NIOSH Analytical Method 5600 *Organophosphorus Pesticides* (NIOSH 1994) and the sampling approach of the California Air Resources Board (CARB) as summarized by Baker et al. (Baker 1996). Modifications to these methods were made to accommodate the requirements of this study and are included in the methods description below.

In accordance with the NIOSH method, we used OVS XAD®-2 sorbent tubes (cat no 226-58, SKC Inc, Eighty Four, PA). These sampling tubes consisted of a 13-mm quartz particulate matter filter, followed by a front and a back up section of XAD®-2 sorbent. Sample flow rates were adjusted to approximately 2.0 liters per minute (lpm) for the receptor and ambient samples and 6.0 lpm for the perimeter samples. Two samples were collected in tandem for each sample period at each site and location.

### **3.1 Sampling apparatus**

The sampling train for all sample pairs was attached to a 2 meter 'T'-shaped mast with a cover for rain protection. Each side of the 'T' held one XAD®-2 parallel to the ground. Flow rates for each sample were monitored and adjusted with dedicated rotameters that were calibrated before and after the study period using a DryCal DC-Lite Primary Airflow Meter (BIOS International Corporation, model no DCLT-12K, Butler, NJ). The DryCal was calibrated to a bubble flow meter (primary standard) prior to the rotameter calibration. (See SOP 1: Sample Apparatus Set-Up, SOP 6:

DryCal Calibration in Laboratory, and SOP 7: Rotameter Calibration in Laboratory in Appendix B.)

Perimeter samples were collected using SKC Hi-Lite 30 air sampling pumps (cat no 228-31, SKC, Inc, Eighty Four, PA). One pump was used for each sample location, with the air flow from the pump split between the two rotameters.

Each near-field receptor and community ambient air sample was collected with a separate SKC Universal Sample Pump (cat no 224-PCXR8, SKC, Inc, Eighty Four, PA). Because of the long sample periods (24 hours), the pumps were equipped with a Battery Eliminator (cat # 223-325, SKC, Inc, Eighty Four, PA) to enable the use of marine deep cycle batteries or a 110 AC for power. These power sources were used because the pump battery was limited to an 8 hr run time before needing to be recharged.

### **3.2 Near-field perimeter site layout and sampling plan**

The sample collection procedures are detailed in SOP 3: Perimeter Air Sample Collection and SOP 3A: Perimeter Air Sample Collection – Addendum, located in Appendix B. The addendum includes modifications for Phase 2. SOP 5: Labeling, covers the unique sample identifiers for each sample.

**3.2.1 Site layout.** For each site, the eight perimeter sampling locations (stations) were set at the same distance from the orchard edge (defined by the outer tree trunks) and were approximately equidistant from each other. Additional factors that influenced the final location placement were as follows:

- One station at approximately each corner of the treated area (up to four)
- Locations not to block orchard access roads that circumvent orchard blocks
- Locations not to interfere with other orchard activities and equipment (e.g. irrigation, other types of applications, thinning, pruning)

Each sample location was documented with GPS coordinates using an EnerTech Global Positioning System Recording Meter (Campbell, CA).

**3.2.2 Sampling plan.** We conducted near-field perimeter sampling following the approach used by the California Air Resources Board (L. Baker, personal communication). The methods were modified to accommodate conditions specific to this project. A four-day sampling schedule was used for each region: pre-spray day; spray day; post-spray day 1; and post-spray day 2. The sampling plan used for both near-field perimeter sites during Phase 1 and the one site during Phase 2 is presented in Table 1.

**Table 1. Near-Field Perimeter Air Sampling Plan**

	Sample Day			
	<i>Pre-spray</i>	<i>Spray</i>	<i>Post-spray 1</i>	<i>Post-spray 2</i>
# Field air sample locations	4	8	8	8
# QC air sample locations <sup>1</sup>	1	1	1	1
# Sample periods per day	1 (morning)	3 (morning, lunch, night)	2 (morning, night)	1 (morning)
Sample period duration	24 hr	2 (6 hr) 1 (12 hr)	2 (12 hr)	24 hr
# Field & QC air samples <sup>2</sup>	10	54	36	18
# Field blanks <sup>3</sup>	2	6	4	2
# Field spikes <sup>3</sup>	2	6	4	2

<sup>1</sup>The QC air sampler was co-located at one of the field air sample locations.

<sup>2</sup>For each sample period at each location two side by side air samples are collected.

<sup>3</sup>Two field blanks and two field spikes were used for each sampling period.

**Note:** Changes in the proposed sampling plan were made to accommodate orchard application schedules and to increase sample volumes. Changes included: *Spray-day:* changed from three 8 hr hour sample periods to two 6 hr sample periods and one 12 hr sample period. *Post-spray day 1:* changed from three 8 hr sample periods to two 12 hr sample periods.

