Passive and Active Air Sampling for Residential Exposures to Airborne Organophosphorus Pesticides and Oxygen Analogs ("Oxons") in Central Washington State

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A dissertation submitted in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

University of Washington

2012

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Abstract

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Organophosphorus (OP) pesticides are some of the most widely used insecticides in the United States, and spray applications are a concern for public health due to potential human exposures from distant transport via off target volatilization and particulate drift. Initial tests on active air sampling methods found the NIOSH recommended sampling matrix (OVS XAD-2 Resin Tubes) to artificially transform substantial amounts of chlorpyrifos (CPF) to its oxygen analog (CPF-O) in the laboratory (up to 32%) and in the field, leading to inaccuracies in reported levels CPF and CPF-O in past field studies. A series of side-by-side tests identified the PUF matrix as a superior sampling medium for OP pesticides and their oxygen analogs.

Passive air sampling methods were developed and tested in a laboratory exposure chamber and in the field to measure airborne exposures to OP pesticides and oxygen analogs in an agricultural community. Results show that the new PUF-PAS method combined with sensitive analysis (LC/MS-MS) may be used to improve our understanding of the continued fate and transport at low levels typical of

residential communities down to method limits of quantification of 0.01to 0.05 ng/m^3. PUF-PAS air sampling rates were similar to other semi-volatile organic compounds (SVOCs), ranging from 1.6-8.4 m^3/day and outdoor rates vary according to wind velocity.

The PUF-PAS devices were deployed in the Yakima Valley region of Washington State and measured cumulative monthly air concentrations during pre-thinning, thinning, and non-application seasons. Results demonstrated that air concentrations of CPF during pre-thinning season were 5-10x higher than AZM during thinning season. Households proximal to tree fruit fields (≤250m) reported significantly higher outdoor air concentrations CPF and AZM than non-proximal households. Indoor air concentrations were significantly reduced compared to outdoors, and farmworker households reported higher mean air concentrations of CPF than non-farmworker households. Very few samples detected oxygen analogs indoors. Indoor surface deposition (ng/m^2) and air concentration (ng/m^3) measurements were correlated.

Higher proportions of oxygen analogs (2-35%) were identified in air, particularly in samples further from potential sources of application and during times of increased cumulative solar radiation (mJ/m^2). This research highlights the ability of oxygen analogs ability to persist in air, resulting from atmospheric transport, photolysis, or reaction with oxidizing agents. Opportunity for exposure to oxygen analogs outdoors is a greater concern than indoor exposures. When considering cumulative and aggregate effects of exposure to OP pesticides in order to protect the unique health needs of children, the inclusion of oxygen analogs in risk assessments is necessary.

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Acknowledgements

This work was supported by the NIOSH Educational and Research Center Grant NIOSH-T42OH00843 (Chapters 2,4) Washington State Department of Health Pesticide Program (Chapter 2,4), the Pacific Northwest Agricultural Safety and Health Center (PNASH) (NIOSH Agricultural Centers Program 2 U50 OH07544) (Chapters 2-5), and the Child Health Center Pesticide Exposure Pathways Project at the Center for Child Environmental Risks Research NEIHS-P01 ES009601, EPA-RD-83451401 (Chapters 2-5).

First, I would like to thank my two primary advisers, Dr. Richard Fenske and Dr. Michael Yost for their ability to provide opportunity, advice, and guidance during my time at the University of Washington. A special thanks to Dr. Fenske for introducing me to the International Society of Exposure Science and for encouraging me to pursue this field of study. To Dr. Yost for supporting me during some tough life transitions and keeping me on track. Thanks to Ming Tsai and Alex Lu for laying the groundwork in this interesting path of research on agricultural chemicals and human health. I thank Dr. Catherine Karr for being a great role model and allowing me to work on her childhood asthma research project. Thanks to my two undergraduate mentees, Angele Zamarron and Lilian Turcios, worked with me over the summer via support from the Environmental Health Sciences Undergraduate Research Program from the National Institute of Environmental Health Sciences, Award Number R25ES16150. Angele helped deploy air sampling equipment during the summer 2011 and Lilian assisted with GIS formatting during summer 2012. I would like to also thank Kit Galvin, Maria-Tchong French, and Maria Negrete for their assistance on field work training and standard operating procedures. Cole Fitzpatrick and Kris Hartin were helpful in geographic analysis. Thanks to Beti Thompson, Elizabeth Carusso, and Ilda Islas from the Fred Hutchinson Cancer Research Center for helping me gain access and inform the local community regarding the air monitoring project (Chapters 5-6), and to all the *promotores de salud* at the Fred Hutchinson Cancer Research Center community office in Sunnyside, Washington for their assistance in helping me

schedule and meet with the families. Thanks to Mark Beaudreau from the University of Washington Field Research and Consultation Group for welding the air sampling masts.

A special thanks to Dow Agro Sciences LLC and Bayer Crop Sciences for supplying labeled internal standards. There was an extraordinary effort and years of dedication to this subject put forth by the University of Washington Environmental Health Laboratory, including Russell Dills, Jianbo Yu, and Jacquie Ahmad. I am especially grateful to Jianbo Yu for her work in developing analytical methods. Thanks to Lucio Costa, PhD and Clem Furlong, PhD for their consultation on toxicity estimates.

Professor Michael Morgan provided much input on papers concerning air monitoring results; he and instructor Janice Camp gave me wonderful professional and career advice. Both were wonderful and inspiring industrial hygiene course instructors. Lee Monteith was the person who originally encouraged me to pursue passive air monitoring and provided many resources and background texts along the way.

I give thanks to my past MPH/Global Health advisers and mentors at the University of Iowa for encouraging me to pursue my PhD at the University of Washington. These include Dr. Maureen McCue, Dr. Naresh Kumar, Dr. Tom Peters, and Dr. Peter Thorne.

Thanks to my fellow students and other good friends Vanessa Galaviz, Travis Cook, Marissa Baker, Ling Cui, Chris Simpson, Gretchen Onstad, Jen Krentz, and Alexander Domesle for their good humor and energy. Especially to my friend Ryan Van Surksum for staying up with me those late nights to construct passive air samplers in our living room and for his words of wisdom, love, and encouragement for 5 years. I brought him a single prototype design and he constructed a passive monitor from scratch using household tools. I would like to thank Stephanie Penn individually for introducing me to the wonderful world of long distance running; and to Susan Beroozi and Jessica Graham for providing many early morning running groups. To the many Seattle yoga studios that allowed me to take many savasanas and helped keep my mental focus and bodily awareness. To the University of Washington Catholic Newman Center for nourishing my spirit and letting me sing.

Personally, I would like to thank my brother Sean, my father Tony, my godparents Randy and Trina Stevens, and my boyfriend Nathan for their support, friendship, love, and generally sticking with me through these years of graduate school. Nathan and Jackie Gibbs provided for me while writing this dissertation at Nathan's home outside Coralville, IA. My family has greatly emphasized humility, a hard work ethic, respect, and the attainment of knowledge in all forms-- whether it is physical, mental, or spiritual. They are truly an inspiration to guide my work now and forever into the future.

Dedication

This dissertation is dedicated to my mother, Teresa Kovarik Armstrong. Thank you for your wondrous spirit, curiosity, encouragement, and love.

"But your mom really meant it. You do have a beautiful mind. And my only ambition for you is that you use it to the best of your abilities. I pray that you discover your talents and gifts and then you go on to better the world a little by using them." –in 1984.

List of Abbreviations

AZM: Azinphos-Methyl

AZM-O: Azinphos-Methyl-Oxon

CV: Coefficient of Variance

CPF: Chlorpyrifos

CPF-O: Chlorpyrifos-Oxon

EHL: Environmental Health Laboratory

GIS: Geographical Information Systems

LOD: Limit of Detection

OP: Organophosphorus

OVS: OSHA Versatile Sampler

PP: Polypropylene

PUF-PAS: Polyurethane Foam Passive Air Sampler

REL: Recommended Exposure Limit

SVOCs: Semi-volatile Organic Compounds

I) Specific Aim of Dissertation

The overall aim of this dissertation is to examine methods of accurate, precise, and sensitive measurement of airborne residential organophosphorus (OP) pesticides chlorpyrifos (CPF), azinphos-methyl (AZM) and their oxygen analogs (CPF-O, AZM-O, also called "oxons") in Central Washington State to improve understanding of critical pathways of residential exposure. This research involved methods testing of current Active Air Sampling (AAS) techniques involving polyurethane foam (PUF) and XAD-2 resin matrices, and development of new Passive Air Sampling (PAS) methods using diffusion and deposition. The findings of this study will be used to: 1) improve cumulative quantitative exposure metrics for a children's health cohort and examining potential household factors leading to increased susceptibility, 2) examine associations of airborne concentrations with environmental factors, and 3) investigate the fate and transport of environmental oxygen analogs that exist in low concentrations in airborne pesticide mixtures.

II) Research Questions

A) Current Air Sampling Methods

The first aim of the research was to evaluate the performance of current recommended air sampling methods.

1. How accurate, precise, and sensitive are the current active air sampling (AAS) methods (NIOSH 5600, ASTM 2011) for airborne OPs and their oxygen analogs? What are the benefits and limitations of active air sampling in epidemiologic studies in agricultural communities?
2. What are the superior methods for sampling airborne OPs and oxygen analogs?
3. Can the precision and sensitivity be improved with new analytical techniques (LC/MS-MS)?

B) New Air Sampling Methods

The second aim of the research was to develop and validate new passive air sampling methods to detect OP pesticides and oxygen analogs in air.

1. Is there a method for passive air sampling (PAS) of airborne OPs and oxygen analogs? What are the benefits and limitations of passive sampling for these compounds compared to the existing active sampling methods in agricultural communities?
2. What are the passive (diffusive) air sampling rates for these compounds?
    a. How are these affected by meteorological and other environmental factors?
    b. What is the variability in sampling rates?
3. Can passive air samplers accurately detect residential OPs and oxygen analogs indoors as well as outdoors?
    a. How do indoor/outdoor performance and sample rates compare?
4. How does passive (diffusive) sampling for vapors compare to passive (deposition) sampling for settled particulate?

5. How do analytical precision and sensitivity from passive air sampling matrices compare with active air sampling matrices using newly devised analytical techniques (LC/MS-MS)?

C) Quantification of Airborne Pesticide Exposures

The final aim of the research was to use new methods to estimate airborne exposure pathway of OP pesticides in a children's health cohort.

1. What are the residential indoor and outdoor exposures to airborne OPs and oxygen analogs for families with children living in agricultural areas of Washington State?
    a. How much oxygen analog is present in airborne pesticide mixtures? What is its dominant pathway of exposure?
    b. Does the presence of oxons substantially increase health risk?
    c. Do air concentrations differ indoors vs. outdoors?
2. What environmental (e.g. geographical, meteorological) factors are associated with higher levels of airborne OPs and oxygen analogs?
    a. Do children living in closer proximity to tree fruit fields experience higher levels of exposure to airborne OP pesticides and oxygen analogs than children living at farther distances?
    b. Do children living in farmworker households experience higher levels of exposure to airborne OP pesticides and oxygen analogs than children living in non-farmworker households?
    c. Are there other household characteristics linked to elevated airborne pesticide exposures?
3. Are levels of settled particulate/dust [surface deposition (ng/cm^2)] related to indoor levels of airborne OP pesticides and oxygen analogs?

Chapter 1: Introduction and Background

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1.1 Organophosphorus Pesticides, Oxygen Analogs, and Health Risk

Organophosphorus (OP) pesticides are some of the most widely used insecticides in the United States. In Central Washington State, OP pesticides such as chlorpyrifos (CPF) (Lorsban™) and azinphos-methyl (AZM) (Guithion™) are often applied in aerosolized form to tree fruits and vegetables. They are typically mixed with oily liquids or water and sprayed on crops at high volume to control for over 200 destructive agricultural pests, including roaches, fleas, termites, cattle ticks, and codling moth. In the state more than 95% of these OP pesticides are applied with an air-blast spray tank pulled behind a tractor (Brunner et al. 2003). In the Yakima Valley region, the primary crops are tree fruits (apples, pears, peaches, and cherries), grapes, and hops, requiring the use of both AZM and CPF with spray application rates averaging 0.5 kg/acre and 1 kg/acre, respectively (USDA, 2002, 2009).

In the past decade, regulatory restrictions have been placed on annual amount of AZM that can be applied and restricted entry intervals have been lengthened, contributing to a steady decline in usage. In 2006, the U.S. Environmental Protection Agency (USEPA) declared that AZM could not be used in apple production after September 2012 (USEPA 2008), but recently extended the usage deadline due to unusual bad weather conditions in 2012 (USEPA, 2012). In contrast, CPF was banned for household use

in 2001 but continues to be commonly used in agriculture. Few alternatives to CPF have been shown to be as effective and CPF continues to be one of the most widely used crop protection products in the world (Dow ArgoSciences©, 2012). During 1989-2000, the dependency on AZM in tree fruit orchards (% acres treated) decreased >40%, but use of CPF increased more than 12% (Beers and Brunner 1991, Brunner et al. 2011). Spray applications of OP pesticides are a concern for public health due to potential human exposures from distant transport via off target volatilization and particulate drift. Human exposure to OP pesticides in air usually occurs through inhalation or dermal pathways, and can be occupational or residential in nature.

The primary target organ for OP pesticide toxicity in humans is the central and peripheral nervous system, similarly to most insects. Acute health effects reflecting acetylcholintesterase (AchE) inhibition are most widely recognized by toxicologists and physicians. AchE is inhibited in target tissues of the nervous system and compromises breakdown of the common neurotransmitter acetylcholine in the synaptic cleft of the nerve junction. This leads to repeated and continuous stimulation observed as: symptoms such as headache, blurred vision, watering of the eyes, runny nose, dizziness, confusion and muscle weakness. Being exposed to high levels may cause symptoms such as severe sweating, loss of bowel control, severe muscle tremors, loss of consciousness or even death (Gallo and Lawryk, 1991).

Recently, toxicological studies have focused on the relative potency of combined OP pesticides and their oxygen analogs in animal models (Costa et al. 2005). Most OPs are regularly undergoing transformation to the oxygen analog (e.g. "oxon") *in vivo* as a metabolic product through breakdown mechanisms involving cytochrome p450 enzymes. For example, chlorpyrifos is broken down into oxons, diethylphosphates, TCPγ, and glucuronide and sulfate conjugates (Timchalk et al 2007). However, some studies have demonstrated direct environmental transformation to oxon in the atmospheric environment (CARB 1998, Fenske et al. 2009, Seiber et al. 1989), as demonstrated in Figure 1.1. The airborne presence of the oxon is a human health concern because *in vivo* toxicity studies have found the toxicity of

the oxon to range from 5 to 100 times higher than the parent OP pesticide (Chambers and Carr 1993; Cole et al 2005; 2011, Huff et al. 1994, Furlong et al. 2005, Timchalk et al. 2007). Chlorpyrifos-oxon (CPF-O) is also believed to pose a special risk for genetically susceptible individuals who have lower levels of the paraoxonase [PON-1(-/-)] enzyme which plays a key role in metabolism of OPs in the body (Shih et al. 1998). The frequency of the PON-1(-/-) allele in a study population of farmworkers in Yakima Valley was 25% of the population (Guerrette et al. 2012, Hoffman et al. 2010). This reported frequency is similar to those found for other primarily Hispanic populations (Lopez-Flores et al. 2009).

Children have been found to be particularly susceptible to exposures to the oxygen analog due to differences in metabolic functioning during development (Costa et al. 2005). Children have also been found to have higher body burden of OP pesticides in general, with studies finding urinary metabolite levels in children are consistently higher than in adults (Barr et al. 2004). Young mice have been found to demonstrate changes in specific brain cells and irregular distribution of neurons in the cortical plate after exposures to chronic low doses of CPF-O (Furlong et al. 2005).

Several *in vitro* and *in vivo* studies have demonstrated the effects of various OPs on neurological development, as well as learning and memory functioning in rodents (Costa 2006, Giordano 2007). Although these studies have demonstrated that high peak exposures to OPs and oxygen analogs can cause long-lasting behavioral effects, the evidence regarding longer-term neurodevelopmental consequences from low chronic exposures is less well defined. Some epidemiologic investigations are in place to look at child health outcomes association with chronic pesticide exposures during prenatal periods and during childhood. For example, the CHAMACOS study (Center for Health Assessment of Mothers and Children of Salinas) in Salinas Valley, California has an ongoing longitudinal birth cohort examining exposures to pesticides and other chemicals to determine impacts on growth and development (Eskenazi et al. 2003)

Among rural and agricultural populations, there is abundant data on occupationally related exposures to OP pesticides—as these individuals are generally thought to be at higher risk.

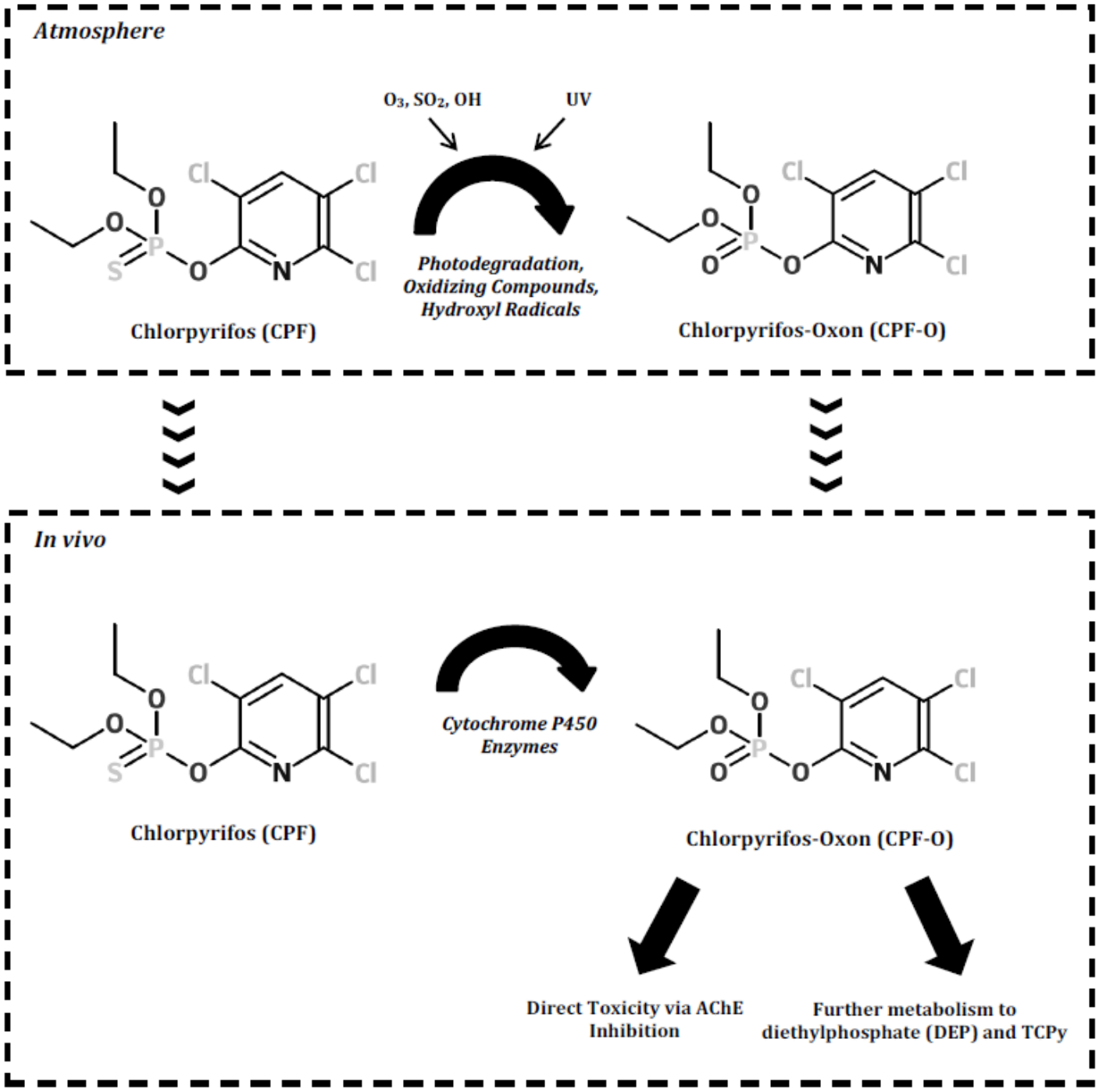
Developmental and long-term health studies have identified possible increased risks for cancer (Daniels et al. 1997, Zahm and Ward, 1998) and neurological impairments (Blain 2001, Young et al. 2005), after environmental exposures to OP pesticides, especially in farmworking and rural communities. Childhood and pre-natal exposures are particularly concerning as they have been linked to hyperactivity [including attention deficit hyperactivity disorder (ADHD)] (Bouchard et al. 2010, Marks et al. 2010), learning disabilities, differences in motor functioning (Eskenazi et al. 2007, Rohoman et al. 2005), lowered IQ (Bouchard et al. 2011) and shortened gestational periods (Eskenazi et al. 2004.) Epidemiologic literature also points to a relatively consistent relationship between pesticide exposure and Parkinson's disease, but the data is insufficient for concluding that such a relationship exists for any particular pesticide compound (Brown et al. 2006). These studies employ questionnaire assessment, biomarker measurement, and environmental dust samples to obtain an exposure estimate; and few studies have included measurements of OP pesticides in air (for past air monitoring studies, see Table 1.1). Pesticide exposure histories are often collected retrospectively, and information/recall bias are inherent limitations. Arcury et al. (1998) argues the challenges in understanding the negative consequences of chronic low level exposures to OP pesticides are due to the lack of good exposure measures that include all potential pathways. In addition, better exposure data is needed to define potential gene-environment interactions. Understanding all specific pathways of exposure are critical for understanding sources and developing prevention strategies.

The failure to analyze for oxygen analogs in atmospheric pesticide mixtures leads to underestimation of total OP pesticide exposures and inaccurate health risk estimates. Although the oxygen analog may be present at much lower concentrations (10-100x) than the parent, it is important quantify because as low as a 1% concentration identified in the air relative to the parent concentration could significantly increase overall toxicity. This subject is discussed in Chapter 2.

Current-use OP pesticides like CPF and AZM are regulated by the Environmental Protection

Agency (USEPA) under the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) of 1947. FIFRA authorizes the EPA to regulate the sale, distribution and use of pesticides, and it requires that industry register pesticides for specified uses and to take actions to mitigate pesticide exposures and protect public health. FIFRA was amended in 1996 by the Food Quality Protection Act (FQPA) which set tougher safety standards for pesticides by requiring the EPA to first, consider the cumulative and aggregate effects of exposure to related pesticides and second, implement safety precautions when it determines the safe exposure levels in order to protect the unique health needs of infants and children (USEPA, 2009). FIFRA regulatory decisions are highly influenced by a Scientific Advisory Panel (SAP) composed of biologists, statisticians, exposure scientists, toxicologists and other experts who provide independent scientific advice. Past action items have included air monitoring programs (primarily in California state), guidelines and regulations on limiting spray drift and tracking pesticide residues into the home, and incentivizing development and adoption of safer alternatives. According to recent proceedings of the FIFRA-SAP (2008), governmental regulatory agencies have become especially interested in vapor/ particulate partitioning, distribution of phases in the environment, and better ways to measure pesticide drift into residential environments. This included a request for better air monitoring data—done efficiently and at low cost.

Figure 1.1/ Example of CPF-O formed *in vivo* and during atmospheric transport. CPF-O is formed *in vivo* as a metabolic product through breakdown mechanisms involving cytochrome p450 enzymes, leading to eventual direct toxicity or metabolism to diethylphosphates (DEP) and TCPy (Timchalk et al. 2007). CPF may undergo photolysis or reaction with oxidizing agents to CPF-O during atmospheric transport in the environment.



1.2 Organophosphorus (OP) Pesticides, Oxygen Analogs, and Environmental Fate and Transport

In recent years AZM, CPF, and their oxygen analogs (AZM-O, CPF-O) have been detected in the air of the surrounding agricultural communities (See Table 1.2, Chapters 2-3). These concentrations are likely the result of vapor and particulate drift from off-target sources, strongly influenced by the physiochemical properties of the compounds and meteorological factors (Harnly et al. 2005, Van den Berg et al. 1999) (See Figure 1.2). Particle drift is the movement of spray droplets produced during the time of application. These droplets may sorb to other particles or dust and settle in near-by areas. Vapor drift is the movement of vapors (i.e. "fumes") after a semi-volatile or volatile pesticide is applied. Volatilization after application may continue from foliar, soil, and particulate residues.

In comparison to other commonly used agricultural chemicals, OP pesticides are semi-volatile, with vapor pressures ranging from 10^{-7} to 10^{2} mmHg at 20°C. These vapor pressures may increase with temperature. For example, the CPF pressure of CPF increases from 10^{-5} to 10^{-4} mmHg at 35°C. OP pesticides also have a Henry's Constant $<10^{-5}$ atm·m^3/mol, allowing volatilization from water. Therefore, volatilization can represent a substantial mass loss from soil, foliar, and water residues during and after application (Popendorf and Leffingwell 1978; Spear et al. 1978). A full review of chemical data for some common-use pesticides, herbicides, and fumigants may be found in the Appendix, Table 9.1(Bowman et al 1983, CDPR 1997-2006, Felsot and Dahm 1979, Lyman et al. 1990, Racke 1993, Rice et al 1997, TOXNET Toxicology Data Network, Van den Berg et al. 1999).

If applied under the wrong conditions, more than 90% of applied material can drift off-target and travel up to 90 km from the source (Harnly et al. 2005, Van den Berg et al. 1999). This is particularly the case during outdoor conditions of high wind turbulence and temperatures. The effects of drift have economic consequences for the orchard operator due to a loss in effectiveness at combating pests at the source of application. In addition, drift may interfere with nearby organic farms, and could result in additional health risk in the surrounding community. As the demand for organic products increases,

neighboring farmers are concerned about spray drift from other sources. Thus, there are many specific guidelines and agricultural extension resources devoted to the means and timing of OP applications (WSDA, WSPRS, 2011) for growers. The EPA requires buffer zones during spray application and has restricted the spray application by the volume spayed, the number of applications per season, the seasonal maximum amounts supplied, and intervals for retreatment (USEPA, 2006).

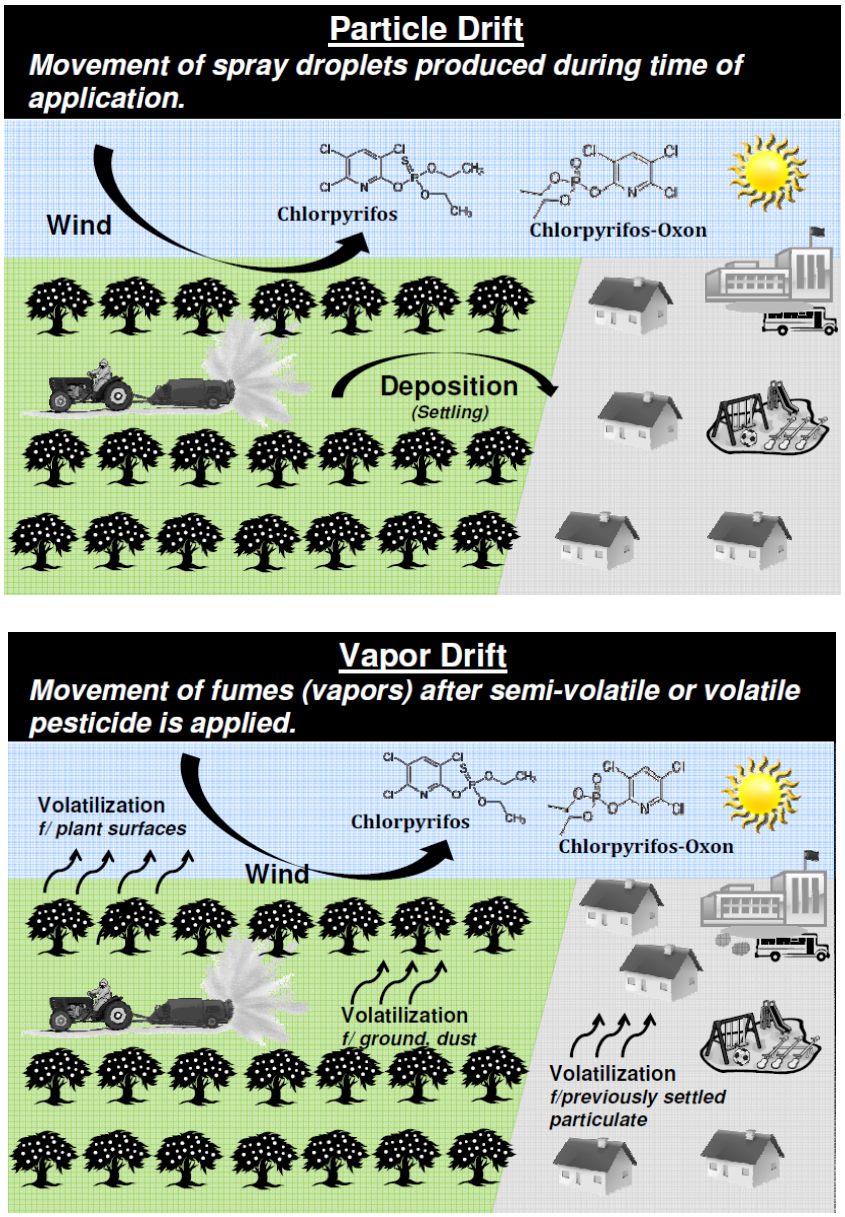
Recently, public health concerns about the oxygen analogs in OP pesticide mixtures heightened when chlorpyrifos-oxon (CPF-O) was identified in virtually all of the 145 air samples collected in agricultural communities of the recent 2008 Washington State Department of Health air monitoring study (Fenske et al. 2009). In fact, higher proportions of oxygen analog were reported at residential locations farther (>250 meters) from agricultural fields, and the oxon represented as much as 94% percent of the total pesticide mixture in some cases. There is little information on the chemical properties of oxons in airborne pesticide mixtures, but some researchers speculate they have slightly higher vapor pressures and greater dispersion than the parent compound (Van den Berg et al. 1999). Their formation in the atmosphere has been associated with higher temperatures, higher levels of ozone, dry weather, interaction with hydroxyl radicals, or photodegradation via ultraviolet light (Fontaine and Teeter 1987, Spear et al. 1978; Aston and Seiber 1997; Bavcon Kralj et al. 2007). CPF and AZM have ultraviolet (UV) absorbencies above 295 nm, further indicating their susceptibility to photo-degradation by sunlight (ASTDR, 1997).

The estimated half-life of CPF and AZM as airborne vapor is 2-4 hours; on foliage, 1-9 days; and in soil, 2-1500 days (Harnly et al 2005). According to Van den Berg et al (1999), the half-life of CPF-O and AZM-O may be slightly higher in air as a vapor than the parent compounds, and lower in soil, foliage, and particulate. Although the parent compound may be detected at low levels, there may a significant amounts of oxygen analog present in the mixture. OP pesticides can also aggregate in soils or dust,

remain on plant surfaces, and eventually re-volatilize back into the air long after the spray period (Eisenreich et al. 1981). The constant process of partitioning and conversion to oxygen analogs may allow OP pesticides to persist for days to weeks outdoors, and up to several months indoors.

Studies have demonstrated that in addition to outdoor infiltration, pesticide residues may be brought indoors on farmworker clothing, shoes, and skin—leading to increased levels in household dust and on surfaces (Simcox et al. 1995, Lu et al. 2000, Curl et al. 2002). Inside the home they may be sorbed onto materials with affinity for the compounds, as demonstrated on household surfaces and in plush toys and furniture (Gurunathan et al. 1998). If sorbed to materials or surfaces indoors, the estimated half-life of these compounds may increase substantially to 30 days or more (CDPR 1997, Davis and Ahmed1998). A recent study conducted by Shin et al. found that residence times of CPF indoors may be up to 7 years (2012). The rate of degradation indoors is slow and results in prolonged presence and increasing chances of detection; although levels may be low and a sensitive method is required. Very little is known about indoor phase partitioning to dust and vapors, and no studies have determined if oxygen analogs are present indoors.

Figure 1.2/ Demonstration of Particle and Vapor Drift of the OP pesticide, CPF and its oxygen analog, CPF-O. Although deposition is important, volatilization can represent a substantial mass loss from soil and foliar residues after application.



1.3 Organophosphorus (OP) Pesticides, Oxygen Analogs, and Air Sampling

1.3.1 Past Air Monitoring Studies

Past air monitoring studies that have measured exposures to both OP pesticides and their oxygen analogs have been primarily outdoor community studies. An overview of past community air monitoring studies is available in Table 1.1. The California Air Resources Board (CARB) and the California Department of Pesticide Regulation (CDPR) have conducted pioneering studies of community pesticide exposures for the past 15 years. In fact, CARB was the first to measure and report oxygen analogs in a residential air monitoring study in 1998 (Tulare County, CA). In recent years, Washington State has also begun to examine airborne community concentrations for large scale exposure assessments. In 2008, an air monitoring study was conducted by the Pacific Northwest Agricultural Safety and Health center (University of Washington) in Central Washington State for the Washington State Department of Health Pesticide Illness Monitoring and Prevention Program (Fenske et al 2009). The initial findings from this particular study led to this dissertation because they led to many questions about the environmental fate and transport of the OP pesticide and oxygen analog mixture, as well as the need for developing new air sampling methods.

Currently, there are three established methods for active air monitoring (AAS) for OP pesticides. They rely on collection and sorption onto polyurethane foam (PUF) or XAD-2 resin matrices and are highly touted for their efficiency at trapping pesticides in gaseous phase (Dobson et al. 2006). Although both matrices have been reviewed and validated for pesticide collection by the US EPA Method TO-10A (USEPA 1999) and by ASTM Method D4861 (ASTM 2011); the NIOSH Method 5600 recommends the use of XAD-2 in OSHA Versatile Sampling (OVS) tubes. The 2008 Washington study used OSHA Versatile Sampling (OVS) tubes, whose methods rely on traditional guidelines from the early 1970s (Lee 1976). In contrast to the traditional occupational exposure sampling methods of using personal sampling pumps or collecting air samples during the pesticide spray; it is challenging to detect residential exposures because

levels may be much lower (e.g. 1 – 30 ng/m^3, Fenske et al. 2009) and transformation to the oxygen analogs may be an important factor. Therefore, a good method limit of detection needs to be 0.5-1 ng/m^3.

In order to deploy active air samples, researchers need to know the timing of pesticide application and have the ability to locate sources. Although this may be possible for occupational settings, these variables are largely unknown and difficult to obtain for broader community studies. Different growers may not apply pesticides on the same day—but often apply in the same season some time before harvest (spring, referred to as "pre-thinning"; and summer, referred to as "thinning"). Often, this leads to labor and resource intensive community air monitoring study designs that rely on active monitoring in tandem samples over the course of many months to seek out peak exposures and cumulative exposure levels. Such an expensive study often only occurs during 1-2 spray seasons even though yearly pesticide-use patterns may be fluctuating.

It is difficult and expensive to maintain active air sampling over the course of many years. Nevertheless, it is currently being attempted by CARB and CDPR in California. Monitoring began in February 2011 (in Ripon, Shafter and Salinas counties) and will last for at least two years. The monitoring relies on the use of XAD resin matrices; and both parent compound and oxygen analogs are being measured (CDPR, 2012).

Table 1.1/ Occupational and community CPF and CPF-O air monitoring studies since 1996.

Air concentration Range >MDL[a] (ng/m^3)		Sampling location	Sampling medium	Analytical method	MDL[a]	Reference
Chlorpyrifos	Chlorpyrifos-oxon		(Resin)		(ng/m^3)	
Occupational Studies						
48 - 2,000	Not Measured	Iowa, North Carolina	XAD-2	LC/MS/MS	NA	Thomas et al. 2010
13,000 - 54,000	Not Measured	Egypt	XAD-2	LC/MS/MS	1.5	Farahat et al. 2010
22,000 - 56,000	Not Measured	Thailand	XAD-2	GC/FPD	1.6	Jaipieam et al. 2010
Community Studies						
10 - 230	Not Measured	Iowa	XAD-2	GC-MS	3.5	Curwin et al. 2005
16 - 1,340	16 - 230	Tulare County, CA	XAD-4	GC-MS	5.25	CARB 1998a, 1999
7 - 150	10 - 28	Parlier, CA	XAD-4	LC/MS	5	CDPR 2006, 2009
83 (Max)	8.5 (Max)	Lompoc, CA	XAD-4	LC/MS	5	CDPR 2003, 2009
1 - 2.9	Not Measured	Iowa	XAD-2	GC-MS	0.13	Peck 2005
5,000 (Max)	Not Measured	Thailand	XAD-2	GC/FPD	1.6	Jaipieam et al. 2010
9 - 494	2 - 108	Washington	XAD-2	LC/MS/MS	0.35	Fenske et al. 2009
Other Studies						
0.05 - 17.5	0.1 – 30.37	Sequoia National Park, CA	XAD-4	GC-MS	$5x10^{-4}$–$8x10^{-4}$[b]	LeNoir et al. 1999

[a] Method Detection Limit

[b] High volume sampling

1.3.2 Passive Air Monitoring

Although passive air sampling has not been commonly used to examine levels of airborne OP pesticides, it is popular for other semi-volatile organic compounds (SVOCs). Some passive samplers, such as the polyurethane foam sampler (PUF-PAS), rely on the properties of atmospheric diffusion to collect contaminants without the use of a pump and the rate of contaminant uptake is controlled by the air boundary layer. This process of accumulation is already understood mathematically, using relatively simple models (Bartkow et al. 2005). A full review of the literature shows that within the past decade, passive sampling with a polyurethane foam disk (PUF-PAS) has been used to study seasonal and spatial trends of polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), polycyclic aromatic hydrocarbons (PAHs), and organochlorine (OC) pesticides. A review of these studies is in Table 1.2. The PUF-PAS has been successful for long term sampling. In comparison, very little research has been dedicated to its performance for sampling semi-volatile OP pesticides and oxygen analogs even though their chemical properties are comparable. A more complete description on theory of passive sampling for SVOCs is explained in Chapters 5-6.

Passive air sampling (PAS) is better suited for providing spatial data when the source location is unknown and electrical power is difficult to obtain—thus it is ideal for remote agricultural areas. Although it provides lower temporal resolution than AAS (e.g days to months rather than in minutes to hours), PAS allows for a measurement of cumulative monthly and seasonal average air concentrations at lower cost and invasiveness to research participants. This is ideal for accumulating longer term exposure data currently lacking for sub-chronic and chronic epidemiological investigations in rural communities. Some advantages and disadvantages of PUF-PAS and OVS-AAS for measuring airborne OP pesticides and oxygen analogs are listed in Table 1.3. Other general advantages and disadvantages of general passive air sampling techniques have been discussed in detail by Shoeib and Harner (2002, 2006).

Table 1.2/ Passive air sampling studies for other SVOCs in the atmosphere since 2002. All studies use a PUF-PAS device.

Compound	Sample Period (days)	Sample Rate (m^3/day)	Location	Reference
PCBs	450	3-5	Indoor/outdoor	Shoeib and Harner (2002)
PCBs, PBDEs, OC Pesticides	42	2-6	Indoor/Outdoor	Harner et al. (2003.2004)
PBDEs	21	2.5	Indoor	Wilford and Harner (2004)
Other SVOCs	NA	1.5-10	Indoor/Outdoor	Bartkow et al. (2005)
PCBs, PBDEs, OC Pesticides	30-90	2-8	Outdoor	Gouin et al. (2005), Jayward et al. (2004), Pozo et al. (2006)
PCBs, OC Pesticides	7-42	2-7	Outdoor	Chaemfa et al (2008)
PAHs, PCBs, OC Pesticides, PBDEs	42-50	2-6	Indoor/Outdoor	Bohlin et al. (2008)
PCBs, OC pesticides	40	2-8	Indoor/Outdoor	Moeckel et al. (2009)
PAHs	1-8	0.5-2	Indoor Outdoor	Bohlin et al. (2008, 2010)
PCBs	21-46	2-3.5	Indoor	Persoon et al. (2009)
Triflurin, Pendimethalin, HCB, Endosulfan, Metolachor, Alachlor, Atrazine	1-365	4-6	Indoor/Outdoor	(Hayward et al. 2010)
Average Sample Rates (m^3/day)				
Outdoors		*3.9*		
Indoors		*2.9*		

Table 1.3/ Advantages and disadvantages of PUF-PAS and OVS (XAD-2 Resin) AAS specific for measuring airborne OP pesticides and oxygen analogs in agricultural community studies.

Advantages	Disadvantages
Polyurethane Foam Passive Sampler (PUF-PAS)	
No electricity, good for remote agricultural areas	Gas and vapors only, fewer particles
Monitors cumulative exposure of entire spray period	Loss of temporal resolution, precision
Non-invasive, quiet	Large sampling matrix
Increases participation rates	Possible matrix effect/cleanup for LC-MS/MS, GC-MS
Low cost of sampling	Sampling rates highly dependent on meteorology
OVS (XAD-2 Resins) AAS	
Gas, Vapors, Particulate	Requires electricity
Good Temporal Resolution	Cumulative exposures measured in tandem sampling
Small size	Invasive, requires pump
Little matrix effect	Requires frequent calibration
Calibrated sampling rates	High cost of sampling

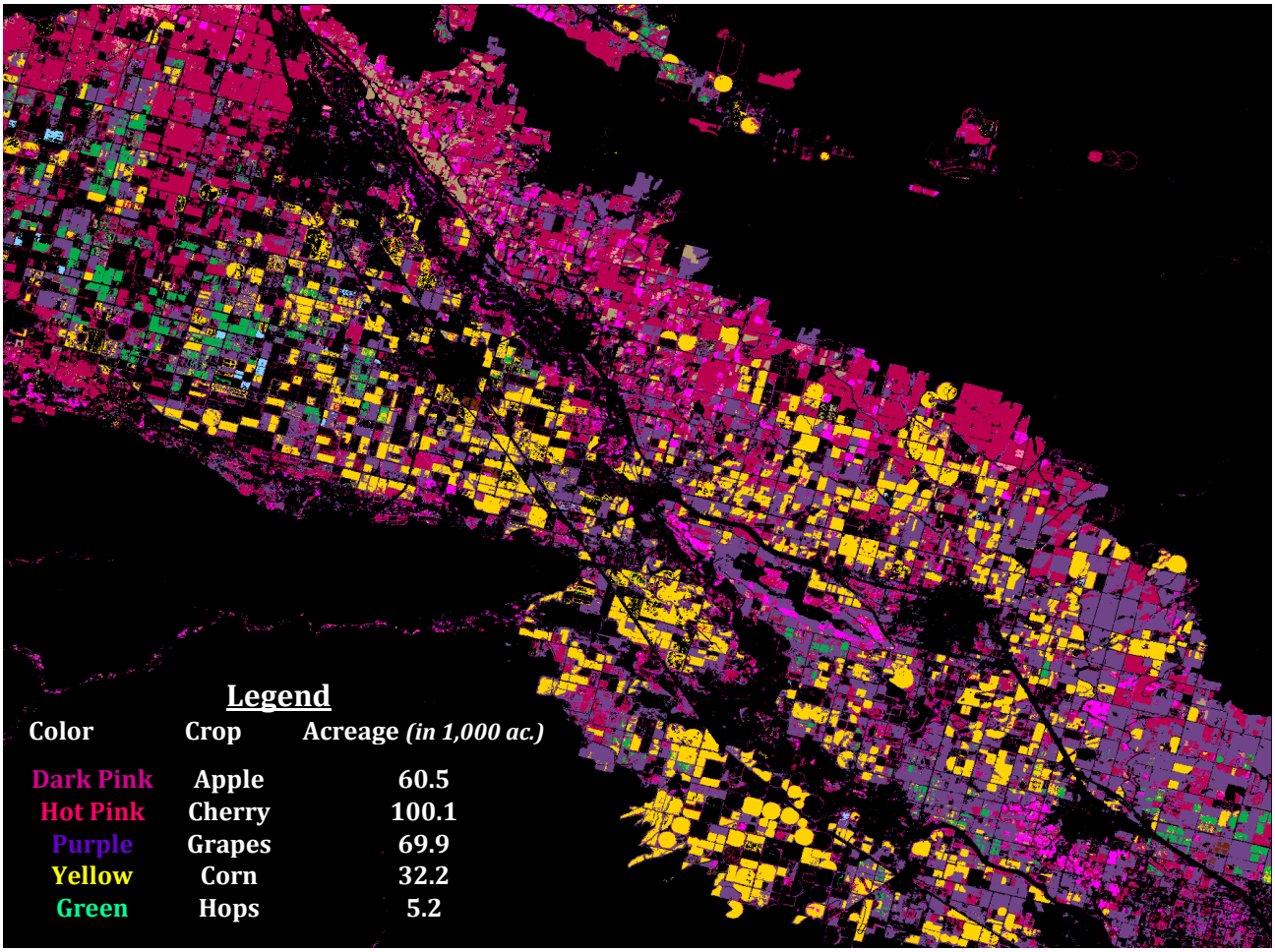
1.4 Study Location and Community

In Washington State, the University of Washington Child Health Center for Environmental Risks Research (CHC) and the Pacific Northwest Agricultural Safety and Health Center (PNASH) have been investigating the linkages of pesticide exposure and health in farmworkers and families since their establishments in 1998 and 1996, respectively. Most research has taken place in the lower Yakima Valley Region of Central Washington State (see map, Figure 1.2), a region that is 150 miles long and 75 miles wide. In this region there are > 1000 orchards covering more than 100,000 acres (USDA 2011, See Figure 1.3). The study area is home to many farmworker families—in fact, > 50% of the population is Hispanic/Latino (as compared to 11% for Washington State) and >30% consists of children and adolescents <18 years of age (US CENSUS 2010). Many members of the Hispanic population are involved in agricultural work, specifically in harvesting, pruning, thinning, and other care of the many crops grown in the region (Thompson et al. 2008).

One of the main goals of the CHC is to use innovative approaches to measure exposures of young children to pesticides, especially in agricultural communities. Initial research in the Yakima Valley has identified increased OP pesticide metabolites in the urine of children and higher measured OP levels in dust than the general population; with the children of farmworkers experiencing the highest exposures (Fenske et al. 2005). The aim of this dissertation is to increase our understanding of the airborne exposure pathway via spray drift and subsequent transport. In past studies, the airborne pathway has not been fully considered. Quantitative airborne measurements are important exposure metrics for epidemiological cohorts investigating both acute and sub-chronic health effects in children and needed to devise future strategies to limit exposures.

Figure 1.2/ Map, State of Washington and Lower Yakima Valley Research Area (in Red)

Figure 1.3/ Map, Lower Yakima Valley Research Area (in Rectangle), 2011Cropland Data Layer. Geographical data for this dissertation was from this cropland data layer, shape-files for ArcGIS are made available to the public from CropScape, NASS/CDL Program (2011).



1.5 Organization of Dissertation

The next 5 chapters (Chapters 2-6) of this dissertation are written as individual scientific publications. For this dissertation, there have been adjustments made to reduce repetitive statements on background, methods, and discussion sections. I am first author on each of these papers. Each chapter begins with a list of figures and tables, a summary, and bulleted highlights for brief reading.

Chapter 2 was published as: Armstrong JL, Fenske RA, Yost MG, Galvin K, Tchong-French M, Yu J. *Presence of organophosphorus pesticide oxygen analogs in air samples.* Atmosheric Environment. This publication reports on the validity of oxygen analog measurements in air samples for the OP pesticide, CPF. It also uses toxicity equivalency factors (TEFs) for chlorpyrifos-oxon to calculate CPF-equivalent air concentrations.

Chapter 3 is to be published as: Armstrong JL, Fenske RA, Yost MG, Tchong-French M, Yu J. *Comparison of polyurethane foam and XAD-2 sampling matrices to measure airborne organophosphorus pesticides and their oxygen analogs in an agricultural community.* Target Journal: Chemosphere. This publication reports on PUF matrices are the superior method for air sampling OP/oxygen analog mixtures to XAD-2. It states that higher levels of the more potent oxygen analogs are detected in air post-application and at distances farther from the source. It also finds that a larger proportion of oxygen analogs are identified in vapors than deposited particulate.

Chapter 4 is to be published as Armstrong JL, Yu J, Dills R, Yost MG, Fenske RA. *A sensitive LC-MS/MS method for measurement of organophosphorus pesticides and their oxygen analogs in community air samples.* Target Journal: Journal of Agricultural and Food Chemistry. It is a chemical analysis methods development paper describing use of a rapid liquid chromatography tandem mass spectrometry (LC-MS/MS) method developed to determine levels OP pesticides and their oxygen analogs on common active and passive air sampling matrices.

Chapter 5 is to be published as: Armstrong JL, Yost MG, Fenske RA. *Development of the*

polyurethane foam passive air sampler (PUF-PAS) to measure airborne organophosphorus pesticides and oxygen analogs in an agricultural community. Target Journal: Environmental Science and Technology. The publication reports on the laboratory and field investigations of new passive air sampling methodologies to sample for exposures to OP compounds and oxygen analogs. The PUF-PAS is identified as a practical alternative to AAS because it results in little artificial transformation to the oxygen analog during sampling, it provides cumulative monthly exposure estimates, and the measured sampling rates are comparable to rates for other semi-volatile organic compounds.

Chapter 6 is to be published as: Armstrong JL, Yost MG, Negrete M, Islas, I, Fenske RA. *Passive air sampling for indoor and outdoor exposures to the organophosphate pesticides chlorpyrifos, azinphos methyl, and their oxygen analogs in rural households.* Target journal: Environmental Science and Technology. The final publication reports on the 2011 passive air monitoring findings in the Yakima Valley community during application and non-application seasons.

Chapter 7 is a discussion and conclusions section, followed by Standard Operation Procedures (SOPs), Supplementary Materials (tables of raw data), and my Vita. The SOPs were written in order to repeat experiments if necessary.

The findings of this dissertation have led to other publications in non-scientific journals and numerous presentations at scientific conferences and meetings, all of which may be found in the Vita. In September 2012, a meeting about this work led to the development of an additional regional methods testing grant with EPA Region 10 for use of PUF-PAS devices to sample herbicides in Central Oregon, which is currently in review. The work may also support a further commentary or review paper discussing the importance of oxygen analogs in health risk assessment.

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Chapter 2: Presence of organophosphorus pesticide oxygen analogs in air samples

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Chapter 2 Summary: A number of recent toxicity studies have highlighted the increased potency of oxygen analogs (oxons) of several organophosphorus (OP) pesticides. These findings were a major concern after environmental oxons were identified in environmental samples from air and surfaces following agricultural spray applications in California and Washington State. This paper reports on the validity of oxygen analog measurements in air samples for the OP pesticide, chlorpyrifos. Controlled environmental and laboratory experiments were used to examine artificial formation of chlorpyrifos-oxon using OSHA Versatile Sampling (OVS) tubes as recommended by NIOSH method 5600. Additionally, we compared expected chlorpyrifos-oxon attributable to artificial transformation to observed chlorpyrifos-oxon in field samples from a 2008 Washington State Department of Health air monitoring study using non-parametric statistical methods. The amount of artificially transformed oxon was then modeled to determine the amount of oxon present in the environment. Toxicity equivalency factors (TEFs) for chlorpyrifos-oxon were used to calculate chlorpyrifos-equivalent air concentrations. The results demonstrate that the NIOSH recommended sampling matrix (OVS tubes with XAD-2 resin) was

found to artificially transform up to 30% of chlorpyrifos to chlorpyrifos-oxon, with higher percentages at lower concentrations (<30 ng m 3) typical of ambient or residential levels. Overall, the 2008 study data had significantly greater oxon than expected by artificial transformation, but the exact amount of environmental oxon in air remains difficult to quantify with the current sampling method. Failure to conduct laboratory analysis for chlorpyrifos-oxon may result in underestimation of total pesticide concentration when using XAD-2 resin matrices for occupational or residential sampling. Alternative methods that can accurately measure both OP pesticides and their oxygen analogs should be used for air sampling, and a toxicity equivalent factor approach should be used to determine potential health risks from combined exposures.

Chapter 2 Highlights

- Chlorpyrifos-oxon is formed during air sampling with matrices containing XAD-2.
- Chemical analysis without measurement of oxon underestimates air concentrations.
- Comparisons of lab and field data suggest that oxon is present in community air.
- Accounting for chemical mixtures of parent OPs and oxons in air is important.
- Small amounts of oxon in air have a large effect on human health risk estimates.

2.1 Introduction

The primary objective of this study was to determine the degree to which the OP pesticide chlorpyrifos (CPF) can be transformed artificially to its oxygen analog form by air sampling with OVS tubes at levels representative of concentrations measured during community sampling at low and high flow rates. It is important to rule out sampling transformation in order to correctly assess health risk from exposure to airborne CPF-O. The second objective was to ascertain the extent to which CPF-O may have been environmentally present in the community air that was sampled in the 2008 Washington study. The final objective was to use this data to include the toxicity of CPF-O and estimate potential changes in community health risk resulting from respiratory exposure to the mixture of both parent CPF and CPF-O.

2.2 Sampling Methods

2.2.1 Laboratory Studies

Sampling was conducted according to NIOSH method 5600 for OP pesticides (NIOSH, 1994). OVS tubes containing XAD-2 sorbent were spiked in triplicates at levels of 0, 42, 210, and 2100 ng of 99.5% pure chlorpyrifos (ChemService, Inc. PS-674) in solution. A 25 µl Hamilton™ positive displacement syringe was used to apply chlorpyrifos in acetone solution directly to the resin by inserting the needle beyond the quartz fiber pre-filter into the first bed of XAD-2. The back-up XAD-2 resin was not spiked because past studies have demonstrated that even higher concentrations of chlorpyrifos (>96%) are primarily trapped on the first resin bed (Shibamoto et al. 1996). Each OVS tube was paired with an SKC air sampling pump (224-PCXR8) operated at a flow rate of either two or six liters per minute (LPM) for approximately 24 hours. Two flow rates were tested to examine potential differences in artificial transformation at higher flow rates and to simulate popular air sampling procedures conducted in past community monitoring studies (CARB 1998, CDPR 2003, Fenske et al 2009). Larger spike masses were applied at higher flow

rates (~6LPM) to account for larger air sampling volumes. Pumps were pre- and post-calibrated between studies using a DryCal DC-Lite and flow rates were calculated separately for each sample in order to calculate the air volumes for each spiked sample. Laboratory blanks, spikes, and storage spikes were included in the experiments for quality assurance purposes.

2.2.2 Field Studies

The following spring, data were collected outdoors at a community air sampling site managed by the Washington Department of Ecology in Yakima Valley, WA. The site was previously utilized in the 2008 Washington State study to collect ambient concentrations and is located >1 km (1405 m) from the nearest tree fruit field. OVS tubes containing XAD-2 sorbent were spiked with chlorpyrifos in triplicates at levels of of 0, 15, 30, 60, 200, 592, and 2628 ng following the procedures described in the laboratory studies. Previous data from the 2008 study emphasized the need to control for small background concentrations of CPF and CPF-O by including non-spiked samples. Triplicate spikes of 0 and 30 ng were deployed with no pump air flow. All SKC air sampling pumps were stored in a weather-proof container and operated at either 2 or 6 LPM for 24 hours. Outdoor temperatures ranged from 4-12°C during the sampling period. Samples were stored at a University of Washington field office in Yakima in a freezer at -10°C until transport to the University of Washington Environmental Health Laboratory. Flow rates were calibrated and calculated separately in order to calculate the air volumes (m^3) for each spiked sample.

The Environmental Health Laboratory performed chemical analysis for both CPF and CPF-O. A new LC-MS-MS method was developed through modifications of methods described by Sancho et al. (2000), Yusa et al. (2009), and NIOSH Method 5600 (the method is described in Chapter 4). The quartz fiber filter and primary resin section was placed in a 10 mL vial, and separated from the secondary resin section to analyze for break-through. All samples were sonicated with an acetone/acetonitrile solution containing stable-isotope labeled internal

standards of chlorpyrifos diethyl-D10, 99% (Cambridge Isotope Labs DLM-4360) and 13C2, 15N-Chlorpyrifos oxon (donated by Dow Agro Sciences LLC). The limit of detection (LOD) for both chlorpyrifos and CPF-O was 1 ng/sample. Fortification/recovery studies involved spiking matrix blanks with CPF and CPF-O at levels ranging from 5 to 1000 ng/sample; recoveries were 86.1 – 94.6% for CPF and 85.8 – 97.6% for CPF-O.

Quality assurance field spikes and blanks were carried into the field and handled in a manner similar to other samples except they were capped and did not have air drawn through them. Field spikes were prepared by introducing low levels CPF (20-50 ng/sample) into the front section of the XAD-2 resin with a micropipette, immediately recapping, followed by storage on ice. Field spike recoveries were 74.4 –101.5% for CPF, and yielded no detectable CPF-O. Field blanks yielded no CPF or CPF-O. Static storage spikes were kept in the laboratory freezer at -10°C for 2 months and recoveries ranged from 84-105%.