**3.2.3 Field quality control samples.** Quality control (QC) samples for each sample period in Phase 1 and Phase 2 consisted of two field blanks and two field spikes. For Phase 1, chlorpyrifos spike loads were 50 ng/tube for the low concentration and 250 ng /tube for the high concentration. For Phase 2 each spike tube was loaded with 50 ng of azinphosmethyl, phosmet, and malathion, and 20 ng of azinphosmethyl-oxon.

**3.2.4 Global Positioning System (GPS).** During the spray event the tractor path was documented with an EnerTech Global Positioning System Recording Meter (Campbell, CA) that recorded the GPS coordinates every 3 seconds. The unit was mounted on the tractor and the distance from the spray nozzles was recorded.

### 3.3 Near-field receptor and ambient community air samples sampling plan

One set of two side-by-side air samples were collected during each sample period for all near-field receptor and ambient community sites. One set of quality control air samples was collected each sample period at one of near-field receptor sites. The sample period was 24-hr. In Phase 1, sampling took place in March and April and sample periods were scheduled daily for 28 days. In Phase 2, the sampling periods were once every three days over a 70 day period during May, June, and July.

Sample collection procedures are described in SOP 4: Receptor & Ambient Air Sample Collection and SOP 4A: Receptor & Ambient Air Sample Collection – Addendum, located in Appendix B. The addendum includes modifications for Phase 2. SOP 5: Labeling covers the unique sample identifiers for each sample.

**Note:** *During Phase 1, the sampling schedule was extended beyond 28 days due to replacement of one site (Region 2) and the delay of the spray period due to cold weather (Region 1).*

**3.3.1 Field quality control samples.** For each region, two quality control air samples were co-located at one of the near-field receptor sites. The field quality control samples for each 24 hr sample period consisted of one field blank and one field spike. The spike load for Phase 1 spike was load 12.5 ng/tube of chlorpyrifos. The spike load in Phase 2 was 50 ng each of azinphosmethyl, phosmet, and malathion/tube.

**3.3.2 Global Positioning System (GPS).** Each site position was documented with an Enertech Global Positioning System Recording Meter (Campbell, CA).

### **3.4 Sample storage and transport**

After each sample period, the tubes were recapped, placed in individual resealable bags, and stored on ice for transportation to the PNASH field office freezer (-10 C). Samples were then transported on dry ice to the Fenske laboratory freezers (-20 C), where they were stored until they were submitted to the laboratory for analysis.

### **3.5 Chain of custody**

After sample collection, and each time custody of samples was transferred, the recipient verified receipt of each sample by matching the identification number on the tube with the number listed on the Chain of Custody data sheets. Also documented were the date, time, temperature, and sample storage method. Each recipient signed for the receipt of the samples. Chain of Custody procedures are detailed in SOP8: Chain of Custody, located in Appendix B.

## **4.0 Air Sample Analysis**

Samples are being analyzed at the University of Washington's Environmental Health Laboratory and Trace Organics Analytical Center, an AIHA-certified laboratory.

### **4.1 Sample analysis plan**

Phase 1 samples are being analyzed for chlorpyrifos and the chlorpyrifos-oxon. Phase 2 samples will be analyzed for azinphosmethyl, azinphosmethyl-oxon, phosmet, and malathion.

The initial analysis will be on a subset of the total number of samples analyzed. One sample from each side-by-side pair will be submitted for analysis. Table 2 describes the sample subset for each phase and sample type.

**Table 2. Sample Analysis Plan**

sample type	sub-set of samples submitted
<b>Phase 1</b>	
• near-field perimeter air samples	1/location/ sample period
• near-field perimeter quality control air samples	1/location/ sample period
• near-field perimeter field blanks and spikes	1 blank and 2 spikes/day
• near-field receptor air samples	1/site/every 2 <sup>nd</sup> sample period <sup>1</sup>
• near-field quality control air samples	1 every 2 <sup>nd</sup> sample period <sup>1</sup>
• ambient community air samples	1 every 2 <sup>nd</sup> sample period <sup>1</sup>
• near-field & ambient field blanks and spikes	1 each/every 4 <sup>th</sup> sample period
<b>Phase 2</b>	
• near-field perimeter air samples	1/location/sample period
• near-field perimeter quality control air samples	1/ sample period
• near-field perimeter field blanks and spikes	1 blank and 1 spike/day
• near-field receptor air samples	1/site/sample period
• near-field quality control air samples	1/site/sample period
• ambient community air samples	1/site/sample period
• near-field & ambient field blanks and spikes	1 each/sample period

<sup>1</sup>If sample was missing for a designated sample period, an alternate was selected from an adjacent day.