2.2.3 Determination of Artificial and Environmental CPF-O

Total chlorpyrifos was calculated for each sample by converting the measured chlorpyrifos-oxon to its chlorpyrifos equivalent using the ratio of molecular weights, and adding this value to the measured chlorpyrifos, as indicated in Equation 1:

$$\mathbf{CPF_{Total} = CPF\text{-}O_m * (CPF_{MW}/CPF\text{-}O_{MW}) + CPF_m} \qquad \textit{(Eq. 2.1)}$$

Where CPF_{Total} = total chlorpyrifos in sample (ng), $CPF\text{-}O_m$ = mass of chlorpyrifos-oxon measured in sample (ng), CPF_{MW} = chlorpyrifos molecular weight (350.6 ng/nmol), $CPF\text{-}O_{MW}$ = chlorpyrifos-oxon molecular weight (334.5 ng/nmol), and CPF_m = mass of chlorpyrifos measured in the sample (ng). To control for small concentrations levels of CPF and CPF-O, outdoor recovery masses were

corrected by subtracting background levels CPF and CPF-O from non-spiked samples in the outdoor environment to calculate total % recovery and % CPF-O.

The percent chlorpyrifos-oxon (% CPF-O) in each sample was calculated by dividing the mass of chlorpyrifos-oxon, expressed as chlorpyrifos equivalent, by total chlorpyrifos and multiplying by 100, as indicated in Equation 2:

$$\textbf{\% CPF-O} = \textbf{CPF-O}_{m} * (\textbf{CPF}_{MW}/\textbf{CPF-O}_{MW})/\textbf{CPF}_{Total} * 100 \qquad \textit{(Eq. 2.2)}$$

Next, % CPF-O (y-axis) was plotted against total mass per unit volume (x-axis), which was estimated by dividing CPF_{Total} by specific air sampling volumes. A quadratic prediction plot with 95% confidence intervals was used to model expected oxon as an artifact of sampling ($R^2 = 0.288$) as a function of total CPF air concentration. Community measurements from ambient sites (> 500 m from orchard) and near-field sites (< 100 m from orchard) from the 2008 Washington State study were directly compared with the laboratory and field experimental data. A non-parametric statistical test was used compare expected values determined from laboratory and field study samples to observed community measurements from Washington State study data. The Mann Whitney U-test was used since sample size and variability of the two groups differed and the observations were independent of each other (Fay and Proschan 2010). The basic assumption of normality was questionable via Shapiro Wilk test and small experiment sample size(Rosner and Grove 1999). Due to the variable nature of the relationship between oxon transformation and total concentration chlorpyrifos, statistical tests were performed for the entire data set and for each data tertile of pesticide concentrations. All calculations were performed using STATA™ 10.1 data analysis and statistical software (StataCorp LP College Station, Texas).

2.3 Results

Data from the laboratory and field experiments are presented in Table 2.1. In the laboratory experiments, samples with low spike masses CPF (42 ng) had an average of 31.6% oxon transformation whereas higher spike masses CPF (~2100 ng) had an average of only 15.4% oxon transformation. Similarly in the field experiments, low spike masses (<30 ng) yielded an average of 24.4% oxon, whereas medium spike masses (60-200 ng) yielded only 9.9% oxon. A similar effect was found at higher flow rates of 6 LPM. Samples hung outdoors with no flow rate (0 LPM) resulted in no conversion to CPF-O. These results further emphasized that artificial transformation was occurring during the action of pulling air through the sampling tube.

Table 2.1/ Spike masses (ng), air volume (m^3), recovery masses total chlorpyrifos (CPF), chlorpyrifos-oxon (CPF-O), and total mixture (CPF +CPF-O) (ng), % recovery total (CPF +CPF-O), and % oxon (CPF-O). In laboratory and field studies measured after 24 hour air sampling with chlorpyrifos-spiked OVS tubes. All reported values are the mean of spiked samples run in triplicates. *Italicized* recovery masses are corrected by subtracting background levels CPF and CPF-O in the outdoor environment from non-spiked samples. These corrected values were used to calculate total % recovery and % CPF-O.

Spike Mass (ng)	Sample Air Volume (m^3)	Recovery Mass (ng)			% Recovery	% CPF-O [b]
		CPF_m	$CPF\text{-}O_m$	CPF_{Total} [a] (CPF +CPF-O)	Total (CPF +CPF-O)	
Laboratory						
Low Flow Rate (2 LPM)						
0	2.81	<LOD	<LOD	<LOD	<LOD	NA
42	2.91	22	9.7	32.1	76.5	31.6
210	2.92	128	37.7	167.5	79.8	25.5
High Flow Rate (6 LPM)						
2100	8.25	1437	256.0	1706	81.2	15.4
Field [c]						
No Flow Rate (0 LPM) [c]						
0	0	<LOD	<LOD	<LOD	<LOD	NA
30	0	25	0	25	83.3	NA
Low Flow Rate (2 LPM)						
0[d]	2.78	16.5	6.5	23.3	>100	30.5
15	3.03	*7.5*	*2.0*	*11.4*	76.0	18.4
30[d]	2.88	*19.5*	*0.5*	*20.6*	68.7	2.5
60	2.86	*52.0*	*3.5*	*55.5*	92.5	6.3
200	3.2	*161.5*	*12.5*	*169.7*	84.9	7.3
High Flow Rate (6 LPM)						
0	10.1	48.5	19.5	70.96	>100	29.5
200	10.21	*150.5*	*27.0*	*177.4*	88.8	16.0

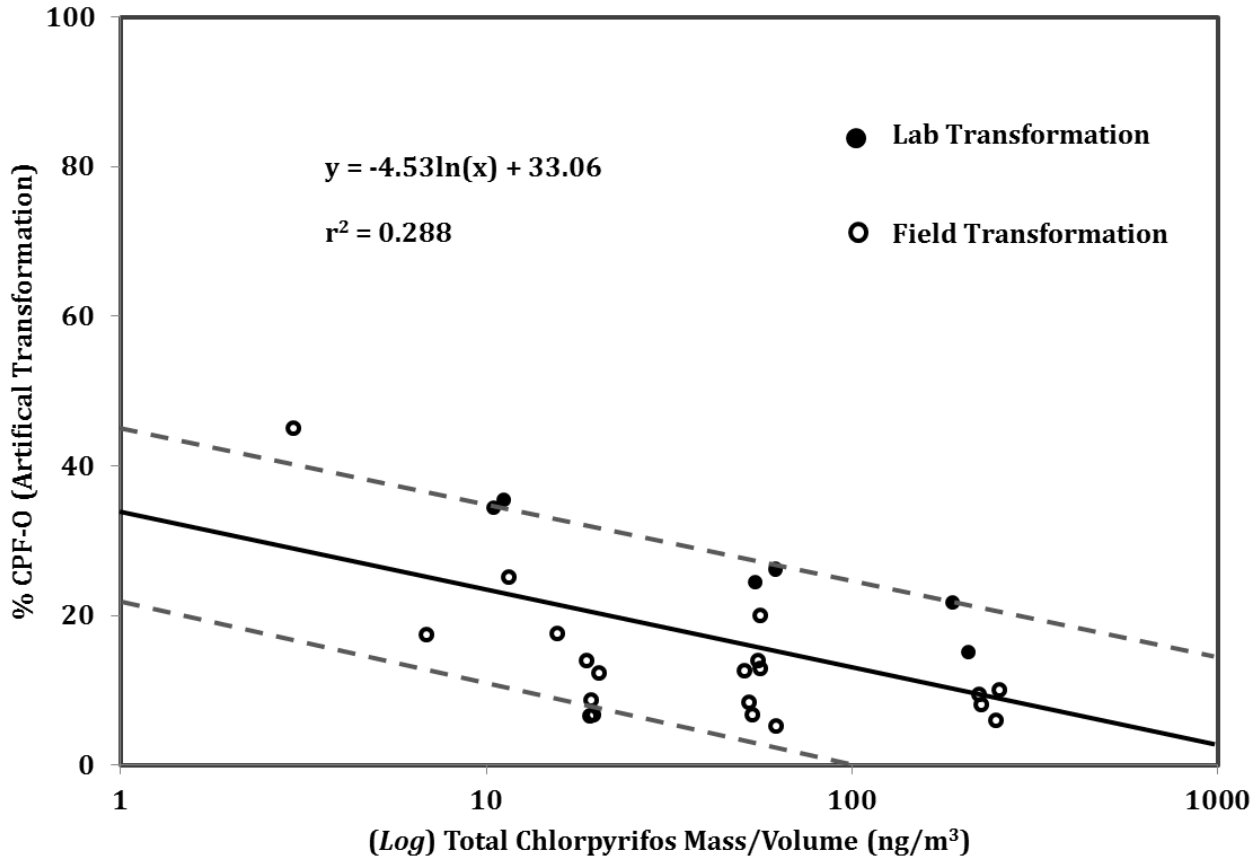
[a] Total chlorpyrifos mass (CPF_{Total}, ng) is the sum of CPF and CPF-O measured in samples, adjusted by molecular weight ratio (see Equation 1 in text).

[b] % CPF-O is the amount of CPF-O divided the amount of total CPF times 100 (see Equation 2 in text).

[c] These samples had no recorded flow rate because they were deployed on a sampling tube with no sampling pump attached.

[d] Duplicate sample resulting from pump failure.

Figure 2.1/ % Artificial Transformation to Oxon by Log Mass per Unit Volume of Total Chlorpyrifos.

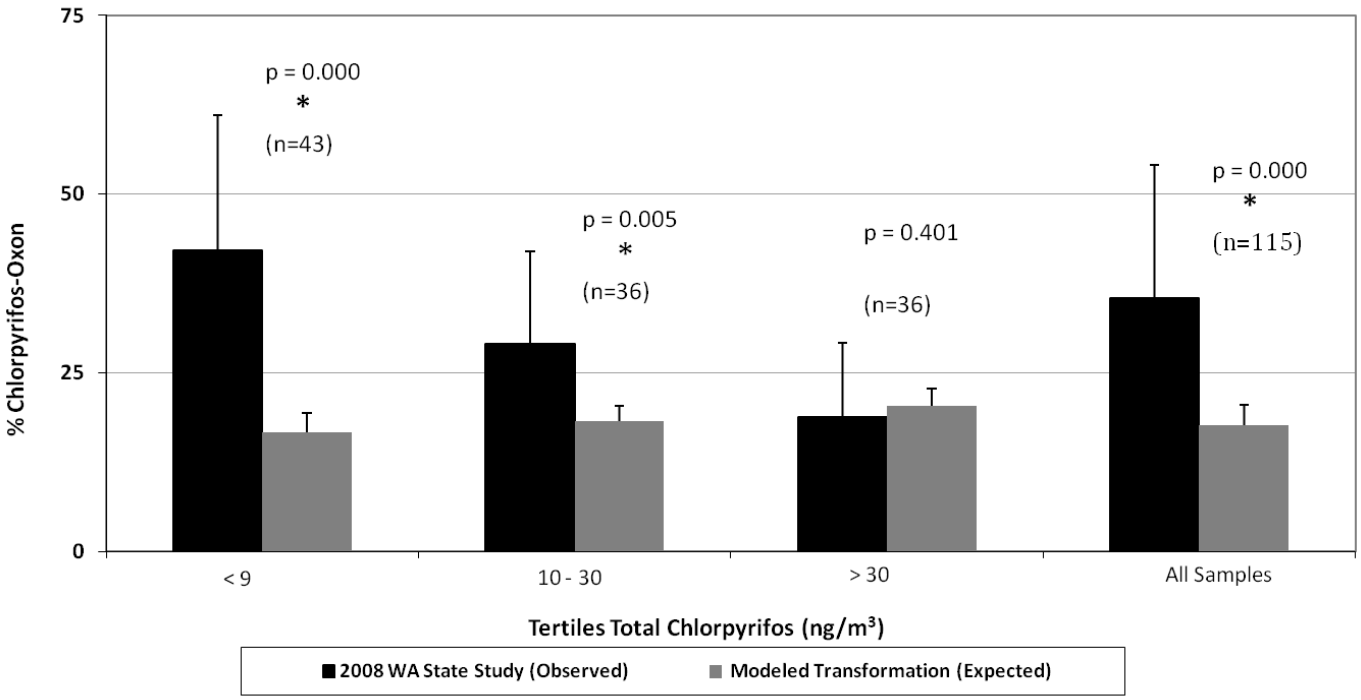


An inverse relationship was observed in both the laboratory and field study experiments between total chlorpyrifos expressed as a mass per unit volume (ng/m^3) and the proportion of chlorpyrifos transformed to oxon on the XAD-2 resin sampling matrix (Figure 2.1). A quadratic prediction plot model accounted for about 29% of the variability in these data (R^2 = 0.288). The 95% confidence intervals were generated from the model to assess differences between the transformation experiments and the 2008 Washington State study. In many instances the proportion of oxon found in the 2008 air monitoring samples exceeded the upper 95% C.I. of the experimental data. This was especially true at low concentrations (≤10 ng/m^3) and in ambient samples that were located > 500 meters from the nearest orchard. In fact, more than half (69%) of the ambient samples (n=32) were higher than the predicted artificial transformation values. These samples warrant further investigation because this means significant airborne CPF-O in residential air. On the other hand, some of the percent oxon was less than expected at medium concentrations and in near-field samples < 100 meters of an orchard. Only 36% of near-field samples (n = 113) had higher percentages chlorpyrifos-oxon than predicted. Higher proportions CPF-O in the air samples farther in proximity from fields may be attributable to physiochemical transformation as pesticides drift further from their source of application. In the past, atmospheric scientists have used the term "aging" to describe similar processes on the local/regional scale for complex mixes of pollutants and transformation products (Demerjian, 2011).

All the community samples from the Washington State study, both ambient and near-field, had a median of 14% greater proportion oxon (95 C.I. 12.8 –20.3%) than could be explained by the artificial transformation experiments in the laboratory and field. This difference was statistically significant in a Mann Whitney test ($\alpha < 0.005$). When broken into tertiles (Figure 2), the Washington study had a 15% greater proportion of oxon than expected (95 C.I. 10.04- 18.9%; $\alpha <$

0.001) at low concentrations (<10ng/m^3) and 10% greater proportion of oxon than expected (95 C.I. 4.8 to 16.97%; α=0.005) at medium concentrations (10-30 ng/m^3). The opposite was true for higher concentrations (>30 ng/m^3); the Washington study actually had 3% less proportion of oxon than expected, but this was not statistically significant (95 C.I. -7.85 to 12.7%; α= 0.401).

Figure 2.2/ Mann Whitney U-test comparing observed vs. expected % chlorpyrifos-oxon at concentration tertiles; * = p value ≤ 0.05.



2.4 Discussion

2.4.1 Artificial Transformation

In this study we found that CPF is artificially transformed on XAD-2 resin to CPF-O, but that it does not account for all CPF-O measured in the air of an agricultural community. This transformation is a major concern because Agency for Toxic Substances and Disease Registry (ATSDR) currently recommends the use of XAD-2 resin air sampling matrices. ATSDR notes that CPF may be converted to its oxygen analog under certain environmental conditions; however, it does not discuss the potential for artificial production of the oxon on the sampling matrix (ASTM, 2011). Neither the EPA/ASTM D 4861 international method nor the NIOSH 5600 method makes any mention of measuring for CPF-O. This study has demonstrated that if the oxon in air samples using XAD-2 resins is not measured, then true CPF air concentrations maybe underestimated by 5-30%.

Woodrow et al. (1978) noted the conversion of parathion to paraoxon on Amberlite XAD-4 resins during one-hour laboratory testing at high air sampling volumes and Seiber et al. (1989) also reported substantial conversion (up to 54%) of methyl parathion to its oxygen analog on XAD. In 1996, the California Air Resources Board (CARB) found substantial amounts of CPF-O in many of the samples collected in Tulare County (1998a; 1998b). CARB reported that when using XAD-4 resin, "conversion of chlorpyrifos to the oxon analogue may take place on the trapping media during sampling." However, CARB also reported that concurrent field spike studies showed "only insignificant conversion taking place under actual field conditions." These results are puzzling in light of our finding of significant conversion of CPF to its oxon on XAD-2 resin in both the laboratory and in the field.

The act of drawing air through the sampling resin may be a causal factor, as demonstrated

by no conversion in XAD resin at zero flow rate (Table 2). In the future, it will be important to test new sampling matrices or examine passive methods using diffusion or deposition to measure CPF and CPF-O in air. Arcury et al (2006) have noted that many researchers and safety personnel continue to collect airborne OP pesticide samples without any harmonized environmental sampling and chemical analysis methods. Not only do problems exist with the current method, there is also a need for new guidelines on how to collect and measure both organophosphate pesticides and their oxygen analogs with minimal sampling artifacts.

2.4.2 Environmental Chlorpyrifos-Oxon (CPF-O)

A direct comparison to the 2008 Washington State study has also demonstrated that transformation of OP pesticides to their oxygen analogs may still be occurring in the atmospheric environment. Under these circumstances, the health risk associated with exposure to airborne OP pesticides will be higher than previously estimated due to increased potency of CPF-O in the airborne mixture.

We have demonstrated this phenomenon by using toxicity equivalence factor (TEF) values, which have been used in the past for compounds such as polychlorinated biphenyls (PCBs) and dioxins (Van den Berg et al 1998) in chemical risk assessment. These numbers are drawn from two main *in vivo* toxicology studies that conducted side-by-side comparisons of brain acetylcholinesterase inhibition for both CPF and CPF-O (Chambers and Carr 1993; Cole et al. 2005).

A toxicity equivalent concentration (TEC) can be calculated for the mixture of CPF and CPF-O by adjusting for the toxicity of the oxon formed in the environment and available for inhalation:

$$\mathbf{TEC_{CPF} = (CPF\text{-}O_e * CPF_{MW}/CPF\text{-}O_{MW} * TEF) + CPF} \qquad \textit{(Eq. 2.3)}$$

Where TEC = toxicity equivalent concentration of chlorpyrifos parent and oxon; $CPF\text{-}O_e$ = mass of environmental chlorpyrifos-oxon (ng); CPF_{MW} = molecular weight of chlorpyrifos (350.6 ng/nmol); $CPF\text{-}O_{MW}$ = molecular weight of chlorpyrifos-oxon (334.5 ng/nmol); TEF = toxicity equivalence factor drawn from toxicology studies; and CPF = chlorpyrifos measured in the sample (ng).

In Table 2.2, we illustrate the possible magnitude of changes in toxicity from respiratory exposure to mixtures of the parent CPF and CPF-O. We conclude that even at low concentrations CPF-O (e.g., 2 ng/m^3), total toxicity can be increased by factors of one to ten. If the higher toxicity equivalence factor values are correct, then toxicity could increase by more than 20-fold, putting some deceptively "low" concentrations above the acute screening level of 1,200 ng/m^3 as defined by the California EPA (CDPR 2006). As little as a 1% concentration of CPF-O relative to the parent CPF concentration could significantly increase overall toxicity.

Table 2.2/ Toxicity equivalent concentrations of chlorpyrifos for selected air concentrations after incorporation of chlorpyrifos-oxon using three toxicity equivalent factors. *Italics are > California EPA Screening Level of 1,200 ng/m³ (CDPR 2006).*

Measured air concentration CPF (ng/m³)[a]	Environmental oxon CPF-O (ng/m³)[a]	Toxicity Equivalent Concentration[b] (ng/m³)		
		5 x TEF[c]	10 x TEF[c]	100 x TEF[c]
15	2	25	36	225
25	2	35	46	235
50	11	108	165	*1203*
150	32	318	485	*3500*
250	25	381	512	*2870*

[a] Corrected for artificial transformation.

[b] $TEC_{CPF} = (CPF\text{-}O_e * CPF_{MW}/CPF\text{-}O_{MW} * TEF) + CPF$ (see Equation 3 in text).

[c] TEF = Toxicity Equivalence Factor; 5-fold value from Chambers et al 1993; 10 and 100-fold values from Cole et al 2005, Sultatos et al 1982.

Since many families in central Washington State live in communities with high agricultural density, we have found that pesticide levels with high concentrations CPF-O (>30 ng/m^3) would be a concern to human health. Neither artificial transformation nor toxicity equivalence of CPF-O was taken into account for the 2008 air monitoring study. Given its high potency, the failure to include analysis for CPF-O in air samples this could lead to considerable underestimates of health risk, especially when considering populations of genetically susceptible individuals and young children.

Future research should continue to investigate the sources and causes of oxon formation in dusts and airborne particles, such as "aging", mixtures, photodegradation, temperature, and the presence of oxidizing compounds such as ozone (O_3) and sulfur dioxide (SO_2). Ozone levels in particular have been predicted to increase substantially in areas like central Washington State as a result of changes in the atmosphere and climate. Although ozone is known to damage vegetation and reduce crop yields, less is known about its potential airborne chemical interactions with pesticides and may become an increasing concern with climate change patterns.

These results will contribute to the much needed explanation of environmental fate and transport of CPF-O to complement recent toxicological and epidemiological studies that have examined numerous health effects. These experiments stress the importance of accurately defining oxon presence in the environment because low concentrations may change health risk assessments—especially at concentrations typical for residential atmospheres farther from agricultural fields, where many families and children live, work and play. These findings call for consideration of the presence of organophosphorus oxons in air when calculating residential risk to pesticide drift and aerial transport.

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Chapter 3: Comparison of polyurethane foam and XAD-2 sampling matrices

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Chapter 3 Summary: Side-by-side active air sampling for the organophosphorus (OP) pesticide, chlorpyrifos (CPF) and its oxygen analog, chlorpyrifos-oxon (CPF-O) was conducted with two recommended air sampling matrices: OSHA Versatile Sampling (OVS) tubes with XAD-2 resin (NIOSH Method 5600) and polyurethane foam (PUF) tubes (ASTM, 2011). The study compared the proportion of artificially transformed chlorpyrifos-oxon (CPF-O) in the laboratory and in outdoor samples near the perimeter of a tree fruit application in Washington State. Laboratory tests demonstrated that the NIOSH-recommended OVS tubes artificially transformed up to 32% of chlorpyrifos to chlorpyrifos-oxon during the sampling process, whereas PUF tubes had little to no artificial transformation (≤ 0.1%) at very high concentrations. In the field, PUF tubes measured higher total pesticide air concentrations than OVS tubes, but the proportion of CPF-O

in the sample was significantly higher on OVS tubes than on PUF tubes ($p < 0.001$). This result confirmed that OVS tubes were converting a significant portion of CPF to CPF-O. In addition, PUF tubes reported measurable levels CPF-O in the field when no artificial transformation was expected. We conclude that the PUF matrix is the superior sampling medium for OP oxygen analogs when compared to OVS/XAD-2 because it resulted in very little artificial transformation. Community samples (150 meters away from orchard perimeter, 24 hours post-application) had considerably higher levels CPF-O than near field samples (<8 meters from orchard perimeter, 6 hours during application), suggesting that the oxygen analog may be formed over time and during atmospheric transport. This study also demonstrated that both CPF and CPF-O may be present at substantial concentrations in community air. It is recommended that both worker and community risk assessments take into consideration the presence of the more toxic oxygen analogs when measuring for OP pesticide mixtures.

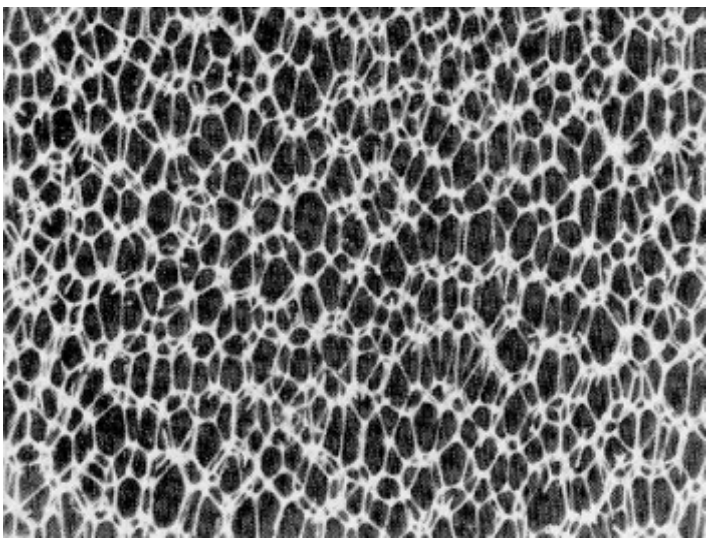
Chapter 3 Highlights

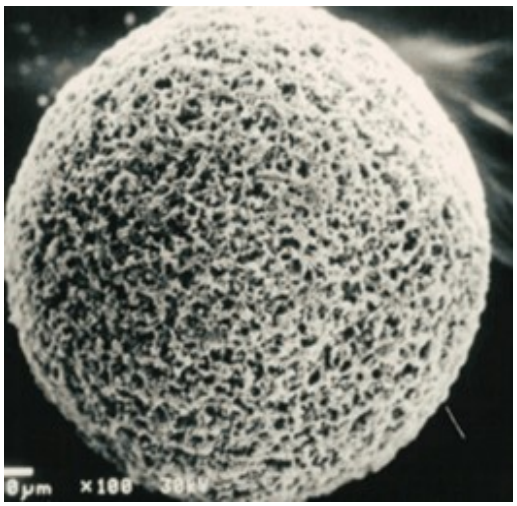
- The PUF matrix has been identified as a superior sampling medium for OP pesticides and their oxygen analogs when compared with the OVS/XAD-2 matrix.
- OP pesticides and their oxygen analogs were measured on PUF matrix in the field, further emphasizing the presence of oxon in community air.
- Significantly higher amounts of oxon were present in community air as it drifted further from the initial source of application.

3.1 Introduction

Currently, three established methods for active air monitoring for OP pesticides rely on collection with polyurethane foam (PUF) or XAD-2 resin matrices. Both matrices have been reviewed and validated for pesticide collection by the US EPA and ASTM, but NIOSH recommends the use of XAD-2 in OSHA Versatile Sampling (OVS) tubes (NIOSH 1994). In the past decade, XAD resin sampling matrices have become more common in active sampling because the XAD macroreticular beads yield larger specific surface area than PUF, allowing the resin to be used in smaller quantities and in light-weight air sampling tubes (See Figure 3.1). Low volume OVS tubes containing XAD-2 may be as small as 8 mm diameter X 75 mm length (140/270 mg sorbent) in comparison to the more common 22 X 100 mm size for PUF tubes (500 mg sorbent) (SKC, Inc.). The difference in size is beneficial when considering options for use with personal air sampling pumps attached near the breathing zone of research participants. However, little is known about how the difference in sampling matrices may affect reported airborne levels of OP pesticides or their oxons.

Figure 3.1/ Micrograph cross-section of PUF sampling matrix (10X) and XAD-2 macroreticular resin bead (100x) (NRC, Canada, Environment Canada).





Concerns regarding the accuracy of sampling results arose after a recent study sampled for the common airborne OP pesticide, chlorpyrifos (CPF) and found that in OVS tubes 5 to 30% of CPF was artifactually converted to chlorpyrifos-oxon (CPF-O), especially at lower concentrations (≤ 30 ng/m^3) that are typical of previously reported community levels (See Chapter 2, Fenske et al. 2009). Spiked field samples with no air flow did not result in this artifact, suggesting that it occurred during the active air sampling process. Previous studies have noted artifactual oxon formation from other OP pesticides (e.g. parathion) when actively sampling with XAD resins (Woodrow et al. 1978, Seiber et al. 1989). None of the three OP pesticide sampling methods discussed earlier (ASTM, USEPA and NIOSH) include chemical analysis for the oxygen analogs. This means that results from studies using OVS tubes are likely underestimating actual OP pesticide air concentrations. There is little knowledge on the cause of artifact formation, and other potential air sampling matrices such as PUF have not been examined for this phenomenon or how it affects reported air concentrations.

The primary aim of this research was to evaluate the ability of two traditional sampling matrices (PUF and XAD) to accurately measure air concentrations of the OP pesticide CPF and its oxygen analog CPF-O. The experiments involved use of spiked laboratory samples and active air samplers exposed to a representative range of environmental air concentrations of CPF and CPF-O in the field during an application.

A secondary aim of the study was to evaluate the performance of a passive sampling method for the OP pesticides. Very few published passive sampling methods for these pesticides exist, so we chose to examine the PUF matrix due to its strong adsorptive capacity. We placed these passive collectors in areas directly near applications side by side with the active samples. XAD-2 resins were not explored passively due to difficulties arising from the physical disturbance of small macroreticular beads. Passive methods have not been formally reviewed by

the EPA or ASTM, but past research has identified that deposition maybe informative for surface area loading 2-4 hours following a pesticide application (Tsai 2007). In addition, such passive methods are very low cost and do not require an electricity source.

3.2 Sampling Materials and Methods

3.2.1 Laboratory

Experiments on spiked samples were conducted in a laboratory fume hood according to NIOSH method 5600 for OVS tubes (NIOSH, 1994) and EPA Method TO-10A for PUF samplers (USEPA 1999). OVS tubes containing XAD-2 sorbent (SKC 226-58) and PUF tubes (SKC 226-92) were both spiked with 99.5% analytical grade CPF (ChemService, Inc. PS-674) in acetone solution with a 25 µl Hamilton™ positive displacement syringe at levels of 0, 40, 60, 200, or 2000 ng. The solution was applied directly to the matrix by inserting the needle beyond the quartz fiber pre-filter of XAD-2 resin and directly into the middle section of the PUF. Each OVS and PUF tube was immediately connected to an SKC air sampling pump (224-PCXR8) operated at a flow rate of two liters per minute (LPM) for 24 hours. Both sets of tubes were situated side-by-side in the hood, drawing air at room temperature (20-22° C). Sampling pumps were pre- and post-calibrated with a DryCal DC-Lite. Flow rates for each were measured and the air volumes (m^3) were calculated separately for each spiked sample.

In the same manner, three passive PUF deposition disks (14 cm diameter, 2.5 cm depth, Tisch Environmental, TE-1014) were spiked with 0, 25, and 400 ng CPF and laid flat on glass petri dishes in a sampling chamber inside the lab hood. Laboratory blanks and storage spikes were included in the experiments for quality assurance purposes and to ensure that the spike solution was not contaminated with the oxygen analog (CPF-O).

3.2.2 Field

Twelve pairs of OVS/PUF tubes were co-located near an apple orchard during an air blast application of Lorsban® (CPF) in Washington State's Yakima Valley in March 2010. Samples were hung side by side on a 1.5 meter (m) air sampling mast (Figure 3.2). All samplers were equipped with calibrated SKC pumps. In order to examine potential transformation to the oxygen analog across a range of possible outdoor concentrations, samples were taken near to and far from the field perimeter. To capture air concentration data representative of higher levels, eight pairs of sampling tubes were co-located 6 to 8.5 m from the orchard perimeter in the four primary wind directions. Pumps were operated at 6 LPM for 6 hours during application. To capture data representative of community air levels, four pairs were co-located 150 m from the orchard perimeter and operated at 2 LPM for 24 hours immediately post-application. This distance was used to represent community exposures because many homes, schools, and local businesses were within this range of proximity to orchards in the area (See Figures 3.2 and 3.3).

Figure 3.2/ Side by side collection PUF and OVS sampling matrices. Samples were co-located, hung from sampling masts, and wrapped with aluminum foil to reduce potential reactions with UV light. Flow rates were recorded using rotameters.

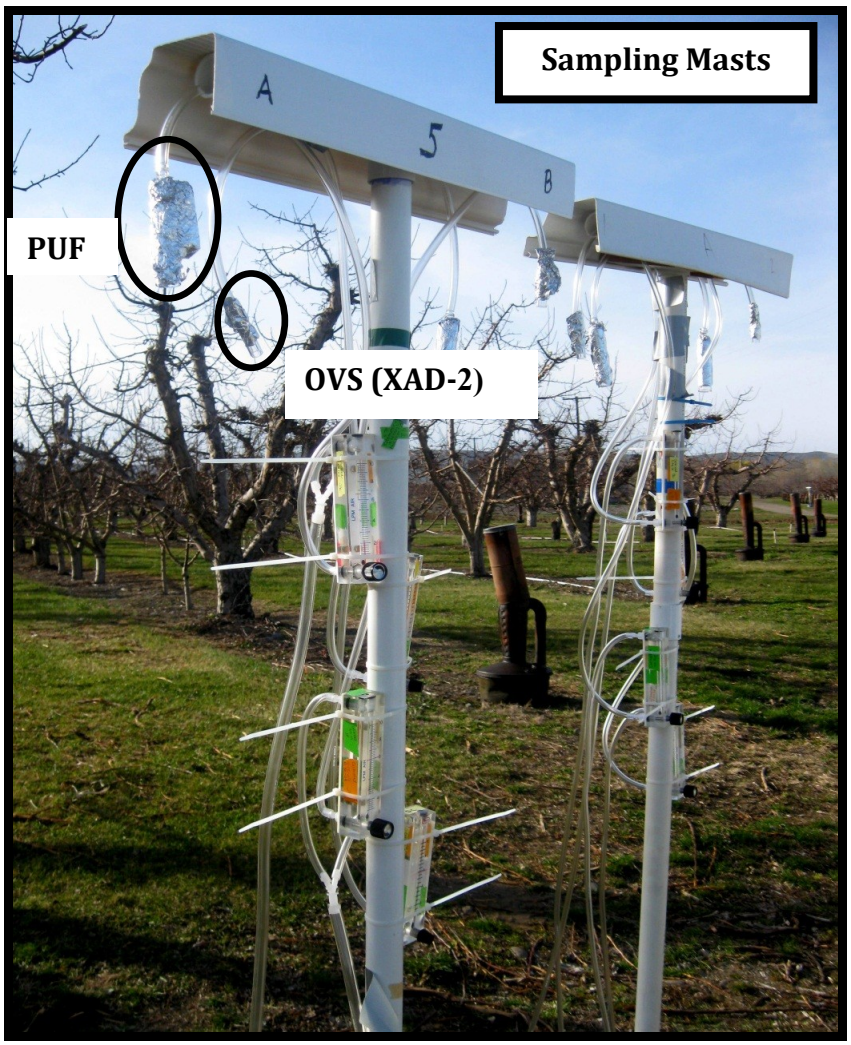
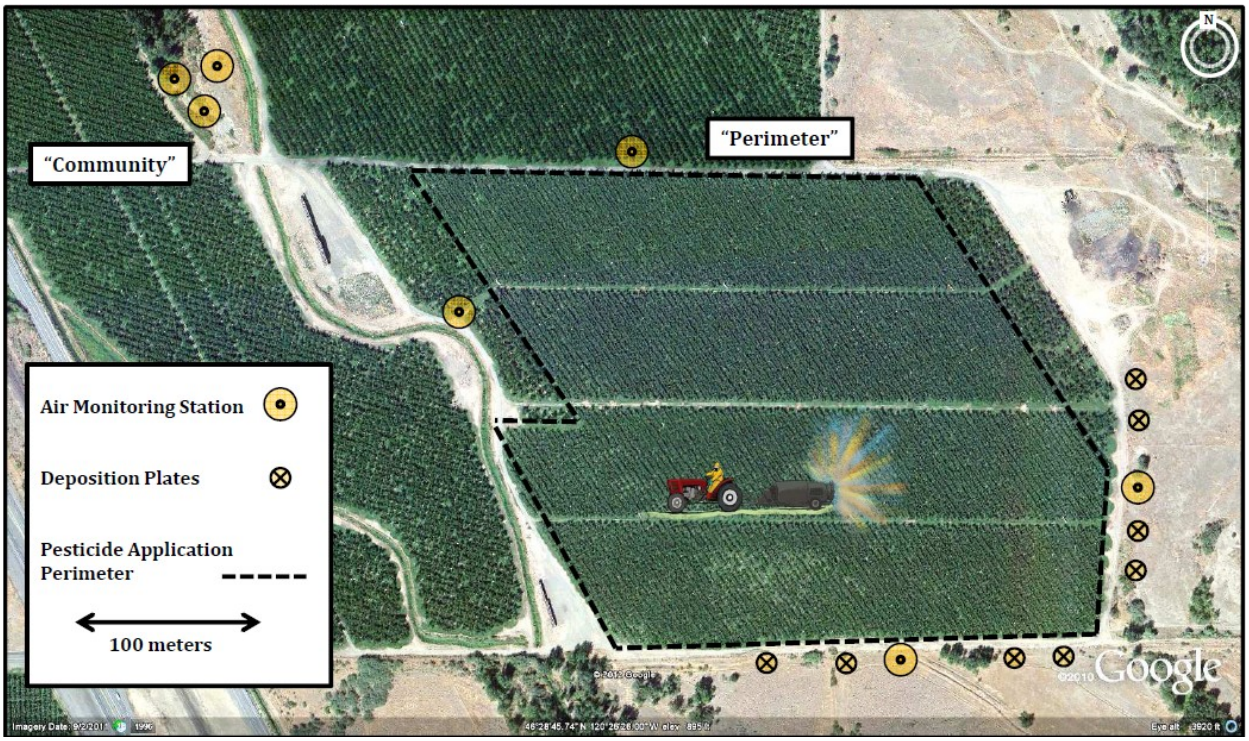


Figure 3.3 / Yakima Valley community and near-field distances of homes, businesses, and schools. 2011 Google Earth Version 6.2, NASA Terra Satellite Imaging, and USDA Farm Survey 2011

Figure 3.4 / Field Placement of community and near-field air monitoring stations and deposition places during and after a pesticide application. 2011 Google Earth Version 6.2, NASA Terra Satellite Imaging.



The community samples were stationed northwest of the orchard because previous wind rose data on prevailing seasonal winds using the Washington State University Agricultural Weather Network monitor < 5 km away (AgWeatherNet 2.0), and the orchard foreman's onsite thermo-wind meter readings (Extech® Mini Anemometer) indicated this site was located upwind. Flow rates were measured and the air volumes were calculated separately for each spiked sample. All air sampling pumps were stored in a locked weather-proof container.

Twelve glass deposition plates (14 cm diameter) were lined with a PUF matrix (14 cm diameter, 2.5 cm depth) and situated 6 m from the orchard perimeter, near the active air sampling masts. These samples were stationed in two downwind directions using the same data on prevailing seasonal winds and onsite thermo-wind meter readings as for the active samples. The plates were laid horizontal at a height of 0.8 m. To examine the effect of time on potential transformation of OP pesticide to its oxon on the matrix, half of the deposition plates were removed following the application, and half were removed 6 hours later. Field researchers wore personal protective equipment upon re-entry to collect the field samples post application.

Meteorological data was obtained during the application and post-application periods using a monitor < 5 km from the application site (AgWeatherNet 2.0), and wind roses during the sampling period were produced using WRPlot View 7.0 (Lakes Environmental™, available in the Appendix). All samples were stored at the University of Washington field office in Yakima in a freezer at -10°C until transported to the University of Washington Environmental Health Laboratory (EH Lab) in Seattle.

3.2.3 Chemical and Statistical Analysis

Chemical analysis was performed for both CPF and CPF-O using LC-MS-MS (Sancho et al. 2000). All samples were sonicated with an acetone/acetonitrile solution (10 ml) containing stable-isotope labeled internal standards of chlorpyrifos diethyl-D_{10}, 99% (Cambridge Isotope Labs DLM-4360) and $^{13}C_2$, ^{15}N-Chlorpyrifos oxon (donated by Dow Agro Sciences LLC). Extraction of the larger PUF deposition plates used higher desorption volumes of solution (50 ml), resulting in higher compound limits of detection (LOD). The limit of detection (LOD) for both CPF and CPF-O was 0.1 ng/sample for both types of active air sampling tubes and 1 ng/sample for the PUF deposition plates.

Blanks and quality control spikes were used in the laboratory and field and handled in a manner similar to other samples. Spikes were prepared by introducing low levels of analytical grade CPF in acetone solution (50 ng) into the middle section of PUF and front section of the XAD-2 resin with a 25 µl syringe. Spiked uncapped tubes were arranged in the laboratory during the sample period to examine samples with no air actively pulled through the tubes. In the field, OVS field blanks yielded no detectable CPF or CPF-O; two PUF tube field blanks yielded CPF-O at the detection limit (0.1ng); and one PUF deposition field blank yielded CPF at the detection limit (1 ng). Samples were corrected for these blanks. No breakthrough was detected on the back up section of the OVS tubes.

GPS coordinates were used to map side by side samplers at perimeter and community site locations in the field using GoogleEarth Version 6.2. For both the laboratory and field studies, statistical comparisons were made comparing the results on PUF and XAD-2 active air matrices using the student's T test for paired samples. Similar to previous studies (Armstrong et al 2012 (Chapter 2), Fenske et al 2009), we estimated the % CPF-O while adjusting for the difference in molecular weight. Another common test to look at differences between two recognized sampling

methods is the Bland-Altman Plot. The Bland Altman assumes that the two methods designed to measure the same parameter should have good correlation. The plots are not in this chapter but can be viewed in the Appendix (Figure S.3.2).

3.3 Results

3.3.1 Laboratory

Recoveries were lower for OVS tubes (mean 78.5%) than for PUF tubes (mean 100.6%) or PUF deposition plates (mean 90.2%), as indicated in Table 1. According to the EPA Method TO-4A (USEPA 1999), recoveries must fall between 60-120%, and all recoveries were in the acceptable range. Recoveries larger than 100% were likely due to spiking error because laboratory blanks demonstrated no contamination with CPF or CPF-O. In spiked OVS tubes 10-15% of CPF was converted to CPF-O at higher spike masses, and 32% was converted at the lowest spike mass. PUF sampling tubes spiked under the same conditions demonstrated artifact formation of CPF-O (0.1%) only at spike levels ≥ 2000 ng. Spiked PUF deposition plates also yielded no detectable CPF-O formation.

Table 3.1/ Total Mass CPF (ng), Percent CPF-O, and Percent Recovery in laboratory measured after 24 hours air sampling at 2 LPM with side-by-side CPF-spiked active PUF and OVS tubes and PUF passive deposition plates.

Spike Mass		Mass Total CPF[a]	% Recovery		Mole % CPF-O[b]
(ng)	N[b]	Mean (ng)	Mean	CV (%)[c]	Mean
Active Samples					
PUF	(11)				
0		<LOD	--	--	< LOD
61		51.3	84	27	< LOD
200		232	116[d]	3	< LOD
2100		2267	108[d]	2	0.1
OVS	(18)				
0		<LOD	--	--	< LOD
42		32.1	77	5	31.6
60		48	80	14	10
200		151.7	74	20	14.6
2100		143.7	68	18	15.4
Passive Samples					
PUF	(8)				
0		<LOD	--	--	< LOD
25		22.6	91	31	< LOD
400		357	89	27	< LOD

[a] Total Mass is CPF+CPF-O, corrected for difference in molecular weight, % chlopyrifos-oxon is the amount of chlorpyrifos-oxon, corrected for difference in molecular weight, divided the amount of total chlorpyrifos, x 100.

[b] Number of spiked samples; includes triplicates at each spike level and two blanks.

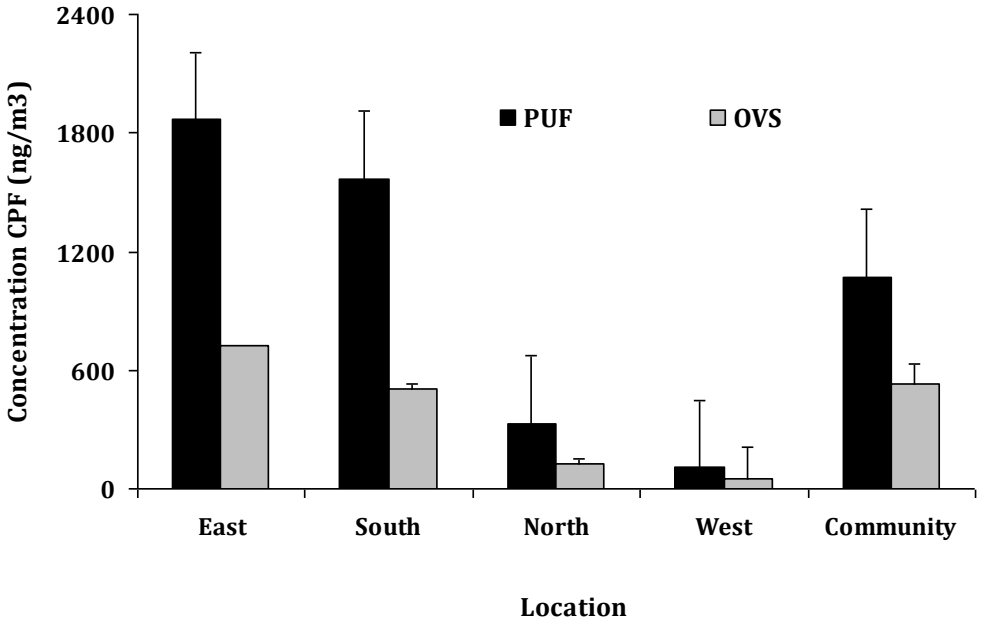
[c] CV = coefficient of variation.

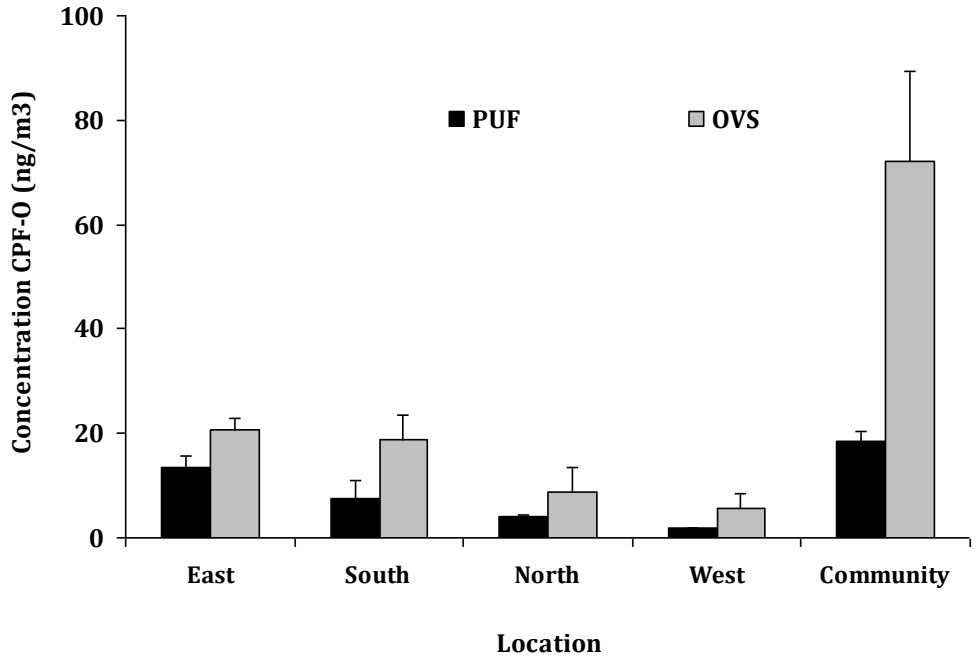
[d] Spike recoveries were considered acceptable between 60-120% (USEPA, 1999).

3.3.2 Field Perimeter Samples

During the pesticide application, outdoor temperatures ranged from 2-14°C and wind conditions were relatively calm, with northwesterly winds at an average speed of 1.3 m/s. As indicated in Figure 3.5, measured CPF air concentrations near the orchard ranged from 32 to 647 ng/m^3 on OVS, and 97 to 2,039 ng/m^3 on PUF. Overall, the mean CPF concentrations on PUF tubes were significantly greater than the mean concentrations on OVS tubes ($p \leq 0.001$). Mean air concentrations on the east and south sides of the perimeter (downwind) were more than four times higher than in the north and west (upwind), consistent with measured wind direction. Wind data is available in Appendix Figure 9.1. CPF-O concentrations were 4-22 ng/m^3 on OVS and 2-14 ng/m^3 on PUF, with concentrations also higher downwind. The proportion of CPF-O to total CPF (% CPF-O) differed dramatically for the two sampling matrices ($p \leq 0.001$): mean values were only 1-2% on the PUF matrix; mean values ranged from 4-13% on the OVS matrix. In both cases, % CPF-O had an inverse relationship to total CPF air concentration.

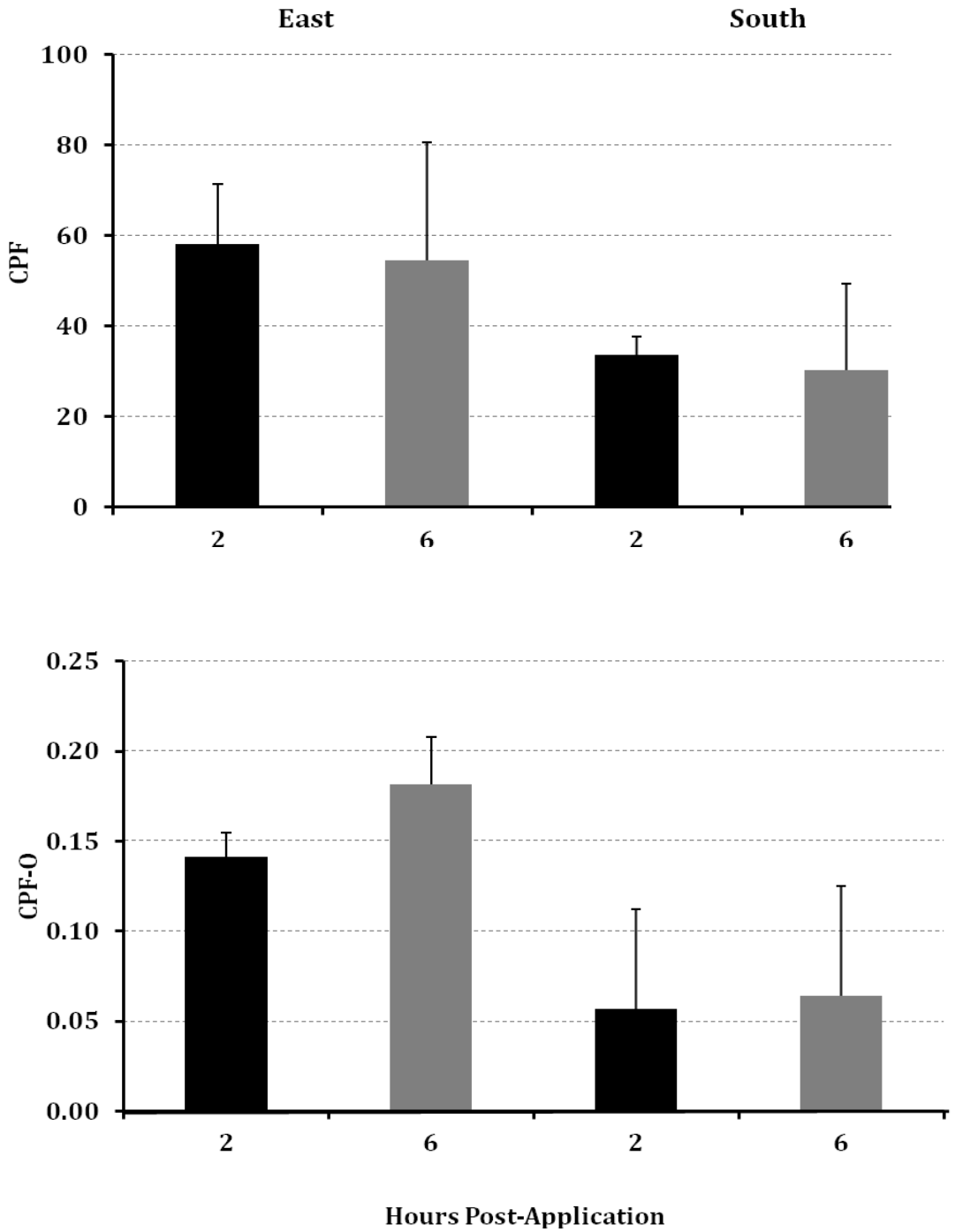
80Figure 3.5/ Side-by-side PUF and OVS Comparison of near field CPF and CPF-O sampling (orchard perimeter) during an application (6 hour sampling period) and far field sampling (community) post application (24 hour sampling period). Bars and whiskers represent mean and standard deviation values, respectively.





For the PUF deposition samples, mean CPF surface area loadings on the east perimeter were higher (50-60 mg/m^2) than those placed south of the orchard (30-35 mg/m^2), as indicated in Figure 3.6 ($p = 0.000$). This was consistent with prevailing wind patterns. CPF-O loadings followed a similar pattern. Unlike the active air samples, the % CPF-O on deposition samples was very low (0.17-0.36%). There was a small increase in the amount of CPF-O after a 6 hour delay in time to removal, but this was not statistically significant. However, this provided insight regarding the potential aging process of CPF to CPF-O on the deposition samples that were left out for longer periods of time. It is worthwhile to note that even these low percentages CPF-O still account for considerable mass loadings of CPF-O (ranging from 0.04-0.21 mg/m^2) near the field.

Figure 3.6: Mass loading (mg/m²) for chlorpyrifos (CPF) and chlorpyrifos-oxon (CPF-O). Particle deposition sampling after removal upon re-entry 2 hours later and an extended 6 hours later, near the orchard perimeter. Bars and whiskers represent mean and standard deviation values, respectively.



3.2.2 Community Samples

The 24-hour post application community samplers measured CPF air concentrations that ranged from 375 to 660 ng/m^3 on the OVS, and 965 to 1,162 ng/m^3 on the PUF, with mean concentrations of 500 and 1,100 ng/m^3, respectively. Mean concentrations on PUF tubes were significantly greater than concentrations measured by OVS tubes ($p \leq 0.001$). Although the samples were located further away than the perimeter samples and continued 24 hours post application, the measured concentrations fell within the range of the orchard perimeter concentrations. During the sampling period following application, outdoor temperatures ranged from 8-18°C and wind speed (1.2 m/s) was low, but wind direction was more variable than during the spray period and may have shifted following application (wind rose data available in supplementary figures).

Concentrations of CPF-O ranged from 50 to 92 ng/m^3 on the OVS and 16 to 21 ng/m^3 on the PUF. Both concentration and % CPF-O were significantly higher on the OVS than PUF, despite the fact that OVS reported lower airborne levels of total pesticide ($p \leq 0.001$, See Figure 3.6). In addition, all community samples had higher %CPF-O than the orchard perimeter samples during application for both matrices ($p<0.01$).

3.4 Discussion

3.4.1 Differences of Measured CPF and CPF-O on PUF and XAD-2

These results highlight some of the complexities of measuring airborne pesticide concentrations of CPF and CPF-O with accuracy and precision. In the laboratory, very little CPF-O was artifactually transformed on the PUF matrix in comparison to XAD-2 resin. There was also no artificial transformation on quality control samples and capped spikes without drawn air. This demonstrated that the transformation was occurring during the process of pulling air through OVS (XAD-2) resins, but not during the process of pulling air through PUF.

These results were replicated in the field. We found that side-by-side samples of PUF and XAD-2 yielded a significant difference in reportable concentrations for both CPF and CPF-O and assume this partially attributable to the artificial transformation of CPF to CPF-O in XAD-2 tubes, but does not entirely explain the phenomenon. A notably smaller difference in reported concentrations may be due to direct blow on of particulate to the frontal surface areas of OVS and PUF sampling tubes in near field samples. This side-by-side difference in the field of measured concentrations is a large concern, given the fact that both methods are recommended by the EPA (Method TO-10A) (1999).

3.4.2 Environmental Chlorpyrifos-Oxon (CPF-O)

Although very little or no CPF-O was artificially transformed on the PUF matrix in the laboratory, small concentrations of CPF-O (2-10 ng/m^3 in near field samples during application and 16 to 21 ng/m^3 in community samples post application) were still observed on PUF tubes in the field. These experiments confirmed that the CPF-O is likely environmentally present in air and unlike measured concentrations of its parent compound, CPF-O can be higher post

application than during application (See Figure 3.5).

The PUF deposition disks further confirmed that CPF-O was present during the sampling period, but proportions collected on particle deposition samplers were less than 1%. There was a noticeable difference in %CPF-O on active PUF and passive PUF samplers. We hypothesize that this may be due either to the inverse relationship between mass total CPF and %CPF-O, or due to a difference in presence of oxygen analogs in the particle and gaseous forms of the OP pesticide. Further tests should examine the presence and levels of environmental CPF-O over time, and if these amounts differ in particulate vs. vapor. Higher amounts of CPF-O in vapor form would be of great concern when considering direct human inhalation exposures.

The 24 hour post application community samples had reported concentrations similar to the near field concentrations at the time of application. This may have been due to the continued volatilization, wind erosion, and drift of CPF and CPF-O 24 hours following application (Zhou et al 2010). In Figure 3.5, the community samples report noticeably higher concentrations CPF-O (ng/m3) and % CPF-O than in the orchard perimeter samples on both PUF and OVS tubes. We hypothesize that this may be due to both the chemical aging process over time and distance of transport, which allows for atmospheric interactions with oxidizing compounds and photolysis.

Both the existence of CPF-O in these representative community samples and high concentrations of total CPF are a concern when considering potential exposures to humans living in nearby residential areas. Therefore, more research should focus on using the PUF sampling matrix in residential air monitoring studies and in environmental fate and transport studies that focus on the meteorological factors like wind and temperature's influence on airborne concentrations and transport of parent compound and their oxygen analogs.

For both methods, whether PUF or XAD-2 resins, CPF-O is an important part of the mixture when considering total concentrations of organophosphorus pesticides. The failure to account for CPF-O will no doubt lead to an underestimation of total CPF pesticide concentrations.