#### **4.2 Analytical methods**

The laboratory followed a modified version of NIOSH method 5600 (NIOSH 1994). The modifications allowed for an increase in sensitivity and included a different extraction solvent and detector. Samples were extracted with 5 ml of ethyl acetate by sonication followed by evaporation in the TurboVap to just dryness, then the residues were re-dissolved in 250 uL 2,2,4-trimethylpentane (TMP), and transferred to GC vials to be analyzed on the GC-MS or stored in a -20 C freezer until analysis. The analysis was done with an Agilent 6890 network gas chromatography system (Santa Clara, CA) equipped with a Restek (Bellefonte, PA) RTX-5 column (30m x 250 um, 0.1 um film thickness) and an Agilent (Santa Clara, CA) 5973V Mass Selective Detector.

**4.2.1 Recovery.** One matrix blank and four fortified (at 5.0 and 50.0 ng/tube) matrix blanks ran with each set of 19 submitted samples. In addition, field QC samples (field blanks, field spikes) were submitted along with the air samples.

**4.2.2 Storage stability.** Storage stability studies are conducted over a nine month period. The fortification levels are 12.5 ng/tube for chlorpyrifos and chlorpyrifos-oxon and 50 ng/tube for azinphosmethyl, azinphosmethyl-oxon, phosmet, and malathion.

#### **5.0 Meteorological Data Collection**

Meteorological data was collected from two sources. One source consisted of temporary meteorological stations set up for the purposes of this study and monitored by the University of Washington. Data was also downloaded from four Washington

State Agricultural Weather Stations (Network Version 2.0: AgWeatherNet) that were near the study sites.

### **5.1 Meteorological station site selection**

**5.1.1 Perimeter.** The UW temporary meteorological stations for perimeter sites were located in proximity to the treated block in an open area away from trees. They were a short distance from the treated area, so the instruments did not have direct contact with the application spray. Stations were set up and run prior to the pre-spray sampling day and taken down at the end of the post-spray day 2.

**5.1.2 Near-field receptor and ambient community.** The UW temporary meteorological station for these two sample types was co-located at the ambient community air sampling sites for each region.

### **5.2 Meteorological data collection methods**

**5.2.1 UW temporary meteorological stations.** 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. During the study period, data was downloaded daily.

The meteorological stations located at the ambient sampling sites were Davis Instruments Vantage Pro2 (either cabled or wireless) instruments (Hayward, CA). Each was equipped to record:

- Wind cup anemometer
- Wind direction vane
- Temperature & relative humidity

Data in both regions was logged at 15 minute intervals. During the study period, data was downloaded weekly.

**5.2.2 Washington State Agricultural Network.** The meteorological data was obtained online through *The Washington Agricultural Weather Network Version 2.0: AgWeatherNe*” 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.



Within this network, we collected data for air temperature, dew point, relative humidity, wind speed, max wind speed, wind direction, solar radiation, and precipitation every 15 minutes at four selected locations covering both Region 1 and Region 2. This information supplemented data collected with the UW temporary meteorological stations and covered the duration of Phase 1 between March 1, 2008 and April 30, 2008 and Phase 2 between May 21, 2008 and July 30, 2008.

## **6.0 Data Management and Analysis**

### **6.1 Data entry and storage**

All data is stored in the offices and password protected computer resources of R. Fenske at the University of Washington. Electronic files are stored on the department server, with password access limited to research team staff. The server provides data security with back-up and archiving. To back-up field data sheets, they were scanned and the PDFs stored on the server. Field and laboratory data are entered in Microsoft Excel using a double data entry system with an error check.

### **6.2 Air sample data analysis**

Basic calculations, such as sample volumes and air concentrations, will be done in Excel and SPSS. Data will be imported from Excel to SPSS for statistical analysis.

### **6.3 Meteorological data summary**

Meteorological data for perimeter sampling will be summarized for each sampling period. Temperature will be summarized using minimum, maximum, and average values. Wind speed and direction for each sampling period will be presented in wind roses.

Similar meteorological parameters will be presented for the meteorological data collected at community ambient sites. Daily averages will be presented initially. Following sample analysis, should further examination of the weather data be warranted, average sampling period data will be summarized.

## **7.0 References**

- Baker LW, Fitzell DL, Seiber JN, Parker TR, Shibamoto T, Poore MW, Longley KE, Tomlin RP, Propper R, Duncan DW. 1996. Ambient air concentrations of pesticides in California. *Environ Sci Technol* 30:1365-1368.
- NIOSH 1994. Organophosphorus Pesticides. In NIOSH Manual of Analytical Methods, 4<sup>th</sup> Ed. National Institute for Occupational Safety and Health DHHS (NIOSH) Publication 94-113.
- Tolbert LA, Yost MG, Kissel JC, Galvin K, Fenske RA. 2008. Ambient air concentrations of organophosphorus pesticides due to volatilization during seasonal pesticide applications. Manuscript in preparation. (See also M.S. Thesis by Lisa A. Tolbert, University of Washington Department of Environmental and Occupational Health Sciences, 2007)