We have found the NIOSH recommended sampling matrix (OVS XAD-2 Resin Tubes) to artificially transform substantial amounts CPF to CPF-O both in the lab (up to 32%) and in the field; and that this leads to inaccuracies in reported levels CPF and CPF-O in field studies. This is problematic because this study has demonstrated that it also leads to statistically significant differences if the results are examined alongside studies relying on air samples taken with PUF matrices. If researchers are interested in measuring human exposures to the more potent CPF-O, it may become difficult to determine how much is artificially transformed or is environmentally present in air if they rely on XAD-2 matrices. However, these findings demonstrate that researchers may be able to use the PUF matrix instead to properly quantify exposures to CPF-O.

Notes to Chapter 3

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Chapter 4: Development of a sensitive LC-MS/MS method

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Chapter 4 Summary: A rapid liquid chromatography tandem mass spectrometry (LC-MS/MS) method has been developed for determination of levels of the organophosphorus (OP) pesticides chlorpyrifos (CPF), azinphos methyl (AZM), and their oxygen analogs chlorpyrifos-oxon (CPF-O) and azinphos methyl-oxon (AZM-O) on common active and passive air sampling matrices. XAD-2 resin and polyurethane foam (PUF) matrices were extracted with acetonitrile solution containing stable-isotope labeled internal standards (ISTD). Analysis was accomplished in Multiple Reaction Monitoring (MRM) mode and analytes in unknown samples were identified by retention time (ą 0.1 min) and qualifier ratio (ą 30% absolute) as compared to mean of calibrants. For all compounds, calibration linearity correlation coefficient was ≥0.996. Limits of detection ranged from 0.5-1 ng/sample for CPF, CPF-O, AZM, and AZM-O on active sampling matrices and ranged 1-5 ng/sample on passive sampling matrices. Spiked fortification recoveries were acceptable according to EPA Method TO-10A (1999): 78 -113% from XAD-2 active air sampling tubes, 71-108% from PUF active air sampling tubes, and 74-113% from PUF passive air sampling disks. Storage stability tests also yielded acceptable recoveries ranging from 74-94% after time periods ranging from 2-10 months. The results demonstrate that LC-MS/MS is a sensitive method for determining these compounds from two different matrices at low

concentrations resulting from spray drift and long range transport in non-target areas. In a laboratory comparison, the limit of detection (LOD) for LC-MS/MS was 100 times less than the currently recommended gas chromatography-mass spectrometry (GC-MS) methods.

Chapter 4 Highlights

- LC-MS/MS is a sensitive, accurate, and precise method to capture organophosphorus (OP) pesticides chlorpyrifos (CPF), azinphos methyl (AZM), and their oxygen analogs chlorpyrifos-oxon (CPF-O) and azinphos methyl-oxon (AZM-O) on two different matrices at low concentrations typical of community sampling.
- Spiked fortification recoveries and storage stability up to 10 months on air sampling matrices is acceptable.

4.1 Introduction

There is growing interest among public health scientists and practitioners in the assessment of community exposures to airborne organophosphorus (OP) pesticides; primarily in geographical regions were they are commonly applied aerially or with a tractor spray tank. Community studies may differ from occupational studies because measurements of exposure to OP pesticides occur in non-target areas. Community samples are collected at varying distances from applied fields rather than at the source and concentrations may be lower.

Studies conducted in Washington and California State have begun to measure the oxygen analogs chlorpyrifos-oxon (CPF-O) and azinphos methyl-oxon (AZM-O) in air samples alongside parent compounds (Seiber et al. 1989; CARB 1996, 1998; LeNoir et al. 1999; CDPR 2003, 2006; Fenske et al. 2009). On average, these studies reported concentrations of oxon that was 10-100x lower than the parent compound. However, in the Washington state study, the oxon represented as much as 94% percent of total pesticide mixture in some cases (Fenske et al. 2009). In Chapter 2, it was demonstrated that the failure to measure for these oxygen analogs in air will lead to the underestimation of total OP pesticide exposures. As little as a 1%

concentration of CPF-O relative to the parent CPF concentration could significantly increase overall toxicity.

The current recommended air sampling matrices for these compounds are XAD-2 styrene-divinylbenzene resin [used in OVS (OSHA Versitile Sampler) tubes (NIOSH, 1994)] and polyurethane foam (PUF) (EPA, 1999, ASTM 2011). A number of studies have provided sufficient data for active air sampling method validation and trapping efficiencies, and some have considered oxygen analogs in the assessment (CARB 1994, Shibamoto 1996). The use passive sampling for semi-volatile compounds is an expanding technology but not much research has been conducted on the ability to passively sample for airborne OP pesticides. Nevertheless, the development of a sensitive analytical method may help move this research forward, as most OP pesticides are semi-volatile compounds.

Current analytical methods are adequate for most worker exposure scenarios in which the goal is to measure airborne concentrations of OP pesticides >1,000 ng/m^3, but these methods were not designed to evaluate the oxons of these compounds. Most methods cite the use of gas chromatography-mass spectrometry (GC-MS) for analysis of air sampling matrices. In regard to community exposures, ambient concentrations of OP pesticides (even during active application seasons) tend to be less than 1 ug/m^3 (Seiber et al. 1989; CARB 1996, 1998; LeNoir et al. 1999; CDPR 2003, 2006; Fenske et al. 2009). Sampling concurrently for the oxons thus requires air concentration limits of detection in the 0.1-10 ng/m^3 range to be relevant for community health risk assessments. In 2006, Alder et al. conducted a literature review to compare gas chromatography-mass spectrometry (GC-MS) and LC-MS/MS methods for the analysis of pesticides and reviewed the use of LC-MS/MS in pesticide analysis. The reported LC-MS/MS methods for CPF and AZ resulted in lower detection limits, but analysis was conducted primarily in water samples

(Hernandez et al. 2001).

This paper has compiled the laboratory method development results stemming from two recent air monitoring studies conducted in Washington state; one study used XAD-2 active sampling matrices and was conducted in collaboration with the Washington State Department of Health Pesticides Program (Fenske et al. 2009), and one used PUF active and passive sampling matrices for the Center for Child Environmental Health Risks Research (see Chapters 2-3). The second study used PUF as a sampling matrix after recent findings highlighted the artificial transformation of ≤32% oxon during air sampling of OP pesticides with sampling devices containing XAD-2 media in the laboratory and outdoors (Chapter 2). Higher percentages of oxon were artificially transformed at lower concentrations (<30 ng/m^3) typical of community levels.

Both studies included an improved laboratory method for quantification of OP pesticides and their oxygen analogs from different types of air sampling media which should prove useful for future studies of these chemicals in community air. The analytical procedures described in this paper were used for the extraction and analysis of organophosphorus compounds including chlorpyrifos (CPF), chlorpyrifos-oxon (CPF-O), azinphos-methyl (AZM), azinphos methyl-oxon (AZM-O) collected on both types of matrices during active and passive air sampling for the two studies.

The paper describes an extraction method that was adapted from NIOSH 5600 method, with the substitution of a solvent compatible with aqueous chromatography (Alder et al. 2006, Aglient 2008, Sancho et al. 2000). Instrumental analysis was developed from published liquid chromatography/mass spectrometry (LC-MS/MS) methods (Alder et al. 2006, Sancho et al. 2000). The procedures desorbed the compounds from XAD-2 and PUF by ultrasonication of the sampling

matrices with acetonitrile solution containing stable-isotope labeled internal standards (ISTD). Extracted samples were then analyzed using Liquid Chromatography/Mass Spectrometry (LC-MS/MS) with Multiple Reaction Monitoring (MRM) detection without any further sample preparation by the University of Washington Environmental Health Laboraty (EH Laboratory).

4.2 Experimental

4.2.1 Chemicals and materials

Spike solutions for fortification and storage recoveries were prepared in acetone using the standards for CPF (99.5%, 1000 µg/mL in Acetonitrile, ChemService, West Chester, PA, PS-674), CPF-O (98.8%, ChemService, 1000 µg/mL in Acetonitrile, MET-674B), AZM (99.5%, 100 µg/mL in MeOH, ChemService, F2055S), and AZM-O (98.5%, 100µg/mL in Toluene, ChemService MET-666A). The internal standards solutions were prepared using CPFdiethyl-D_{10} (99%, neat, 100 µg/mL in Acetonitrile, Cambridge Isotope Labs, Andover, MA, DLM-4360), $^{13}C_2$, ^{15}N-CPF-O (99%, solid, donated by Dow Agro Sciences, Indianapolis, IN), AZM-D6 (98.5%, 1000 µg/mL in Toluene, EQ Laboratories, Atlanta, GA,XA10365100AC), and AZM-Odimethyl-D6 (99.3%, solid, Bayer Crop Science, Research Triangle Park, NC, K-176). Solvents and mobile phase components were pesticide or LC-MS grade. Deionized water (Barnstead Nanopure II, 18 mΩ) was used.

The active air sampling matrices were XAD-2 [OSHA Versatile Sampler (OVS), 13 x 75mm (outer diameter x length), 270/140 mg sorbent, SKC, Fullerton, CA,226-58] and PUF (22 x 100mm (outer diameter x length), 76 mg sorbent, SKC Catalog #226-92); and the passive air sampling matrix was the PUF-PAS disk commonly used with the TE-200 PAS air sampler (14 cm diameter x 2.5 cm depth, 4,200 mg sorbant) Cat. # TE-1014, Tisch Environmental, Cleves, OH). The active air

sampling tube XAD-2 and PUF matrices are pre-cleaned with acetone by SKC (Fullerton, CA) and the PUF-PAS disk was cleaned in a soxhlet extractor with ethyl acetate for 30 minutes (~16 cycles) prior to use.

4.2.2 Instrumental Analysis

Apparatus and chromatography were performed by the EH Laboratory. A full description on the system is available in the Appendix.

4.2.3 Recovery assays

Matrix spike recovery was performed for XAD-2, PUF active sampling matrices, and PUF passive sampling matrices at spike mass loadings of 5, 50, and 1000 ng. An additional spike mass loading of 500 ng was performed on PUF active and passive matrices. PUF matrices were spiked *in situ* into the approximate center of the matrix using a 50 µl Hamilton positive displacement syringe. XAD-2 matrices were spiked *in situ* by inserting the needle beyond the quartz fiber pre-filter into the first bed of XAD-2.

4.2.4 Sample Preparation

After spiked solutions were applied for fortification recoveries, all samples were immediately capped and stored in a -20°C freezer if extractions took place the following day. After freezer removal, sampling matrices were allowed to equilibrate at room temperature (20-23°C) in a lab hood for 30 min prior to extraction. Active air sampling media were placed in 50 uL Corning® centrifuge tubes, with ISTD solution (25µL of 100 ng/mL CPF-diethyl-D_{10}, $^{13}C_2$, 100 ng/mL ^{15}N-CPF-O, 4,000 ng/mL AZM-D_6, 1,000 ng/mL AZM-OD_6) and acetonitrile (5-10mL

for XAD-2 and PUF) .and sonicated for 1.5 hours at room temperature (20-23°C). The front and back section of the XAD-2 tubes were extracted separately to simulate procedures from NIOSH method 5600 (1994). The inside of the glass active sampling tubes and the glass Petri-dishes (used to store passive sampling matrices) were rinsed with 5mL of acetonitrile, which was added to the extract. The larger passive PUF disks were sonicated in 10-50mL acetonitrile solution with the same ISTD mass as active sampling matrices. The extract was evaporated at 60°C in a nitrogen stream (TurboVap II, Biotage, Charlotte, NC) to concentrate to 1.5 mL. When particulate was present, the extract was filtered with a PTFE syringe filter (all polypropylene syringe, 13mm, 0.2 μm porosity, Whatman). Quality control included matrix blanks and reagent blanks (acetonitrile, ISTD, and no air matrix).

4.2.5 Sensitivity

For each compound, the mass per sample (ng/sample) limit of detection (LOD) was determined by taking three spiked samples near the LOD and calculating their standard deviations. The LOD was defined as 3 times the standard deviation, and the limit of quantification (LOQ) was defined as 10 times the standard deviation. The LOD and LOQ, expressed in air concentrations, were calculated by dividing the mass LOD and LOQ by typical air sampling volumes. For active samples, this was 2L/min for 24 hours = 2.88 m^3 (Fenske et al. 2009, Chapter 3). In contrast, passive samples are deployed for much longer periods of time, ~30 days, and typical air volumes are 3.4m^3/day (102m^3) for CPF and CPF-O and 3.6 m^3/day (108m^3) AZM and AZM-O (Shoeib and Harner 2002, Hayward et al. 2010). It should be noted that passive sampling air volumes are dependent on variable meteorological conditions, and these were not considered when calculating these typical passive sampling rates. Therefore, the estimates should be regarded as approximate, not exact. More research on passive sampling is conducted in Chapters 5 and 6.

4.2.6 Storage Stability

The storage stability results on XAD-2 active sampling matrices and PUF active and passive sampling matrices are aggregate results from the two recent air monitoring studies conducted in Washington State. The timing of the storage stability analysis was dependent on analysis of field sampling results, which are not presented in this study. For the first study, the XAD-2 active air sampling matrices were spiked in the same fashion as for the matrix spike recovery experiments at mass loadings CPF and CPF-O of 25 ng, AZM and AZ>-O of 50 ng, and stored for 171-236 days. For the second study, the PUF active air sampling matrices were spiked at mass loadings CPF and AZM of 20-50 ng, and stored for 72 days. Finally, the PUF passive air sampling matrices were spiked at mass loadings CPF 500-1500 ng and stored for 158 days, and AZM 125-500 ng and stored for 112 days. Smaller storage spike levels (20-50 ng) were used for active air sampling tubes than the passive PUF disks (125-1500 ng because passive samplers had in larger masses of OP pesticides on the matrix due to prolonged sampling periods (Table 4). No storage blanks were included.

4.3 Results

4.3.1 LC-MS-MS Determination

Analysis was accomplished in Multiple Reaction Monitoring (MRM) mode and analytes in unknown samples were identified by retention time (ą 0.1 min) and qualifier ratio (ą 30% absolute) as compared to mean of calibrants. The precursor and product ion mass/charge (m/z), fragmentation (volts), and collision energy (volts), and retention time (min) information is available in the Appendix.

4.3.2 Linearity of Response and Detection Limit

Calibration curves and resulting limits of detection and quantification are shown in Table 4.1. Calibration performance was based on the linearity of the calibration curve. LOD values ranged from 0.5-1 ng/matrix for CPF, CPF-O, AZM, and AZM-O on active sampling matrices and were slightly larger on passive sampling matrices, ranging from 1-5 ng/sample. The same was true for LOQ values, ranging from 1.5-2 ng/sample on active sampling matrices and ranging from 2-10 ng/sample on passive sampling matrices. In addition, we report some optimal detection limits for these compounds in air, dividing by typical sampling volumes. Since typical passive sampling volumes (~30 day sample duration) are much greater than active sampling volumes (24 hour sample duration) in community studies, it results in lower LOD values (0.01-0.05 ng/m^3) on passive PUF disks than active air samples (0.17-0.35 ng/m^3).

Table 4.1/ Linearity of response and detection limits. Includes calibration curves, LOD, and LOQ values for CPF, CPF-O, AZ, and AZ-O on three types of air sampling matrices.

	Calibration Curve	Limit of detection		Limit of quantification	
	(r^2)	(ng/sample)	(ng/m3)	(ng/sample)	(ng/m3)
XAD-2 (OVS) Tubes					
CPF	>0.999	1	0.35	2	0.69
CPF-O	>0.999	1	0.35	2	0.69
AZ	>0.999	0.5	0.17	1.8	0.62
AZ-O	>0.999	0.5	0.17	1.5	0.52
PUF Tubes					
CPF	>0.999	1	0.35	2	0.69
CPF-O	>0.999	1	0.35	2	0.69
AZ	0.998	1	0.35	2	0.69
AZ-O	0.997	1	0.35	2	0.69
PUF Disk					
CPF	>0.999	1	0.01	2	0.02
CPF-O	>0.999	5	0.05	10	0.1
AZ	0.997	1	0.01	2	0.02
AZ-O	0.996	5	0.05	10	0.1

4.3.3 Recovery and repeatability of the extraction method

Table 4.2 presents the fortification spike recoveries on active XAD-2 (OVS) tubes, PUF tubes, and passive PUF disks. Four replicates were analyzed at each fortification spike level for XAD-2, and three replicates were analyzed at each fortification spike level for PUF tubes and PUF disks. Individual recoveries ranged from 78 -113% from XAD-2 active air sampling tubes, and were slightly higher for AZM and AZM-O than for CPF and CPF-O. Individual recoveries ranged from 69 - 108% from PUF active air sampling tubes and recoveries were higher at larger spike volumes. The recoveries were similar on PUF passive sampling disks, ranging from 74-113%. The acceptable range for fortification spike recoveries in EPA Compendium Method TO-10A for pesticides and PCBs in ambient air using low volume sampling is between 65-135% (1999), and recoveries from all air sampling matrices were well within this range.

The PUF active sampling tubes and PUF passive sampling disks are slightly bulkier than the previously used XAD-2 (OVS) tubes recommended by NIOSH. During chemical extraction, the PUF matrices require a larger desorption volume and some require concentrated evaporation to achieve similar LOD/LOQ values. However, the difference in size of matrix did not substantially interfere with the ability to recover low levels (ng) per sample. In Table 3, the PUF disk has a LOD of 1 and 5 ng for CPF and CPF-O, respectively. This is comparable to the XAD-2 resin, which has a LOD of 1 for both CPF and CPF-O. When we take into account the typical air sampling volumes for the active vs. passive PUF disk samples; we find that the LOD/LOQ values (ng/m^3) are significantly reduced on the passive sampling devices.

Table 4.2/ Percent Recoveries and coefficients of variation (C.V. %) at different spiking levels for CPF, CPF-O, AZ, and AZ-O from XAD (OVS) tubes, PUF tubes, and PUF-PAS disk. Each spiking level was performed in triplicate unless otherwise noted.

Spike Level (ng)		XAD (OVS) Tubes		PUF Tubes		PUF-PAS Disk	
		Recovery	C.V.	Recovery	C.V.	Recovery	C.V.
		Mean (%)	(%)	Mean (%)	(%)	Mean (%)	(%)
Chlorpyrifos (CPF)							
Low	**5**	94.6	5.2	71.2	8.6	85.8	7.7
Medium	**50**	92.3	2.1	84.9[a]	NA	102	25.5
Medium	**500**	NA	NA	93.9	3.6	89.8	26.4
High	**1000**	86.1	3.4	89.5	3.7	75.8	10.2
Chlorpyrifos-oxon (CPF-O)							
Low	**5**	97.6	3.3	82.6	1.0	86.1	3.4
Medium	**50**	93.9	3.6	92.3	2.1	NA	NA
High	**1000**	85.8	7.7	107	7.5	77.8	8.7
Azinphos methyl (AZ)							
Low	**5**	109	4.8	NA	NA	93[a]	NA
Medium	**50**	103	1.9	77.2	5.7	83.5	9.2
High	**1000**	89.7	1.6	102[a]	NA	90	14
Azinphos methyl-oxon (AZ-O)							
Low	**5**	111	2.0	NA	NA	NA	NA
Medium	**50**	104	3.0	86.3	7.3	81.3	10.1
High	**1000**	94.7	1.5	108[a]	NA	74.3	11.1

a – Duplicate sample. No quantifiable C.V.

4.3.4 Storage Stability

Storage stability tests also yielded acceptable recoveries ranging from 73-98% after time periods of 2-10 months (Table 4). There was no measurable difference in percent recovery between samples that had been stored for ~10 months (294 days) or samples that had been stored for ~2 months (72 days).

Table 4.3/ Storage Stability for 2-10 months: CPF, CPF-O, AZ, AZ-O on three air sampling matrices. PUF disks were spiked at higher levels (ng/sample) typical of passive air monitoring.

	Replicates	**Spike Level**	**Storage Time**	**Recovery**	
	N	**ng/sample**	**(days)**	**Mean (%)**	**(CV %)**
XAD-2 (OVS) Tubes					
CPF	18	25	171-236	83.5	3.12
CPF-O	9	25	171-181	74.4	0.35
AZM	21	50	209-294	92.1	7.35
AZM-O	21	50	209-294	80.8	6.18
PUF Tubes					
CPF	4	20-50	72	85.6	10.2
AZM	4	20-50	72	94.3	8.3
PUF Disk					
CPF	7	500-1500	158	82.0	13.1
AZM	7	125-500	112	86.6	10.7

4.4 Discussion

This is the first published method of extraction and analysis method via LC-MS/MS while focusing on the quantification of OP pesticides and their oxygen analogs in air sampling matrices. We have compiled laboratory results from two recent air monitoring studies conducted in Washington State to demonstrate that LC-MS/MS is a sensitive, accurate, and precise method to capture these compounds from two different matrices at low concentrations typical of community sampling. The LOD/LOQ values reported in this study are lower than in past community studies using GC-MS (Method Limits of Detection reported in Table 1.1, Chapter 1).

It should be noted that in 2008, an inter-laboratory comparison was done with the California Department of Pesticides Regulation laboratory (CDPR). The CDPR laboratory found <1% difference between its own standards and the UW standards when measured by GC-MS (0.97% for CPF; 0.45% for CPF-O). The method performed well when compared to the traditional GC-MS method used by CDPR and it may be an appropriate alternative.

Analysis with LC-MS/MS with Multiple Reaction Monitoring (MRM) requires the use of labeled internal standards. The internal standards for CPF and AZM, chlorpyrifos diethyl-D_{10} and azinphos-methyl-D6, are available from Cambridge Isotope and EQ Laboratories. However, there is a lack of commercially available internal standards for the oxon compounds ($^{13}C_2$, ^{15}N-chlorpyrifos-oxon, AZM-O dimethyl-D6), and these were donated by industry for these experiments. The chemical synthesis of these oxon internal standards may be costly. Nevertheless, we have demonstrated that LC-MS/MS is a good alternative for measuring OP pesticides and oxygen analogs in community samples with low limits of detection and good repeatability and that these results do not differ when extracting from three different types of air sampling matrices.

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Chapter 5: Development of the polyurethane foam passive air sampler (PUF-PAS)

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Chapter 5 Summary: This paper reports on the investigation of new passive air sampling methodologies using the polyurethane foam passive air sampling (PUF-PAS) device to measure cumulative monthly airborne concentrations of organophosphorus (OP) pesticides chlorpyrifos (CPF), azinphos-methyl (AZM), and their oxygen analogs (i.e. "oxons") for the Pesticide Exposure Pathways Project of the University of Washington Child Health Center for Environmental Risks Research. Passive sampling rates, or $R_{PUF\text{-}PAS}$ (m^3/day), were determined by theoretical calculations using chemical properties, measuring the loss of labeled depuration compounds, and calibration with side-by-side active air sampling (AAS) in a dynamic laboratory exposure chamber and in the field. We examined the effects of temperature, relative humidity, and wind velocity on measured outdoor $R_{PUF\text{-}PAS}$ at 23 sites in the agricultural community of Yakima Valley, Washington. For both CPF and AZM, indoor $R_{PUF\text{-}PAS}$ were lower than outdoors. This may be attributable to the significant relationship between increased average wind velocities and outdoor RPUF-PAS, with extremely high rates (>4 m^3/day) observed above 8 m/s. In addition, there was a linear relationship between increased $R_{PUF\text{-}PAS}$ and relative humidity for azinphos methyl, but not for chlorpyrifos. In the exposure chamber, very little oxygen analog was observed on the PUF-PAS during sampling: only 2 of 30 spiked samples reported <1 ng chlorpyrifos-oxon and no azinphos methyl oxon was detected. In comparison, substantial proportions of chlorpyrifos-oxon and azinphos methyl oxon were present on PUF-PAS after outdoor deployment. These experiments identify PUF-PAS as a practical alternative to AAS because it results in little artificial transformation to the oxygen analog

during sampling, it provides cumulative monthly exposure estimates, and the measured sampling rates ($R_{PUF\text{-}PAS}$) were comparable to rates for other semi-volatile organic compounds.

Chapter 5 Highlights

- It is possible to passively sample for CPF, CPF-O, AZM, and AZM-O using PUF-PAS devices.
- Measured indoor passive sampling rates are lower than outdoor sampling rates.
- Outdoor sampling rates are influenced by wind velocity and may be influenced by relative humidity.

5.1 Introduction

Chapter 1 introduced past community air monitoring studies relying on AAS matrices, as well as some advantages and disadvantages of using passive (PUF-PAS) and active (OVS-AAS) for measuring airborne OP pesticides and oxygen analogs. In Chapter 3, we found that the PUF matrix is ideal for sampling the oxygen analogs of these pesticides because it results in very little artificial transformation during sampling. In comparison, the XAD resins were found to result in artificial conversion to oxygen analogs during sampling. The PUF has been identified as a reservoir for the accumulation of OP pesticides indoors in plush toys, pillows, couches, and mattresses (Gurunathan et al. 1998). If we are able to define the uptake rates, PUF may be a good passive sampling matrix. This chapter reports on the investigation of new passive air sampling methodologies [PUF-PAS (polyurethane foam passive air sampler) used with the TE-200 PAS (Cat. # TE-1014, Tisch Environmental)] to measure for the airborne semivolatile organophosphourus (OP) pesticides CPF, AZM, and their oxygen analogs, CPF-O and AZM-O on a broader, regional scale.

This research on new passive air sampling methods involves both laboratory exposure chamber and outdoor field sampling results to report on the performance of the PUF-PAS. The specific aim of the study was to quantify passive sampling rates, or $R_{PUF\text{-}PAS}$, (m^3/day) and examine OP pesticide recoverability and potential conversion to the oxon transformation on the PUF-PAS matrix. These were determined by theoretical calculations using chemical properties, measuring the loss of labeled depuration compounds, and calibration with side-by-side active air sampling (AAS) in a dynamic laboratory exposure chamber and outdoors in the field. Environmental factors such as temperature, relative humidity, and wind velocity have also been found to affect sampling rates and performance of outdoor passive samplers (Brown 1999, Gouin et al 2008). We examined the effects of outdoor temperature, relative humidity, and wind velocity on sampling rates ($R_{PUF\text{-}PAS}$) determined with labeled depuration compounds.

5.2 Methods

5.2.1 Theoretical Sampling Rates

The theory of passive sampling and mass transfer across the PUF-PAS disk interface has been explained in numerous past studies and does not need to be revisited for this study (Shoeib and Harner 2002, Harner et al. 2004, Bohlin et al. 2008). In summary, it is based on free flow according to Fick's first law of diffusion of analyte molecules from a sampled medium (e.g. air) to a collecting medium (e.g. PUF). Data is reported and compared as the mass taken up per sampler per unit time, or simply converted to estimated air concentration (ng/m^3) using uptake rates from side-by-side calibration studies.

Similar to Shoeib and Harner (2002, 2004) , we calculated passive sampler air partition coefficients ($K_{PUF-PAS}$) for the OP pesticides CPF and AZM by using reported octanol-air partition coefficients [K_{oa} (Noble 1993)] as surrogates and using effective passive sampling rates from published literature on other current-use semi-volatile pesticides (Gouin et al. 2008, Hayward et al. 2010). It is also possible to estimate K_{oa} from the octanol-water partition coefficient (K_{ow}) and Henry's Law Constant (H) using the following equation (Harner and Bidleman 1998, Meylan and Howard 2005, Shoeib and Harner 2002):

$$\mathbf{K_{oa} = K_{ow}\,(RT)/H} \qquad \textit{(Eq. 5.1),}$$

where R is the ideal gas constant and T is the absolute temperature (K). The computed log K_{oa} values for CPF and AZM were 8.36 and 11.33, respectively (unitless). Chemical data on octanol-air partition coefficients for the oxygen analogs are not available, so it was assumed that the sampling rates for CPF-O and AZM-O were similar to the parent compounds. Shoeib and Harner found that the log K_{oa} may be used to calculate the passive sampling media/air partition coefficient (K_{PUF}) (2002):

$$\mathbf{\log K_{PUF} = 0.6366 \times \log K_{oa} - 3.1774} \quad \textit{(Eq. 5.2).}$$

We modeled expected sampling volumes (m^3) for time (t_{days}) ranging 0-30 days for comparison with observed experimental results. We used the following equation (Eq. 5.1) from Shoeib and Harner, 2002:

$$\mathbf{\text{Expected Air Volume } (m^3) = (K'_{PUF\text{-}PAS}) \times (PUF\text{-}PAS_{volume}) \times \{1 - \exp[-(t_{days}) \times (k_A)/(K'_{PUF\text{-}PAS})/(D_{film})]\}}$$

(Eq. 5.3)

where $K'_{PUF\text{-}PAS}$(dimensionless) $= K_{PUF\text{-}PAS}[(ng/m^3_{PUF})/(ng/m^3_{Air})] \times (PUF\text{-}PAS_{density})$ (g/m^3); $K_{PUF\text{-}PAS}$ = PUF Side Mass Transfer coefficient, $PUF\text{-}PAS_{Volume}$ = Volume of the PUF disk (m^3); t_{days} = Sampling time (days), k_A =Air side mass transfer (m/day) estimated from past effective sampling rates of pesticides (Gouin et al 2008, Hayward et al 2010) divided by surface area of the PUF (m^2), D_{film} = PUF film thickness (m), and $PUF\text{-}PAS_{density}$ = density of PUF-PAS (g/m^3). All calculations were performed in Excel 2010 using supplementary materials made available by the Environment Canada Hazardous Air Pollutants (HAPs) Laboratory. An example calculation is in Table S.5.1 of the Appendix. For CPF and AZM, the expected air sampling rates were calculated to be approximately 3.37 and 3.69 m^3/day at room temperature (25 °C), respectively. These are within the range of values identified in Chapter 1 for other SVOCs (See Table 1.3).

5.2.2 Laboratory Sampling Rates

The PUF-PAS disk is 14 cm in diameter and 1.4 cm thick. It is deployed in the TE-200 PAS sampler housing constructed from two overlapping stainless steel bowls to protect the matrix from precipitation, sunlight, and high wind speeds (Harner et al. 2004). The PUF-PAS disks were pre-cleaned by soxhlet extraction with ethyl acetate at 77°C for 1 hour (~20 cycles) or rinsed with acetone and ultrasonicated for 1.5 hours (2 cycles). They were then dried in a clean lab hood and stored in glass petri dishes sealed with Parafilm® prior to deployment.

A dynamic exposure chamber was constructed of chemically inert materials such as polytetrafluoroethylene (PTFE) tubes, connectors, rubber stoppers (with two holes to allow insertion of PFTE tubing) caps, and glass inlets. The rubber is chemically resistant to many corrosive and other reactive compounds. The chamber was a cylindrical glass mixing container (volume = 549 cm^3) with three outlets for inlet carrier/dilution flow, outlet flow, and one for connection with two active sampling devices. The PUF-PAS disks were reduced to quartered sections (92.5 cm^2 surface area) to fit in the chamber. Indoor laboratory temperatures ranged from 21-23 °C.

We deployed spiked triplicate samples of 99.5% analytical grade CPF (ChemService, Inc. PS-674) and 98.5% AZM (ChemService, Inc. F2055S) in acetone for time periods of 0, 5, 15, and 30 days in the exposure chamber with a steady dry laboratory air flow of 2 liters per minute (LPM). The spike solution was applied with a positive displacement syringe at levels of 0, 25 (low) and 400 (high) ng directly into the middle of the PUF matrix. After spiking, the PUF was allowed to equilibrate at room temperature (21-23 °C) in the laboratory hood for 30 minutes. The disk sections were laid flat on steel mesh wire, spaced 3 cm, and covered with an aluminum lid to simulate conditions in the PUF-PAS sampler.

In the same fashion, we deployed triplicate samples spiked with 210ng of chlopyrifos-methyl-D_6 and 450ng of azinphos ethyl D_{10} (EQ Laboratories, Inc) for 30 days in the chamber. The theory on measuring loss of deuterated compounds (i.e. depuration compounds) has been described in detail by

Gouin et al 2005 and Harner et al 2006; and it states that the steady loss of depuration compounds occurs at approximately the same rate as the uptake for target compounds. The loss [$\ln(C/C_o)$, where C = final concentration depuration compound, and C_o = initial spiked concentration depuration compound] from the PUF matrix is another way to measure passive sampling rates, $R_{PUF\text{-}PAS}$. Ideally, the depuration compounds should have recoveries ranging between 20-80% of their initial amount to ensure a linear sampling rate during the time of deployment (Soderstrom and Bergqvist, 2004; Gouin et al. 2005). We expected the loss of depuration compounds to be comparable to the loss of parent compounds. All calculations for depuration compounds were performed with Excel 2010 using supplementary materials made available by the Environment Canada Hazardous Air Pollutants (HAPs) Laboratory. An example calculation is in Table S.5.2 of the Appendix.

To conduct side-by-side calibration with active air sampling methods, a temperature-controlled DynaCalibrator® (Model 230, VICI, Inc) was used to deliver gas phase concentrations of OP pesticides ranging from 10-50 ng/m^3 in the exposure chamber. The concentrations were set to replicate past background community levels recently measured in central Washington State in a study for the Washington State Department of Health (Fenske et al. 2009). The permeation tube was made by capping 99.5% CPF (ChemService, Inc., solid) inside a PTFE tube with 10.7 cm active length. It was sealed by plugging on the ends with packed glass fiber, PTFE cap, and crimp band. The permeation tube was placed in the DynaCalibrator® and weighed each day for one month to observe equilibrium and calculate emission rate of 5.5 ng CPF/min at 35 °C. The measured loss in mass from the permeation tube is reported in the Appendix. AZM was not well generated in the chamber due to difficulties in achieving consistent volatilization rates from a permeation device at low concentrations. This may be attributable to the lower volatility of AZM

($4.7*10^{-9}$ mmHg at 20-25 °C) as compared to chlorpyrifos ($1.9*10^{-5}$ mmHg at 20-25 °C).

A range of carrier and dilution flow rates was calculated for the generation of concentrations of chlorpyrifos in the chamber (VICI Metronics 1993, 2011), and these data are available in Figure S.5.1 of the Appendix. For the chamber tests, we paired a carrier flow of 10 LPM with a dilution flow rate of 5 LPM. The DynaCalibrator® was operated for 8 hours prior to experiments to create a well-mixed atmosphere.

Three sets of duplicate PUF active air sampling tubes and PUF-PAS drew air for a 24 hour sample period inside the chamber (n=6). The active PUF tubes were hung inside the chamber and connected to outside SKC air sampling pumps (224-PCXR8) with PFTE tubing through a rubber stopper. The sampling pumps operated at a flow rate of two LPM. Sampling pumps were pre- and post-calibrated with a DryCal DC-Lite® and the air volumes (m^3) were calculated separately for active sample. We used the following equation (Eq. 2) to estimate $R_{PUF\text{-}PAS}$ from air concentrations, $C_{PUF\text{-}AAS}$, determined via AAS:

$$\boldsymbol{R_{PUF\text{-}PAS} = M_{PUF\text{-}PAS}/(C_{PUF\text{-}AAS} \times t_{days})} \qquad \textit{(Eq. 5.3)}$$

Where $R_{PUF\text{-}PAS}$ = Passive sampling rate (m^3/day), $M_{PUF\text{-}PAS}$ = Mass on PUF-PAS (ng), $C_{PUF\text{-}AAS}$ = Air concentration from AAS (ng/m^3), and t_{days}= Sample time (days). Observed laboratory sampling rates from depuration compounds and side-by-side calibration were compared using two sample t-tests. All observed laboratory sampling rates were compared to expected rates from theoretical calculations using a one sample t-test.

Figure 5.1/ Laboratory Exposure Chamber for PUF-PAS devices. Temperature-controlled DynaCalibrator® used to deliver gas phase concentrations of CPF.

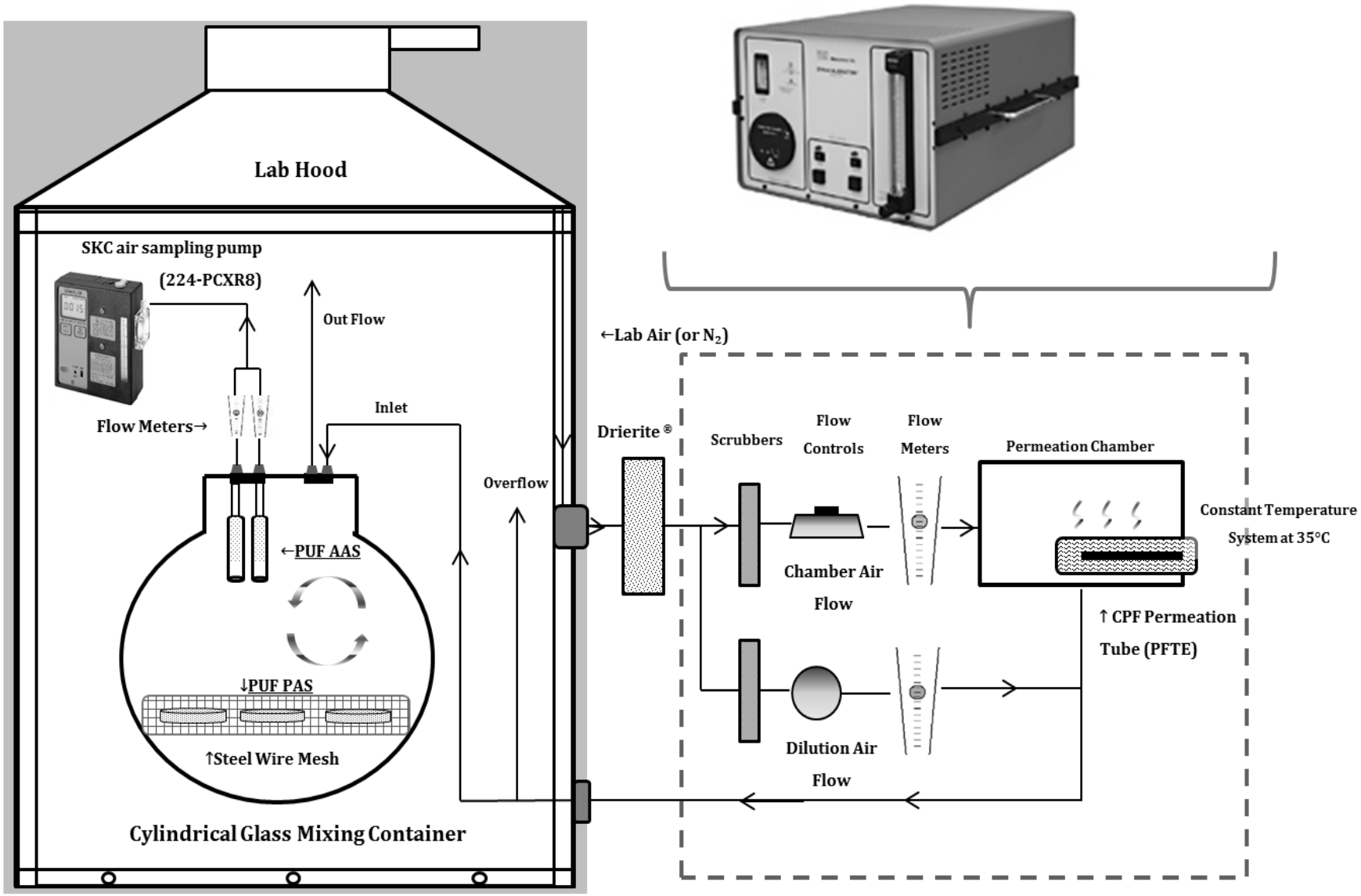


Figure 5.2/ Outdoor Testing Sites of PUF-PAS devices. The figure on the left is a testing site in Seattle, WA. The figure on the right is in Yakima Valley, WA. The device is located near an orchard and a WSU AgWeatherNet Meteorological Station.

5.2.3 Outdoor Sampling Rates

As part of the Pesticide Exposure Pathways project of the Child Health Center for Environmental Risks Research, we deployed 66 outdoor PUF-PAS air samplers across Yakima Valley, WA at twenty research participant homes and three community air monitoring sites. The sampling took place during 2011 spring (CPF, n=36) and summer (AZM, n=30) application seasons. Each PUF-PAS sampler was deployed in stainless steel housing at 1.5 meters in height (Figure 5.1). Inside the PUF-PAS housing, a LogTag® Temperature Recorder (Model# TRIX-8) logged temperature data (°C) in 15 minute intervals throughout the sampling period. All sites were ≤ 5 km to the nearest Agricultural Weather Net station (Washington State University) recording relative humidity and wind velocity at hourly intervals. Each PUF-PAS was spiked with masses of depuration compound chlopyrifos-methyl-D6 (210ng) or azinphos ethyl D10 (450 ng) for time periods ranging 5-30 days. Duplicate PUF-PAS were deployed at 4 sites.

In addition, we conducted side-by-side calibration with active air sampling methods outdoors for 5 days at three community sites fitted with a Washington State University Agricultural Weather station (AgWeatherNet 2.0). One site was operated by the Washington State Department of Ecology, and the other two were operated by Washington State University. After collection, the samplers were stored in glass petri dishes sealed with Parafilm®, placed in a -20°C freezer in a Yakima Valley field office, and transferred to the University of Washington Environmental Health Laboratory on dry ice.

Past studies have found that outdoor meteorological factors can influence sampling rates and that they may differ from sampling rates determined under ideal conditions (e.g. in the laboratory). Observed outdoor sampling rates from depuration compounds and side-by-side calibration were compared using two sample t-tests. All observed outdoor sampling rates were compared with observed laboratory sampling rates using two sample t-tests. All sampling rates were compared to environmental factors such as temperature, wind speed, and humidity using linear and exponential regression. All statistical

calculations were performed in STATA 11.2 (StataCorp LP, College Station, TX).

5.2.4 Extraction and Analysis

PUF-PAS devices were sonicated for 1.5 hours at room temperature (20-23°C) in 10-50mL acetonitrile solution containing stable-isotope labeled internal standards (ISTD) and then placed in a turbovap at 60°C until evaporated to 1.5 mL. If particulate was present, the extract was quantitatively transferred to a leur-lock 3 mL polypropylene syringe, and filtered with a PTFE syringe filter (13 mm, 0.2 μm porosity).

Sample analysis was conducted using the liquid chromatography tandem mass spectrometry (LC-MS/MS) method described in chapter 4. The internal standards solutions had to differ from depuration compounds, and were prepared using 100μg/mL solutions of chlorpyrifos diethyl-D10 (99%, neat, Cambridge Isotope Labs, DLM-4360), 13C2,15N-chlorpyrifos-oxon (neat, donated by Dow Agro Sciences LLC), azinphos-methyl-D6 (98.5%, EQ Laboratories Inc. XA10365100AC), and azinphos-methyl oxon dimethyl-D6 (99.3%, solid, Bayer Crop Science K-176). Internal standards solutions for depuration compounds were chlopyrifos-methyl (ChemService, Inc., 100ug/ml in Acetonitrile) and azinphos ethyl (SigmaAldrich® 45332-250MG). Four samples were analyzed without chlopyrifos-methyl and azinphos ethyl internal standard solutions to check for the presence of these compounds in environmental air, but neither were detected in the Yakima Valley region. Reagents were acetonitrile (pesticide grade), acetone (reagent grade), deionized water (Barnstead Nanopure II, 18 mΩ), and formic acid (certified, ACS, 88%).

The limits of detection (LOD) for chlorpyrifos and azinphos-methyl were 1 and 5 ng/sample, respectively; and for chlopyrifos-methyl-D6 and azinphos ethyl D10, 1 ng/sample. If samples were <LOD, they were divided by $\sqrt{2}$ (resulting in values of 0.71 and 3.54). The samples <LOD for chlorpyrifos and azinphos-methyl samples <LOD were then divided by the effective air sampling volume for analysis.

5.2.5 QA/QC

Corrections for fortification spike recoveries reported in Chapter 4 were not used. Spike fortification recoveries at t_{days}= 0 for depuration compounds chlopyrifos-methyl-D_6 and azinphos ethyl D_{10} were 82 (78-86%) and 87 (70-97%), respectively. Corrections were used for depuration compound recoveries because sampling rate is highly dependent on loss occurring only during deployment.

No laboratory blanks, field blanks, or reagent blanks reported measurable amounts of OP pesticides or oxygen analogs. To check for reproducibility, all laboratory experiments were conducted in duplicate or triplicate samples. In the field, duplicates were 20% of samples.

5.3 Results

5.3.1 Recovery of OP Pesticides and Transformation to Oxygen Analogs

Percent recoveries for CPF from the PUF-PAS ranged from 61-100% for large spike masses (400 ng) and from 52-116% for low spike masses (25 ng) after time periods ranging 5-30 days in the exposure chamber. Percent recoveries for AZM ranged from 71-105% for large spike masses (400 ng) after time periods ranging 15-30 days (Figures 5.2a and 5.2b).

There was little to no conversion to the oxygen analog on the PUF-PAS after prolonged deployment in the chamber up to 30 days. Only 2 of 30 spiked samples CPF reported CPF-O of 1 ng (<2%) after the time period of 30 days and no spiked samples of AZM reported detectable AZM-O. These recoveries were in the acceptable range for large spike masses (ASTM 2011), but the lowest spike recovery (25ng) for CPF was 63% (S.D. 4%) after 30 days (Figure 5.3A). This may have been due to the difficulty of recovering low spike masses from the larger PUF matrix (disk) with precision, spiking error, or greater loss of spiked masses at low levels (25 ng).

Figure 5.3A/ % Recoveries CPF from PUF-PAS after t_{days}= 0, 5, 15, and 30.

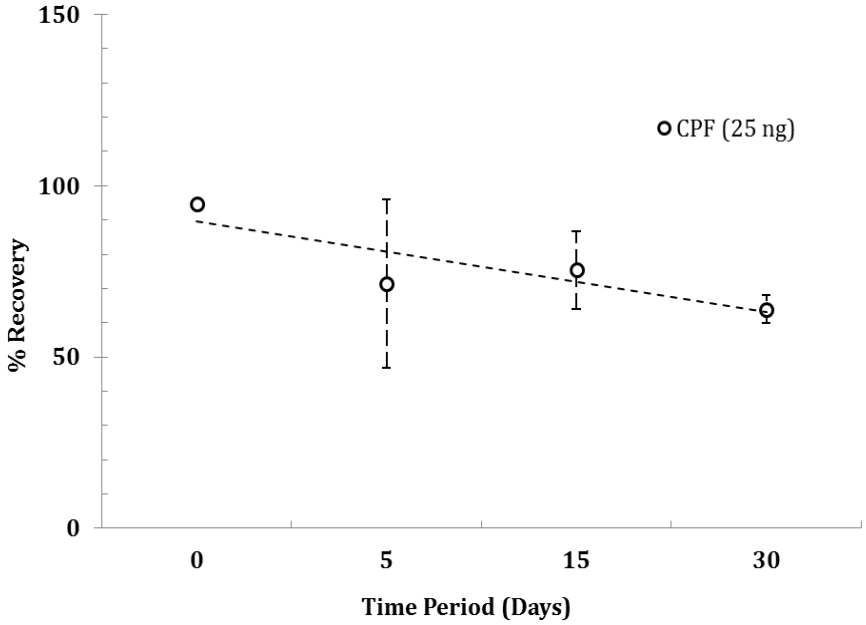


Figure 5.3B/ % Recoveries CPF from PUF-PAS after t_{days}= 0, 5, 15, and 30.

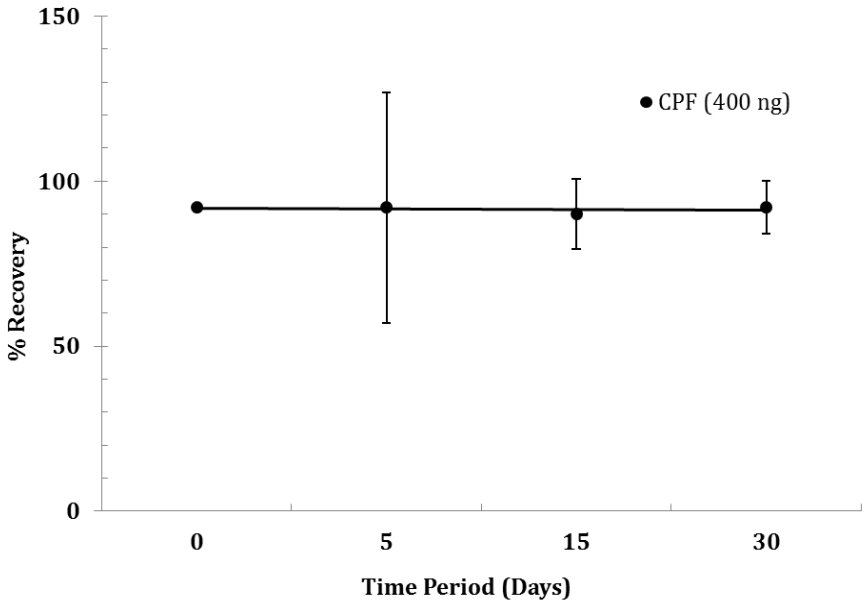
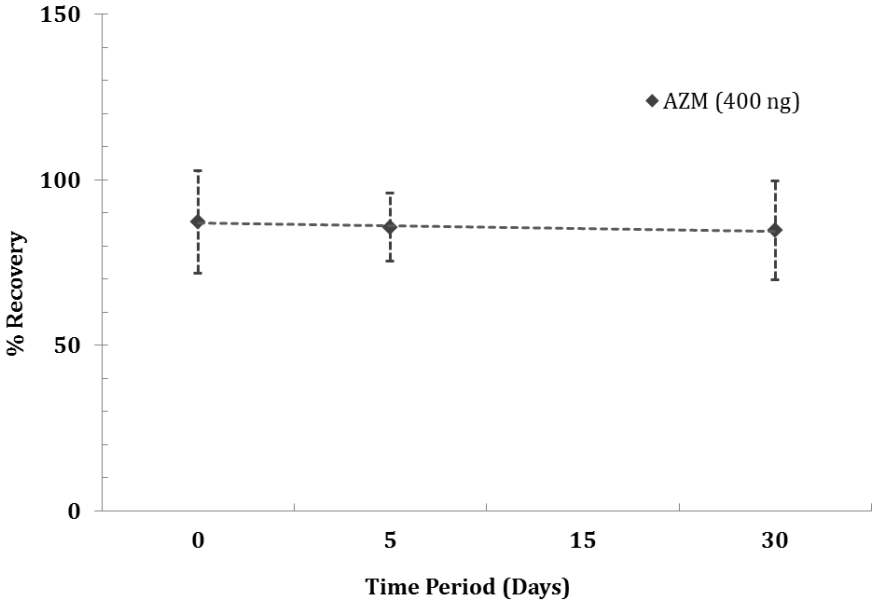


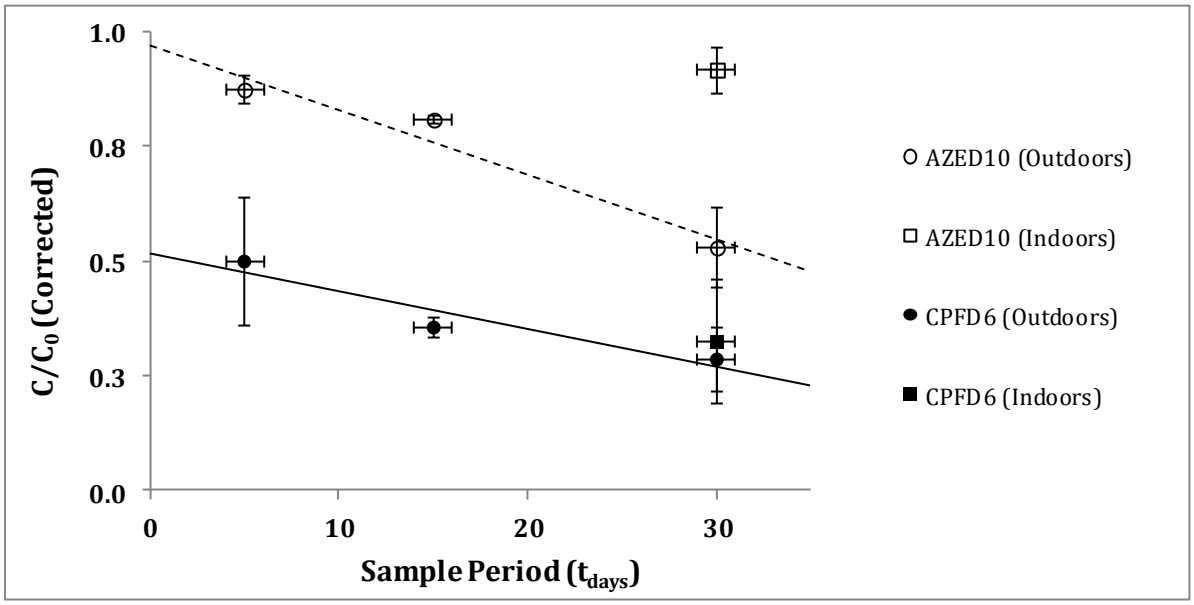
Figure 5.3C/ % Recoveries AZM from PUF-PAS after t_{days}= 0, 5, and 30.



5.3.2 Exposure Chamber and Outdoor Air Sampling Rates

Figure 5.3 reports indoor and outdoor sampling rates determined by the loss of depuration compounds chlopyrifos-methyl-D_6 and azinphos ethyl D_{10}. The final concentration, C, was corrected for the recovery of chlopyrifos-methyl-D_6 and azinphos ethyl D_{10} after sample period t_{days}= 0 [C/C_0(Corrected)]. All sampling was occurring in the linear phase, and measured loss of depuration compounds was less in the exposure chamber than outdoors. For CPF, the loss of depuration compounds corresponded to an indoor mean sampling rate, $R_{PUF\text{-}PAS}$, of 2.25 m^3/day in the exposure chamber (1.42-2.89). This was not significantly different from the mean outdoor 3.12 m^3/day (2.10-7.49). For AZM, the loss of depuration compounds corresponded to a $R_{PUF\text{-}PAS}$ of 3.04 m^3/day in the exposure chamber. This was significantly lower than the outdoor sampling rate of 4.72 m^3/day (2.29-8.42), $p<0.05$. On average, all sampling rates in the exposure chamber were lower than outdoor sampling rates. We would expect the loss of these depuration compounds to be comparable to the loss of parent compounds in Figures 5.3A and 5.3B. This was the case for AZM inside the exposure chamber, but the loss of $CPFD_6$ was greater than expected.

Figure 5.4/Measured loss of depuration compounds [C/C_0 (Corrected)], Chlorpyrifos Methyl D_6 and Azinphos ethyl D_{10} in the exposure chamber and outdoors. Outdoors, loss of depuration compounds was measured at sampling periods, t_{days}= 5, 15, and 30. In the exposure chamber, loss of depuration compounds was measured at one sample period t_{days}=30. The final concentration, C, was corrected for the recoveries after sample period t_{days}= 0.



The observed air sampling rates determined using depuration compounds and side-by-side calibration with AAS are compared with the expected theoretical air sampling rates in Table 5.1. For CPF, all observed $R_{PUF\text{-}PAS}$ were similar to the expected calculation of 3.37 m^3/day. In the exposure chamber, the mean $R_{PUF\text{-}PAS}$ determined by depuration compounds 2.25 m^3/day (1.42-2.89) was not statistically different from the mean $R_{PUF\text{-}PAS}$ determined by side-by-side calibration 2.34 m^3/day (1.6-2.99). Outdoors, the mean $R_{PUF\text{-}PAS}$ determined by depuration compounds was 3.12 m^3/day and highly variable (2.10-7.49), but not statistically different from the mean $R_{PUF\text{-}PAS}$ determined by side-by-side calibration 3.23 m^3/day (2.47-4.39). For example,an outdoor 4 week sample period for CPF would correspond to an air sample volume of 63 to 225 m^3.

Table 5.1/ Sampling rates, *R* (m³/day) for CPF and AZM. Laboratory and field sampling rates were compared to theoretical sampling rates using a one-sample t-test.

Test Step in Passive Methods Development		Chlorpyrifos $R_{PUF-PAS}$ m³/day, (Range)		Azinphos Methyl $R_{PUF-PAS}$ m³/day, (Range)
Expected				
Theoretical Estimates		3.37		3.69
Observed				
Laboratory performance, Depuration Compounds	3	2.25 (1.42-2.89)	3	3.04 (1.12-4.78)
Laboratory comparison with traditional method (AAS)	6	2.34 (1.6-2.99)		NA
Field comparison with tradition method (AAS) [a]	6	3.23 (2.47-4.39)		4.92[b] (4.36-5.50)
Field performance, depuration compounds	22	3.12 (2.10-7.49)		4.72[b] (2.29-8.42)

[a] Outdoor side-by-side calibration occurred with duplicate PAS/AAS sampling at three sampling sites during application season.

[b] Differences between observed and expected sampling rates were statistically significant in a one-sample t-test, α=0.05.

For AZM, the mean $R_{PUF-PAS}$ in the exposure chamber using depuration compounds 3.04m³/day (1.12-4.78), was close to the expected calculation 3.69 m³/day. Side-by-side calibration did not take place in the exposure chamber since it was difficult to achieve steady low levels of vapor AZM. Sample rates were found to be significantly higher outdoors. The mean outdoor $R_{PUF-PAS}$ determined by depuration compounds was 4.72 m³/day and highly variable (2.29-8.42), and was not statistically different from the mean $R_{PUF-PAS}$ determined by side-by-side calibration 4.92 m³/day (4.36-5.50). For example, an outdoor 4 week sample period for AZM would correspond to an air sample volume of 69 to 252 m³.

5.3.3 Outdoor Factors Influencing Air Sampling Rates

During the spring and summer application seasons, we examined potential meteorological conditions of wind velocity, temperature, and relative humidity with potential effects on sampling rates using simple linear regression. For CPF, there was no statistically significant relationship between $R_{PUF\text{-}PAS}$ and temperature (R^2 = 0.0005) or humidity (R^2=0.010). There was an exponential relationship between wind velocity and sampling rate (R^2=0.9370, p=0.000). Two samples had very large air sampling rates and had recoveries chlopyrifos-methyl-D_6 <15%. For AZM, there was also no statistically significant relationship between air sampling rates and temperature (R^2 = 0.035). There was a linear trend toward small increases in $R_{PUF\text{-}PAS}$ (0.12 m3/day, 95% C.I. 0.004- 0.2262, p=0.042) with each percent increase in relative humidity (R^2=0.1685), but this was not significant (p=0.167). There was an exponential relationship between wind speed and sampling rate (R^2=0.9198, p=0.000).

For AZM, the reported $R_{PUF\text{-}PAS}$ in the chamber was higher than expected from the exponential relationship, but this was not significant. The results from exponential regression and a quadratic prediction plot between wind velocity and sampling rate are shown in Figure 5.5.

Figure 5.5A/ Scatter plots with exponential fit demonstrating the effects of average wind speeds (t_{days}=30) and measured sampling rates CPF, R_{PUF_PAS} with depuration compounds CPFM-D_6. Average monthly spring wind velocities were greater than summer wind velocities. For comparison, the average sample rate determined in the exposure chamber is in the clear diagonal box and was assumed to be representative of windspeeds near 0 m/s. Two data points >8 m/s had recoveries of depuration chlopyrifos-methyl-D_6 <15%. R^2 and P values are results from exponential regression.

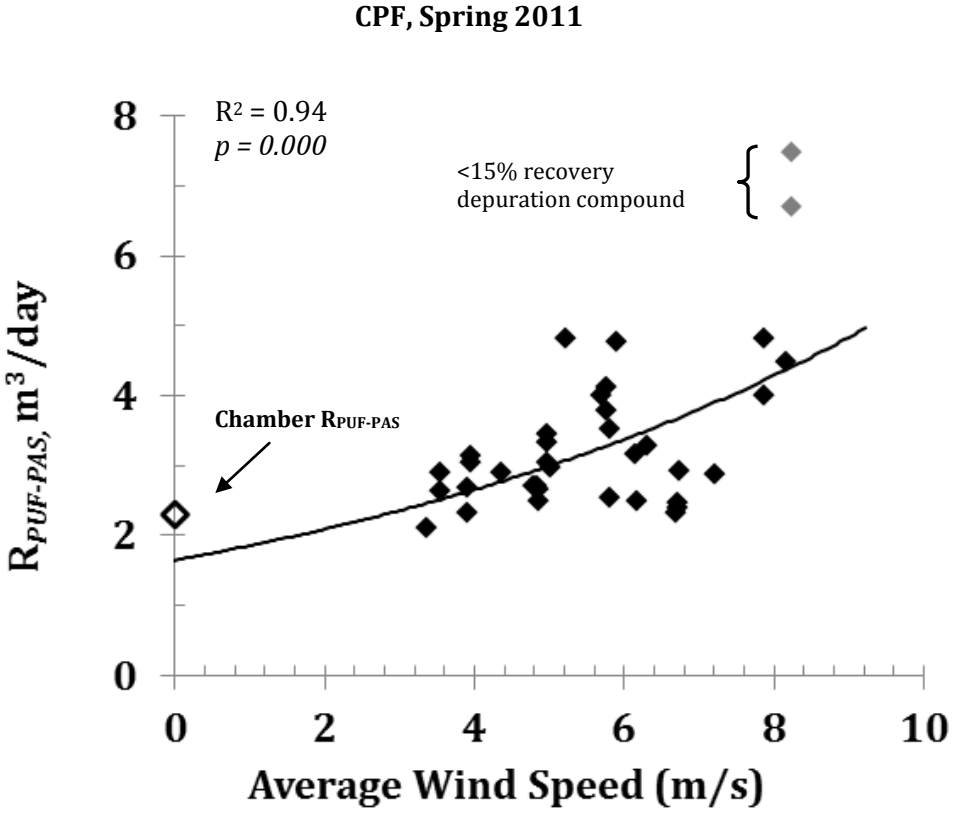
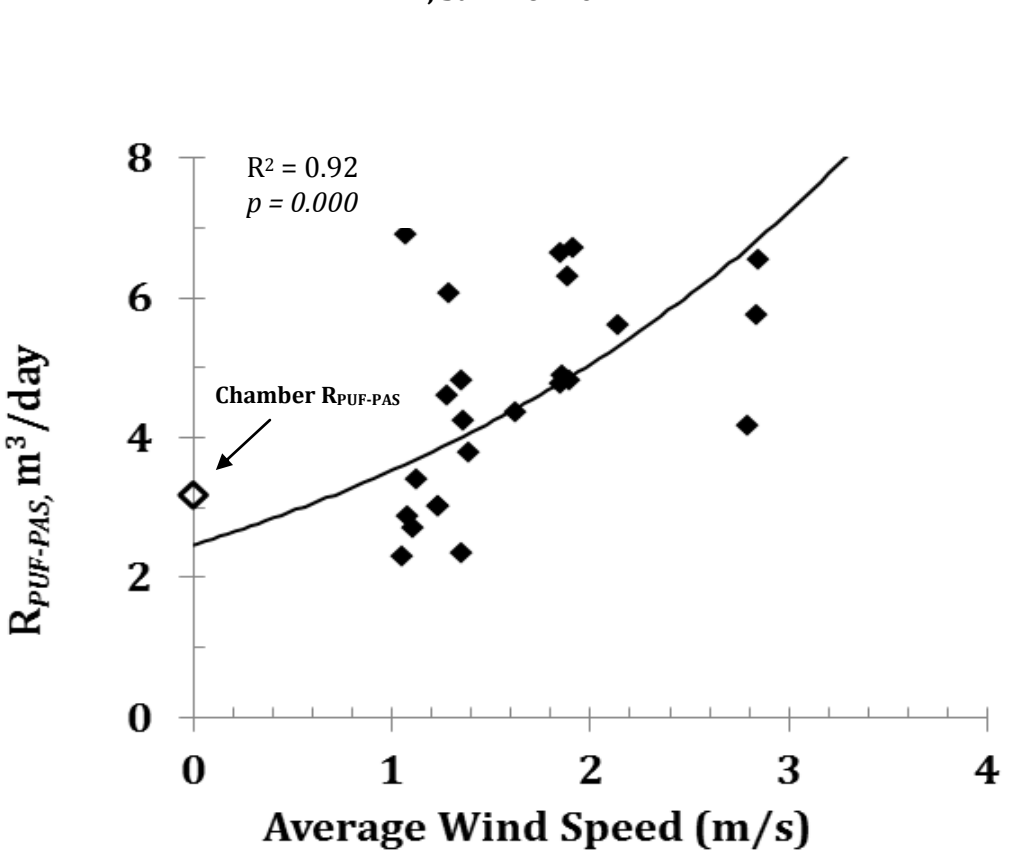


Figure 5.5B/ Scatter plots with exponential fit demonstrating the effects of average wind speeds (t_{days}=30) and measured sampling rates AZM, R_{PUF_PAS} with depuration compounds AZE-D_{10}. For comparison, the average sample rate determined in the exposure chamber is in the clear diagonal box and was assumed to be representative of windspeeds near 0 m/s.



5.4 Discussion

This study included theoretical calculations, laboratory and field performance tests, and side-by-side comparison with traditional AAS methods to identify if PUF-PAS was appropriate for measuring airborne OP pesticides. Although airborne exposure measurements with AAS can be helpful for locating peak exposures, the PUF-PAS is an attractive option for gaining insight on monthly cumulative airborne concentrations of OP pesticides and their oxygen analogs. In the exposure chamber, only 2 of 30 CPF-spiked samples reported <1 ng CPF-O and no AZM-O was identified. In comparison, substantial proportions of CPF-O and AZM-O were present on PUF-PAS devices after outdoor deployment. All PUF-PAS deployed in the spring (n=36) reported levels of CPF-O that were 9-35% of total CPF concentrations, and 30% of the samples deployed in the summer (n=32) reported levels of AZM-O that were 1-13% of total AZM concentrations. The difference in measured oxygen analogs in the laboratory compared to in the field demonstrates that the PUF matrix is ideal for sampling oxygen analogs in the outdoor atmospheric environment. It is recommended that a sampling plan should be designed with the aim of achieving diffusive mass loadings >25 ng on the PUF-PAS device, given that recoveries at low levels decrease over time (see Figure 5.2A).

In the dynamic exposure chamber, indoor $R_{PUF\text{-}PAS}$ results for both pesticides were not different than calculated theoretical estimates. There was good agreement between $R_{PUF\text{-}PAS}$ calculated via depuration compounds and side-by-side calibration with AAS. On average, all measured sampling rates ($R_{PUF\text{-}PAS}$) in the exposure chamber were significantly lower than those measured in the outdoor field. Outdoor $R_{PUF\text{-}PAS}$ determined by depuration compounds was highly variable for both pesticides.

Previous studies have demonstrated higher outdoor sampling rates due to meteorological factors influencing uptake (Hazrati and Harrad, 2007). Higher variability in sampling rates was expected, given the multiple sampling locations and frequent high wind periods in the Yakima Valley. We observed a

significant exponential relationship between increased $R_{PUF\text{-}PAS}$ and wind velocities, with some extremely high rates observed above 8 m/s. In fact, two CPF samples above 8 m/s had recoveries chlopyrifos-methyl-D_6 <15%. Although these samples are valid for approximate measurements of air concentration, we cannot state with confidence that these samples were in the linear sampling stage throughout the time of deployment. There was a small linear relationship between increased $R_{PUF\text{-}PAS}$ and relative humidity for AZM, but it was not significant. AZM has a slightly lower octanol/water partition coefficient at 20-25 °C (log K_{ow}=2.70) than chlorpyrifos (log K_{ow} = 4.96) (Noble 1993, Rice et al 1997), and it is slightly more hydrophilic. This may affect the partitioning from to the PUF-matrix. There was no statistically significant relationship between air sampling rates and temperature. However, average monthly temperatures during the testing period had a very narrow range. During the spring, temperatures ranged 6-14 °C and during the summer they ranged 20-23 °C. Larger variability in mean temperatures and higher temperatures overall (>25 °C) may be required to measure potential effects on sampling rates.

A limitation of this study is that the theoretical estimates and calculations using depuration compounds for $R_{PUF\text{-}PAS}$ consider primarily the gas-phase of OP pesticides. This may capture distant transport via volatilization but does not account for the OP pesticides bound to smaller particles acquired by the passive and active sampling methods. Therefore, when relying on $R_{PUF\text{-}PAS}$ to calculate air concentrations, it is important to remember the concentrations should be regarded as approximate, not exact.

Another limitation is the lack of data on chemical properties of oxygen analogs. We did not have the data to calculate theoretical rates for these compounds and assumed their sampling rates were equivalent to the parent compound. Nevertheless, we have identified PUF-PAS as a practical alternative to AAS because it results in little artificial transformation to the oxygen analog during sampling, provides

cumulative monthly exposure estimates, and we found measured sampling rates ($R_{PUF\text{-}PAS}$) to be comparable to rates for other semi-volatile organic compounds. As we continue to obtain new chemical data on the oxygen analogs, these properties should be incorporated into new calculations of sampling rates.

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Chapter 6: Passive air sampling for indoor and outdoor exposures in an agricultural children's health study

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Chapter 6 Summary: This study presents passively sampled ambient indoor/outdoor air for OP pesticides and oxygen analogs at 20 households and 3 community sites in Yakima Valley, WA during spring/summer application seasons and one winter non-application season. PUF-PAS devices and polypropylene (PP) deposition plates were analyzed for CPF, AZM, and oxygen analogs. Cumulative monthly outdoor air concentrations ranged from 1.40 to 199 ng/m^3 CPF, 0.03 to 20 ng/m^3 CPF-O, 0.02 to 7.32 ng/m^3 AZM, and 0.02 to 0.75 ng/m^3 AZM-O. Households proximal to tree fruit fields (≤ 250 m) reported significantly higher mean outdoor air concentrations CPF ($p=0.01$), CPF-O ($p=0.014$), and AZM ($p=0.012$) than non-proximal households (>250 m); and there was an observable trend of higher outdoor air concentrations with increasing field proximity and in census blocks with high densities of tree fruit acreage. The measured proportions of oxygen analogs in outdoor air increased with average monthly solar radiation (MJ/m^2). Indoors, air concentrations of CPF and AZM were 5-10x lower than outdoors; little to no CPF-O or AZM-O was detected indoors. Farmworker households reported higher indoor mean air concentrations of CPF ($p=0.009$) than non-farmworker households. This trend was similar for AZM but not statistically significant. Overall there was correlation between surface deposition (ng/m^2) and air concentration (ng/m^3) values for CPF ($R^2=0.68$) and AZM ($R^2=0.67$) inside the home. This study demonstrates the ability to passively sample for these compounds in a rural community, and is the first of its kind to measure for both parent and oxygen analog compounds in a residential setting.

Chapter 6 Highlights

- Average monthly air concentrations of CPF were 5-10x higher than AZM.
- Indoor air concentrations were significantly reduced compared to outdoors.
- Households proximal to tree fruit fields reported significantly higher outdoor air concentrations of CPF, CPF-O, and AZM than non-proximal households.
- Proportion of oxygen analogs in outdoor air mixtures increased with solar radiation.
- Farmworker households reported higher mean air concentrations CPF than non-farmworker households.
- There was correlation with surface deposition (ng/m^2) and air concentration measurements.

6.1 Introduction

Previous studies have detected AZM, CPF, and their oxygen analogs in the air of the surrounding agricultural communities (CARB 1998, CDPR 2006, 2009, Fenske et al. 2009) and the mechanisms and factors influencing pesticide drift in air were introduced in Chapter 1. However, few environmental epidemiological health studies have incorporated the direct measurements of OP pesticides in air for exposure metrics. Current AAS methods are high cost and can be invasive to research participants, especially if taking place inside the household. In comparison, polyurethane foam passive air samplers (PUF-PAS) provide a good means of comparison of air concentrations across many different locations (i.e. epidemiology studies) because larger numbers (n) of samplers can be deployed over longer time periods. This spatial resolution is particularly useful for studies incorporating the use of geographical information systems (GIS) because it allows for more samplers to be deployed in a geographic region. The PUF-PAS devices may be used to test models incorporating crop-use data and meteorology to characterize participant household locations into high, medium, or low airborne exposure groups.

These benefits led to the testing of the PUF-PAS device (Chapter 5) for its performance when sampling OP pesticides and oxygen analogs. The tests demonstrated that PUF-PAS can serve as a practical alternative to AAS. In addition, the use of passive polypropylene (PP) deposition plates inside the home may be a good surrogate measurement for exposure if air sampling is not feasible (Keenan et al. 2010). This paper reports on the use of both new passive air sampling methodologies to obtain residential measurements for airborne OP pesticides and oxygen analogs.

6.2 Study Design

6.2.1 Location and Timeline

This study was conducted in the Yakima Valley region during the spring (March- April 2011) pre-thinning season, summer (June-August 2011) thinning season when CPF and AZM are in use, and winter non-spray season (November-December 2011). We scheduled 23 air monitor site locations in collaboration with the *Para Niños Saludables* community-based participatory research project (see timeline, Figure 6.1).

Figure 6.1/ 2011 Sample Collection Time-Line. Air sampling occurred during the spring (March- April 2011) CPF application season, summer (June-August 2011) AZM application season, and a series of quality control (QC) samples in winter (November-December) dormant season.

The *Para Niños* community project involves working with a cohort of 60 farmworker, 40 non-farmworker families, and their children to determine how they may be exposed to OP pesticides through inhalation, dermal, and ingestion routes. At the end of the project, detailed information may be given to the local communities in the Yakima Valley on how to protect families from pesticides. Details about the community project are reported by Thompson et al. (2003, 2008).

For this air monitoring study, all participant household addresses were geocoded in ArcGIS 10.0 and a subset of 20 households were asked to participate in the air monitoring study. These households were selected to be geographically representative of all households in the larger study (See Map, Figure 6.2). Of all approached homes, only one refused to participate in the air monitoring study so we identified another nearby household to participate. The pre-thinning and thinning application and non-application seasons were defined by the frequency of OP pesticide use. Product information regarding CPF and AZM was accessed through the WSU Decision Aid System (DAS, at http://das.wsu.edu). The DAS uses recent meteorological and entomology data to predict optimal application periods.

The passive air monitoring was conducted indoors and outdoors at the selected households and outdoors at three "community" air monitoring sites (See Table 6.1). The three "community" sites were ≤ 100 m of a participant household in the *Para Niños* community project. At these homes, the outdoor "community" measurements were used as surrogate outdoor exposure estimate. One community site was operated by the Washington State Department of Ecology, and two were operated by Washington State University's Agricultural Weather Network system.

6.2.2 PUF-PAS Deployment

Households were grouped *a priori* into proximal (≤ 250 m of nearest tree fruit field) and non-proximal (> 250 m), and farmworker/non-farmworker households (Table 6.1). This table includes the households where no indoor air monitoring occurred and the "community" samples were relied on for

outdoor exposure estimates. It was difficult to obtain non-farmworker residences that were proximal to tree fruit fields (n=2).

We collected a total of 66 outdoor samples (CPF, n=36; AZM, n=30) and 53 indoor samples (CPF, n=27; AZM, n=26) during the application seasons. Only 7 outdoor and indoor samples were collected at 3 households and 2 community sites during the non-application season. All PUF-PAS and PP deposition plates were deployed for approximately 1 month (24-32 days).

Prior to household sampling, a local *Para Niños Saludables* community health worker (*promotora*) notified the research participants of a potential air monitoring project. After obtaining consent, a meeting was scheduled with the family to set up the air monitors when a household member could be present for their input on determining sample location. Outdoors, the PUF-PAS were located away from children's play, livestock, and other high foot traffic areas. Indoors, the PUF-PAS and PP deposition plates were set up in locations to minimize interference or contact with humans or other surfaces.

6.3 Sampling Materials and Methods

6.3.1 Theory of Passive Sampling for Organophosphate Pesticides

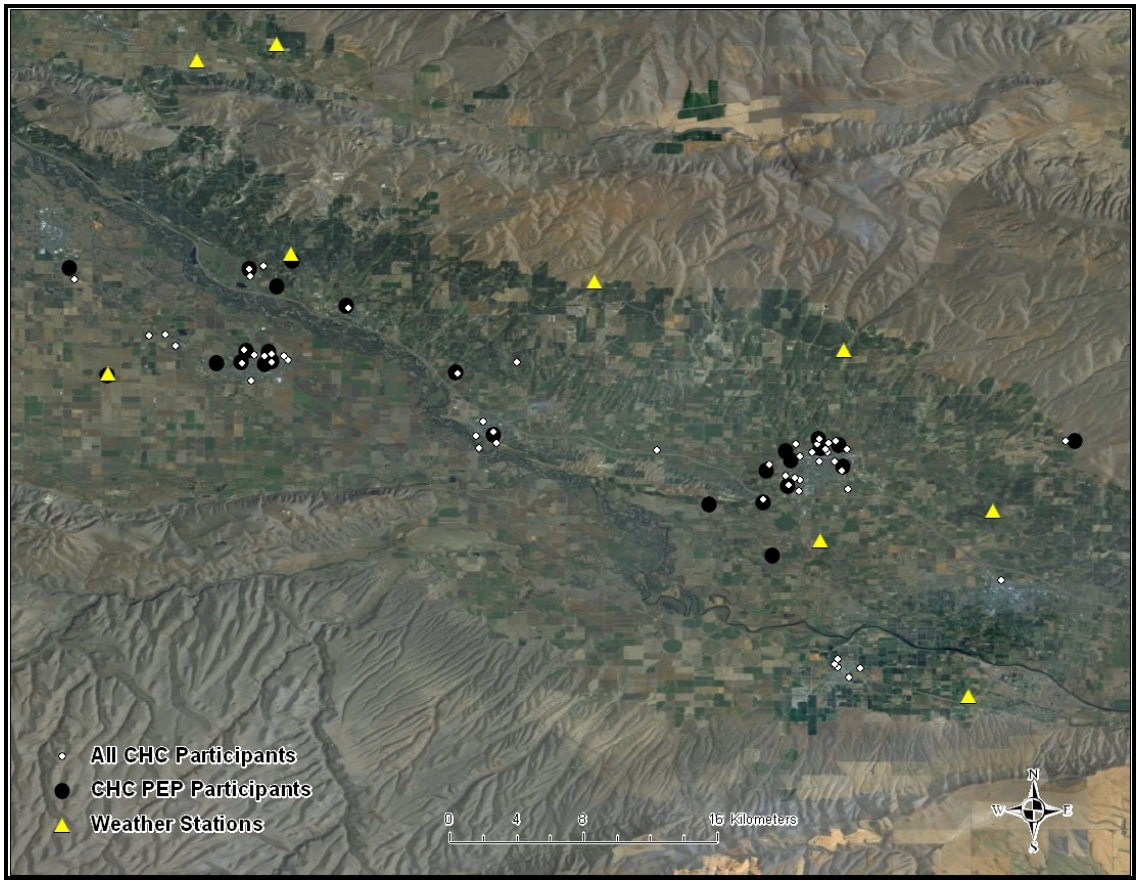
The PUF-PAS relies on the properties of atmospheric diffusion to collect contaminants without the use of a pump and sampling rate is controlled by diffusivity in the air boundary layer (Hourani and Underhill 1988, Shoeib and Harner 2002). Method development of PUF-PAS devices for detection of OP pesticides was previously validated in the laboratory and in the field environment (Chapters 4-5). Calculated sampling rates were linear and similar to those obtained for other volatile organic compounds. Average air concentrations (**Cair,** ng/m^3) are derived from the sampling rate, $\mathbf{R_{PUF\text{-}PAS}}$ (m^3/day), and the mass of chemical collected on the matrix $\mathbf{M_{pas}}$ (ng), where **t** = time, in days:

$$\mathbf{C_{air} = M_{pas}/(R_{PUF\text{-}PAS}*t)} \qquad \textit{(Eq. 6.1)}$$

Outdoor sampling rates were previously calculated using the loss of depuration compounds chlorpyrifos-methyl D_6 and azinphos ethyl D_{10} from the PUF matrix and through calibration with side-by-side active air sampling (AAS) (Chapter 5). Depuration compounds are spiked onto the PUF disks prior to field deployment. Outdoor sampling rates ranged from 1.28-8.49 m^3/day and were comparable to rates for other semi-volatile organic compounds (Chapter 5).

Deposition plates for indoor particulate collection have been used in previous studies using polyethylene plates, Whatman® chromatography paper, and glass slides (Edwards et al. 1998, Keenan et al. 2010), and double-layer gauze pads backed by aluminum foil (Lu et al. 1998).Passive deposition sampling is performed by collecting the deposited particulate after a pre-determined time period (Butte and Heinzow, 2002) dividing collected mass by surface area (cm^2) to obtain surface mass loading. Other residential surface exposure estimates have been conducted with a PUF roller or surface swipe samples (Lu et al. 1998, 1999; Lewis et al 1994).

Figure 6.2/ 2011 Air Monitoring Location Map. Air Monitoring locations are in black; there is an additional site due to the fact that one household re-located during the study. All participants enrolled in the child health center community-based participatory research project are in white and Agricultural Weather Net (WSU) stations are yellow triangles.



(K. Hartin, DEOHS 2012).

Table 6.1/ Number of homes selected at the sample locations were defined as proximal/farmworker, non-proximal/farmworker, proximal/non-farmworker, and non-proximal/non-farmworker.

	Proximal (≤ 250 m)	Non Proximal (> 250 m)	**Total**
Farmworker	7[a]	7	14
Non-Farmworker	2	7[b]	9
Total	9	14	**23**

[a] (n=6) for indoor air concentration and surface deposition;

[b] (n=5) for indoor air concentrations and surface deposition.

6.3.2 Outdoor Air Sample Collection

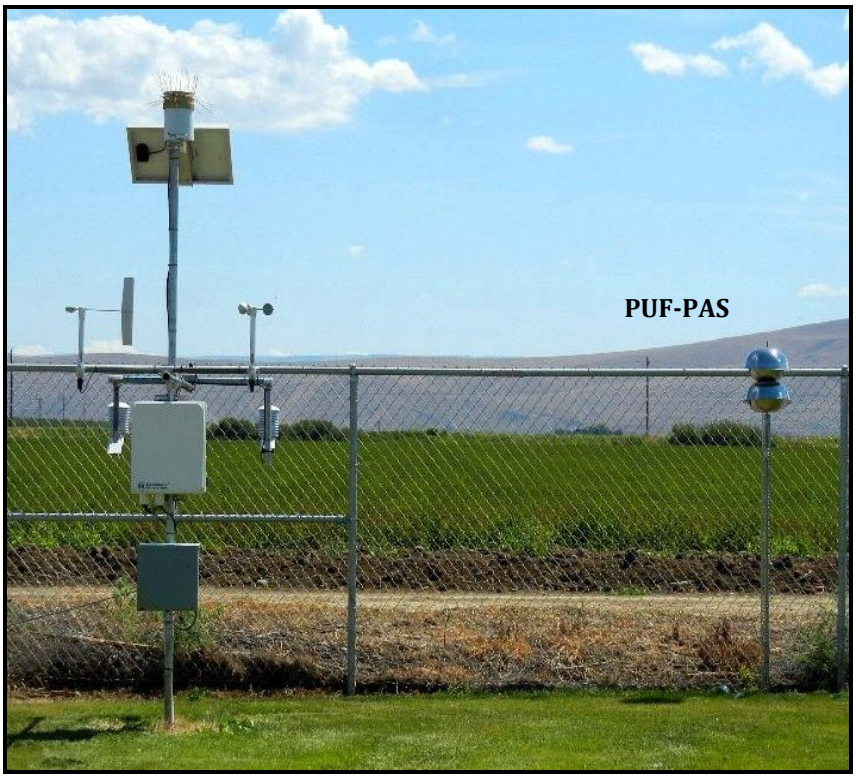
Outdoors, the PUF-PAS disk (Tisch, Environmental, 14 cm in diameter, 1.3 cm thick, surface area 370 cm^2) was placed in a stainless steel, domed chamber (i.e. "flying saucer" model, Shoeib and Harner 2002, Schuster et al. 2012, 22 cm diameter) to protect it from wind, precipitation, direct particle deposition, and sunlight (Tuduri et al. 2006). Air was allowed to flow over the PUF disks through a 1.5 cm gap between the chamber encasements. The sampling housing was hooked to a steel sampling mast at 1.5 -2.0 m height, and flexible plumber's putty was used to waterproof the seal between the sampling housing and mast. Each sampler was located ≥ 8 m from the residence. GPS coordinates were obtained for all outdoor locations PUF-PAS devices using a Garmin™ Wrist Unit 110.

Prior to deployment, each outdoor PUF-PAS was spiked with 210ng chlopyrifos-methyl-D_6 and 450ng azinphos ethyl D_{10} as depuration compounds. These compounds were not used indoors to insure the safety of the participants inside the home, and indoor air sampling rates were determined using the laboratory exposure chamber results and side-by-side calibration with active air samplers (AAS)

(Chapter 5).

Prior to the study, we hypothesized that increased levels of oxygen analogs would be found during periods of higher temperatures and solar radiation. Therefore, an outdoor LogTag® Temperature Recorder (2.3" x 1.3" x 0.9", Model# TRIX-8) was attached to the PUF-PAS chamber and recorded temperature data (°C) in 15 minute intervals. All sample sites were ≤ 5 km to the nearest Agricultural Weather Net station (Washington State University) recording relative humidity (%), solar radiation (MJ/m^2), and wind velocity (m/s) and direction at hourly intervals (See Figure 6.3). After collection, the samplers were stored in glass petri dishes sealed with Parafilm®, placed in a -20°C freezer in a Yakima Valley field office, and transferred to the University of Washington Environmental Health Laboratory (EHL) in Seattle on dry ice.

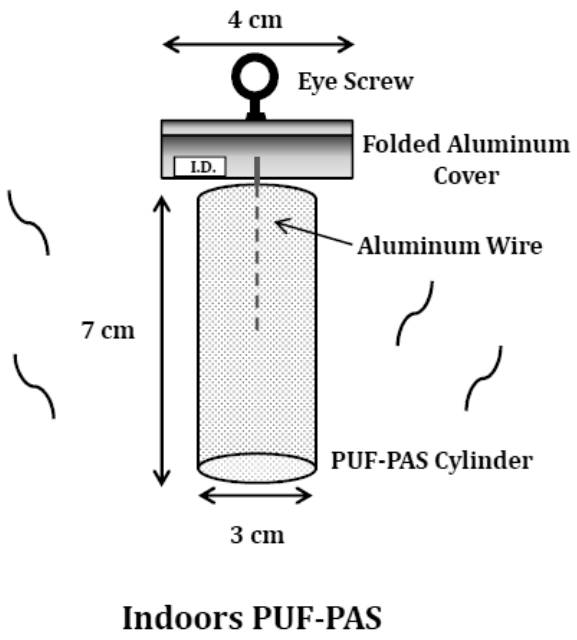
Figure 6.3/ Duplicate PUF-PAS device at a community site situated near a WSU Agricultural Weather Network Meteorological Station.



6.3.3 Indoor Air and Surface Collection

All PUF-PAS devices are made of an accumulating medium (e.g. PUF) that has demonstrated high retention for OP pesticides, allowing the shape and surface area of the device to be altered. Therefore, indoor PUF-PAS devices were designed similar to the 'mini-PUF' introduced by Bohlin et al. (2010). They are cylindrical (7 cm long, 3 cm diameter, surface area 74 cm^2), and placed on a 22 cm free-standing hook with a 10 cm diameter base. To capture primarily vapors and small particles, the top of each 'mini-PUF' was sheltered with a 4.5 x 4.5 cm aluminum covering. The indoor sampler was placed in a main living area of the house at a height ≥ 1m. Next to the PUF-PAS, a small deposition plate consisting of a Petri dish (6 cm diameter, Cat# 89000-300 VWR®) lined with a Whatman® Polypropylene (PP) filter (5 µm Pore Size, 4.7 cm diameter) to collect deposited dust particulate throughout the course of the sample period (See Figure 6.4). The LogTag® Temperature Recorder (2.3" x 1.3" x 0.9", Model# TRIX-8) was placed near both passive sampling devices. After collection, indoor PUF-PAS cylinders were samplers were stored in labeled zipper-sealed bags and PP deposition plates were covered and sealed with Parafilm®. Both were stored, and transferred to the EHL similarly to outdoor samples.

Figure 6.4/ Indoor PUF-PAS device and free-standing base.



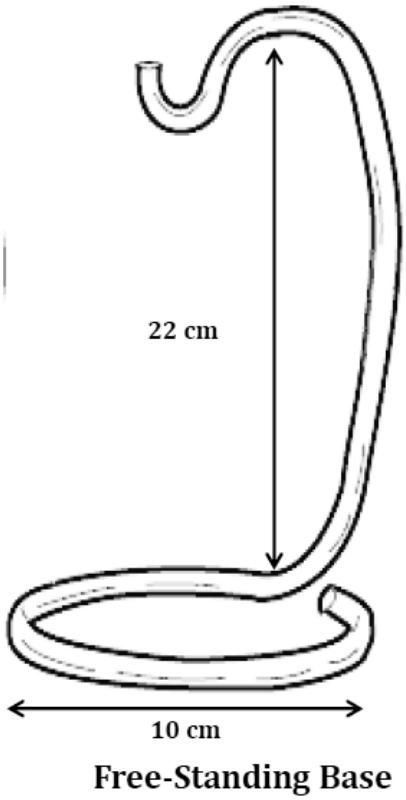
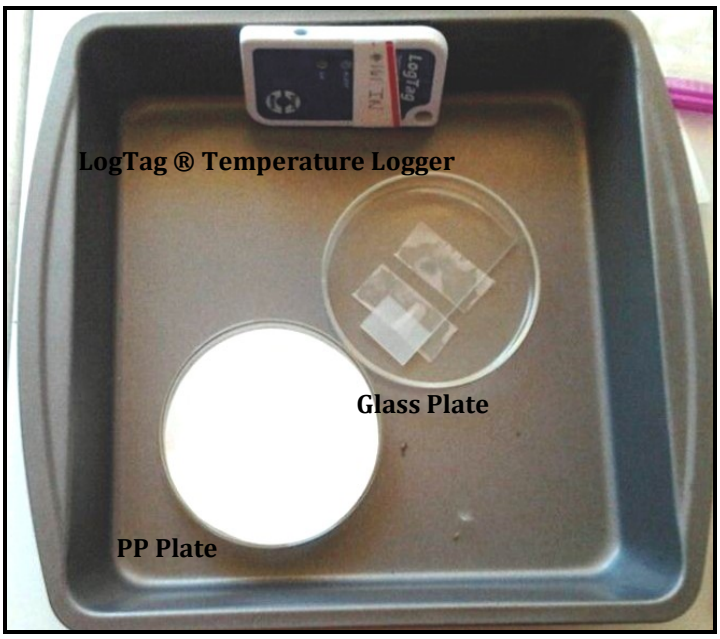


Figure 6.5/ PP deposition plates deployed inside the home. Deposition plates and temperature data loggers were placed in a baking pan to allow for easy deployment in the home.



6.3.4 QA/QC

Preparation and storage of PUF-PAS matrices followed the same procedures in previous literature (Bohlin et al. 2010, Shoeib and Harner, 2002) (See Standard Operating Procedures). To assess variability of the sample method, duplicate PUF-PAS and PP deposition plates were deployed at 4 sample locations. For each site location, the arithmetic mean of the duplicates was used for statistical analysis. Outdoors, triplicate PUF-PAS devices were deployed at 2 locations. For PUF-PAS, the agreement between replicate samples was consistent; coefficient of variation (CV) values were ≤ 19 % for CPF and less ≤ 37% for AZM. For the PP deposition plates, COV values were ≤ 15% for CPF; all replicates for AZM were <LOD. All field blanks (12 outdoor, 6 indoor) reported <LOD for CPF, CPF-O, AZM, and AZM-O. The trip spikes (9 outdoor, 5 indoor) were performed at the sample site with a 50uL syringe and recoveries were acceptable, ranging from 68 to 118%. Storage stability and spike fortification recovery results were within 80 to 120 % for all measured compounds, and all laboratory reagent blanks were <LOD. A duplicate PUF-PAS was deployed at an urban test site in Seattle, WA and reported small air concentrations for CPF, AZM, and CPF-O; but all were <1 ng/m^3. All samples of AZM-O were <LOD in Seattle.

6.3.5 Chemical Analysis

PUF-PAS and PP filter matrices were removed from storage and sonicated for 1.5 hours at room temperature (20-23°C) in 10-50mL acetonitrile solution containing stable-isotope labeled internal standards (ISTD) and then placed in a turbovap at 60°C until evaporated to 1.5 mL. If particulate was present in the extract, it was quantitatively transferred to a leur-lock 3 mL polypropylene syringe and filtered with a PTFE syringe filter (13 mm, 0.2 µm porosity).

Sample analysis was conducted using the liquid chromatography tandem mass spectrometry (LC-MS/MS) method described in Chapter 4. The internal standards solutions were prepared using 100µg/mL solutions of chlorpyrifos diethyl-D10 (99%, neat, Cambridge Isotope Labs, DLM-4360), 13C2,15N-chlorpyrifos-oxon (neat, donated by Dow Agro Sciences LLC), azinphos-methyl-D6 (98.5%, EQ Laboratories Inc. XA10365100AC), and azinphos-methyl oxon dimethyl-D6 (99.3%, solid, Bayer Crop Science K-176). Internal standards solutions for depuration compounds were chlopyrifos-methyl (ChemService, Inc., 100ug/ml in Acetonitrile) and azinphos ethyl (SigmaAldrich® 45332-250MG). Reagents were acetonitrile and operating parameters were the same. Instrument limits of detection (LOD) were 1 ng/sample CPF and CPF-O, and 1 to 5ng/sample for AZM and AZM-O. The instrument LOD for chlopyrifos-methyl-D6 and azinphos ethyl D10 (depuration compounds) was 1 ng/sample. If air samples were <LOD, a substitution LOD value was assigned by dividing by the $\sqrt{2}$ (resulting in values of 0.71 and 3.54 ng/sample). The <LOD samples for chlorpyrifos and azinphos-methyl were then divided by the effective air sampling volume for analysis. After accounting for sample volume of PUF-PAS and surface area of PP deposition plates, this corresponded to PUF-PAS method LOQ ranging from 0.01-0.02 ng/m^3 for CPF/CPF-O and 0.02-0.03 ng/m^3 for AZM/AZM-O; and a PP deposition plate method LOQ of 0.03 ng/cm^2 for CPF/CPF-O and 0.17 ng/cm^2 for AZM/AZM-O. These values were used in statistical analysis.

6.4 Statistical Analysis

6.4.1 Farmworker/Non-Farmer and Proximal/Non-Proximal Household

This study reports on the air concentrations of AZM, CPF, AZM-O, and CPO-O from all indoor and outdoor sample locations. Air concentration data were not lognormal based on the Shapiro-Wilk test, so non-parametric statistical methods were used. The data was skewed right. We assumed that both proximity and farmworker status may affect air concentrations. Therefore outdoor and indoor air concentrations (ng/m^3) and indoor surface deposition (ng/m^2) among proximal farmworker, proximal non-farmworker, non-proximal farmworker, and non-proximal non-farmworker groups were compared using a 2-way non-parametric Friedman test, which is similar to a parametric repeated measure ANOVA (Zimmerman et al. 1993). Next, outdoor and indoor air concentrations (ng/m^3) and indoor surface deposition (ng/m^2) in proximal vs. non-proximal and farmworker vs. non-farmworker variables were compared using a non-parametric Kruskal-Wallis one way analysis of variance test. We also specifically examined the potential correlation of air concentration (ng/m^3) with indoor surface deposition of household dust (ng/cm^2) using linear regression after log transformation of the data. All statistical calculations were performed in STATA 11.2 (StataCorp LP, College Station, TX).

6.4.2 Land Use Regression with Cropland Data

All sample site locations were geocoded into ArcGIS 10.0 to perform simple calculations to look at associations of air concentration values and geographical characteristics of the sample location. The aim was to use publically available crop-use data to characterize participant households into high, medium, and low airborne exposure groups. Tree fruit acreage data for GIS and remote sensing may be obtained using the 2011 USDA Cropland Data Layer from the NASS website (www.nass.usda.gov/research/Cropland/SARS1a.htm). A limitation was that there was no available

data on exact pesticide use patterns per acre, so the analysis assumed all tree fruit fields were potential sources. Each sample location was assigned a Census Block; this data was obtained from the U.S. Census Bureau Geography MAF/TIGER database (www.census.gov/geo/www/tiger/shp.html). The land-use estimate of tree fruit density ($\rho_{tree\text{-}fruit,}$ %) was calculated by taking combined tree fruit acreage (e.g. apples, cherries, peaches, etc) and dividing by the total acreage of each 2010 census block (n=5) in the lower Yakima Valley.

$$\rho_{tree\text{-}fruit}\,(\%) = [N_{Acres\ Tree\ Fruit} / N_{Acres\ Census\ Block}] \times 100 \qquad (Eq.\ 6.2)$$

In addition, the 2011 USDA Cropland Data Layer was used to calculate residential distance (m) of sample site to nearest tree-fruit field for the statistical comparisons of *a priori* proximal (≤ 250 m) vs. non-proximal homes (>250 m) and to generate scatter plots of air concentration (ng/m^3) by proximity (m) after log transformation of the air concentration data. We also tested the linear relationship of log transformed concentrations by log transformed proximity to examine potential exponential decay with field distance.

Since the majority (>70%) of outdoor samples were <LOD for AZM-O, the scatter plot could not be generated without distortion of the regression line. To avoid this, we imputed data <LOD for AZM-O using maximum likelihood estimation (MLE) with a lognormal distribution (also referred to as "left-censored lognormal distributed data") using the Microsoft Solver tool in Excel. Exposure data are often right-skewed and assumed to follow a lognormal distribution (Leidel et al. 1977). This MLE method has been demonstrated to result in less bias and performs well even for censoring up to 80% (Jin et al. 2010). The imputed data was used for the scatter plot, but not used for the non-parametric Friedman and Kruskal-Wallis tests. For both substitution values and imputed values <LOD, there was no statistical significance in difference among groups for concentration and surface deposition of AZM-O.

6.4.3 Factors Influencing Oxon Formation: Linear Regression

To examine meteorological and geographical factors influencing the formation of oxygen analogs in air samples, simple linear regression was used to model potential relationships between the measured proportion of outdoor air CPF-O and AZM-O as dependent variables and average monthly wind speeds (m/s), temperature (°C), solar radiation (mJ/m^2), relative humidity (%), and distance from nearest tree fruit field (m) as explanatory variables. These variables were selected based on their potential to influence interaction with hydroxyl radicals or photodegradation (Fontaine and Teeter 1987, Aston and Seiber 1997, Bavcon Kralj et al. 2007). Multiple regression was also attempted but many of the combined effects were insignificant. The % CPF-O and AZM-O was calculated as in Chapter 2 (Eq. 2.2, where the percent chlorpyrifos-oxon (% CPF-O) in each sample was calculated by dividing the mass of chlorpyrifos-oxon, expressed as chlorpyrifos equivalent, by total chlorpyrifos and multiplying by 100 while adjusting for the difference in molecular weight from the parent compound.

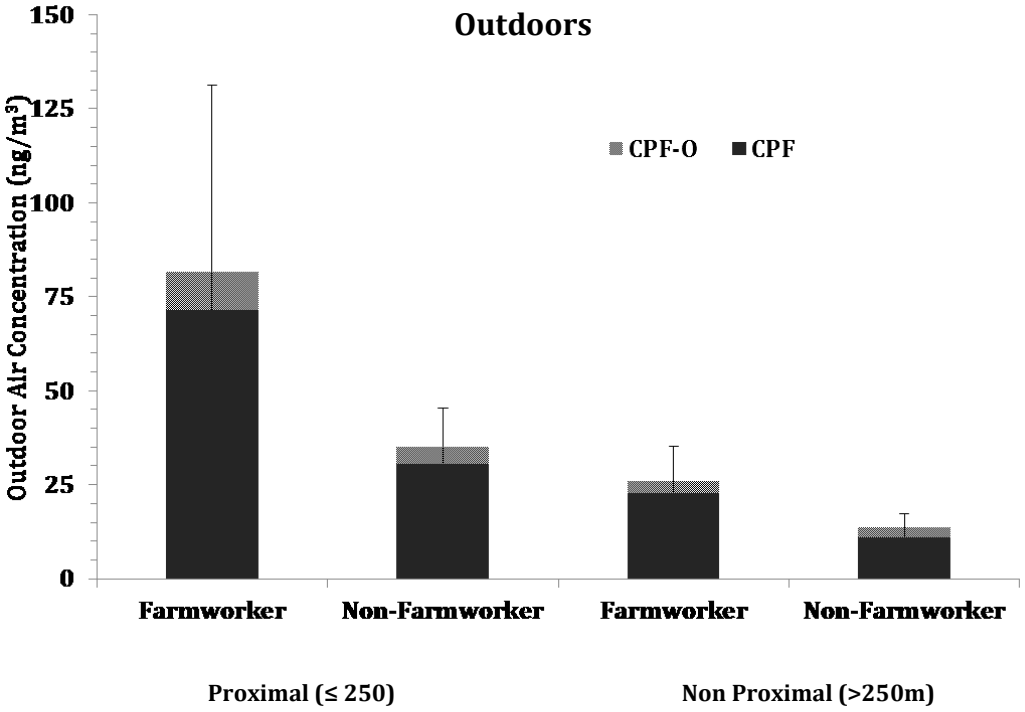
6.5 Results

6.5.1 Outdoor Air Concentrations

The outdoor PUF-PAS air monitoring results are shown in Table 6.2 and graphically in Figure 6.5. During the spring, cumulative residential air concentrations CPF ranged from 1.40 to 199 ng/m^3, and CPF-O ranged from 0.03 to 20 ng/m^3; all samples were >LOD for CPF and > 95% were positive for CPF-O. During the summer, air concentrations of AZM were much lower, ranging from 0.02 to 7.32 ng/m^3 and AZM-O from 0.02 to 0.75 ng/ m^3. Although 98% of samples were >LOD for AZM, only 31% of samples were >LOD for AZM-O. During the winter non-application season, there was low air concentrations of CPF ranging from 0.6 to 5.8 ng/m^3, and CPF-O ranged from 0.02 to 0.44 ng/m^3. In the winter, all samples were <LOD for AZM and AZM-O.

During the spring, there were significant differences in outdoor air concentrations of CPF, CPF-O, and AZM between proximal-farmworker, proximal non-farmworker, non-proximal farmworker, and non-proximal non-farmworker homes (Table 6.2). In the Kruskal-Wallis test, proximal households experienced significantly higher mean outdoor air concentrations CPF ($p = 0.016$), CPF-O ($p=0.012$) and AZM ($p=0.000$) than non-proximal households. Unlike CPF-O, there was very little AZM-O detected in air. Farmworker homes experienced significantly higher mean outdoor air concentrations CPF ($p = 0.013$) and CPF-O ($p=0.012$) than non-farmworker households.

Figure 6.5A/ Outdoor and Indoor Average Monthly Air Concentrations (ng/m^3) of CPF and CPF-O during the spring pre-thinning season. Bars and arithmetic means and whiskers are standard deviations.



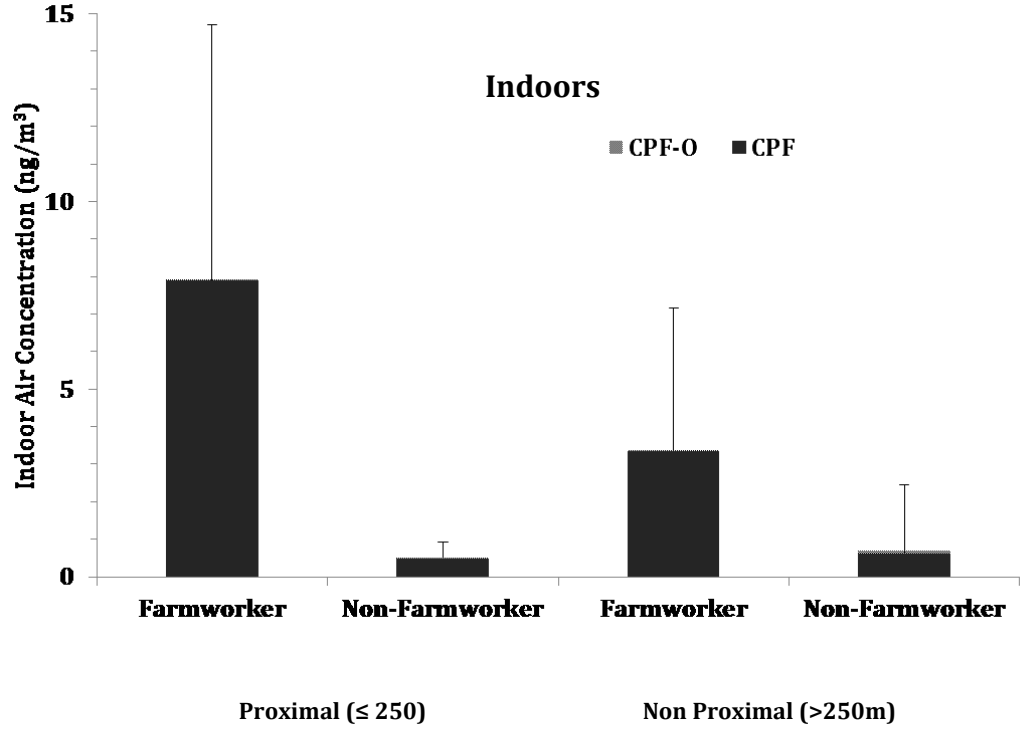
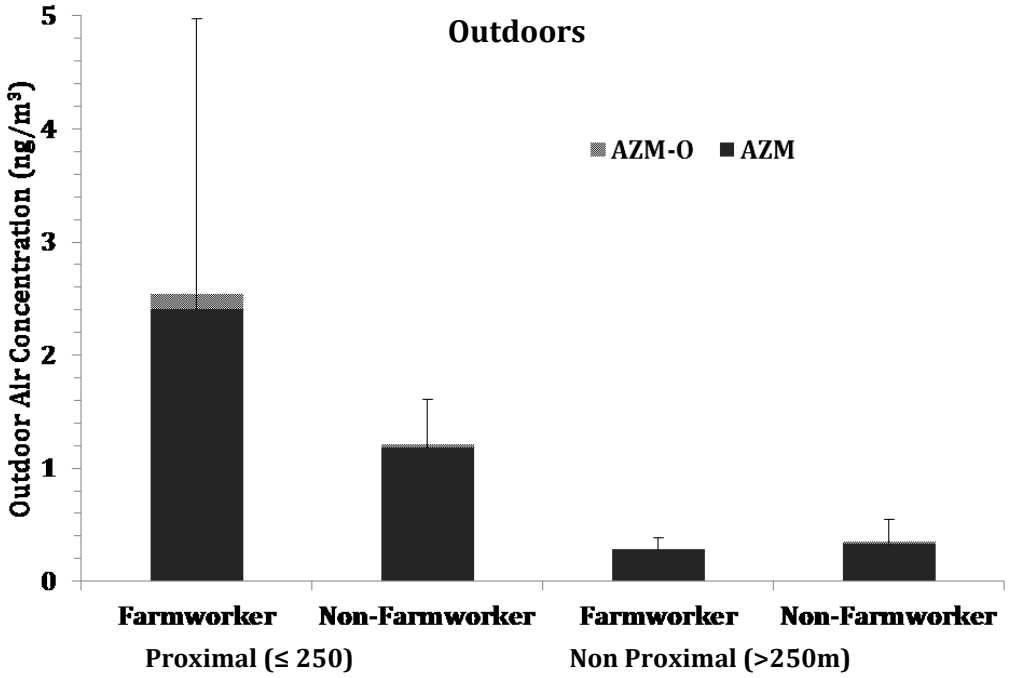


Figure 6.5AB/ Outdoor and Indoor Average Monthly Air Concentrations (ng/m^3) of AZM and AZM-O during the summer thinning season. Bars and arithmetic means and whiskers are standard deviations.



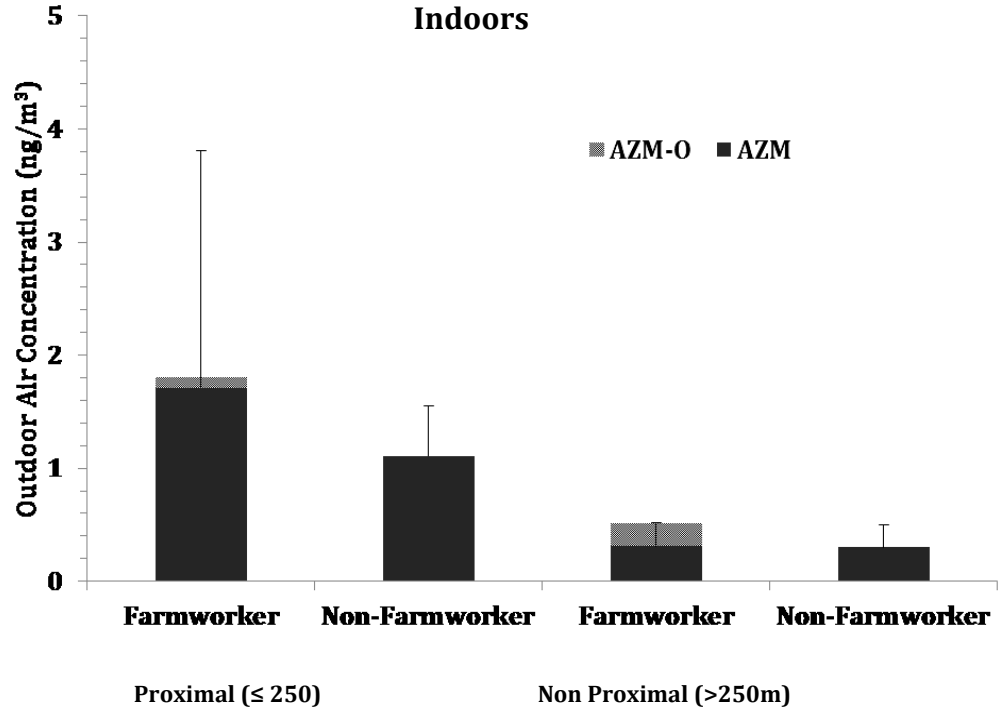


Table 6.2/ Results Passive Air Monitoring, Spring Pre-thinning and Summer thinning seasons, 2011. Arithmetic Mean Values (SD) of Air Concentration (ng/m^3), PFTE Deposition Surface Loading (ng/cm^2); and 2-way Friedman's Test P-Values.

	Proximal (≤ 250 m)		Non-Proximal (> 250m)		
	Farmworker (n=7)[a]	Non-Farmworker (n=2)	Farmworker (n=7)	Non -Farmworker (n=7)[b]	2-way Friedman's Test P-Value
Outdoor Air Concentration (ng/m^3)					
Chlorpyrifos (CPF)[c]	71.5 (59.9)	30.7 (14.6)	22.8 (12.5)	11.2 (6.2)	***0.016***
Chlorpyrifos-Oxon (CPF-O)	10.3 (5.5)	4.5 (4.2)	3.2 (3.2)	2.5 (1.5)	***0.012***
Azinphos Methyl (AZM)[d]	2.41 (2.57)	1.18 (0.43)	0.28 (0.10)	0.33 (0.22)	***0.000***
Azinphos Methyl-Oxon (AZM-O)	0.13 (0.25)	0.03 (0.06)	<LOD	0.02 (0.03)	0.685
Indoor Air Concentration (ng/m^3)					
Chlorpyrifos (CPF)	7.91 (6.80)	0.50 (0.42)	3.5 (3.8)	0.64 (1.82)	0.115
Chlorpyrifos-Oxon (CPF-O)	0.03 (0.05)	0.01 (0.01)	0.01 (0.12)	0.07 (0.19)	0.515
Azinphos Methyl (AZM)	1.71 (2.10)	1.11 (0.44)	0.31 (0.21)	0.30 (0.20)	0.460
Azinphos Methyl-Oxon (AZM-O)	0.1 (0.04)	<LOD	0.2 (0.3)	<LOD	NA
Surface Deposition (ng/cm^2)					
Chlorpyrifos (CPF)	1.71 (2.63)	0.15 (0.13)	0.32 (0.60)	0.06 (0.11)	0.332
Chlorpyrifos-Oxon (CPF-O)	0.09 (0.12)	<LOD	0.03 (0.06)	<LOD	NA
Azinphos Methyl (AZM)	0.46 (0.58)	0.07 (0.10)	0.32 (0.29)	0.04 (0.04)	0.246
Azinphos Methyl-Oxon (AZM-O)	0.04 (0.06)	<LOD	<LOD	<LOD	NA

[a] (n=6) for indoor air concentration and surface deposition; [b] (n=5) for indoor air concentrations and surface deposition.

[c] CPF and CPF-O Measurements were taken during the spring (pre-thinning) season; [d] AZM and AZM-O measurements were taken during the summer (thinning) season.

Table 6.3/ Results Passive Air Monitoring, Spring Pre-thinning and Summer thinning seasons, 2011; 1-way Kruskal-Wallis Test P-Values.

	Kruskal-Wallis Test (P-Value)	
	Proximal (n=9) vs. Non-Proximal Households (n=14) [a]	Farmworker (n=14) vs. Non-Farmworker Households (n=9) [b]
Outdoor Air Concentration (ng/m³)		
Chlorpyrifos (CPF)[c]	***0.016***	***0.013***
Chlorpyrifos-Oxon (CPF-O)	***0.012***	***0.012***
Azinphos Methyl (AZM)[d]	***0.000***	0.184
Azinphos Methyl-Oxon (AZM-O)	0.685	0.481
Indoor Air Concentration (ng/m³)		
Chlorpyrifos (CPF)	***0.031***	***0.009***
Chlorpyrifos-Oxon (CPF-O)	0.961	0.196
Azinphos Methyl (AZM)	0.819	0.124
Azinphos Methyl-Oxon (AZM-O)	NA	NA
Surface Deposition (ng/cm²)		
Chlorpyrifos (CPF)	***0.014***	0.366
Chlorpyrifos-Oxon (CPF-O)	NA	NA
Azinphos Methyl (AZM)	***0.026***	0.085
Azinphos Methyl-Oxon (AZM-O)	NA	NA

[a] (n=8) Proximal, (n=12) Non-Proximal for indoor air concentration and surface deposition.

[b] (n=13) Farmworkers, (n=7) Non-Farmworker for indoor air concentrations and surface deposition.

[c] CPF and CPF-O Measurements were taken during the spring (pre-thinning) season; [d] AZM and AZM-O measurements were taken during the summer (thinning) season.

Overall, residential proximity to the nearest tree fruit field was associated with higher outdoor air concentrations of AZM and CPF (ng/m^3), but this relationship was not as clear with AZM-O or CPF-O (see Figure 6.6). This was also the case when both air concentration and distance data was log transformed (log-log transformation figures are available in the Appendix, Figures S.6.1-S.6.4). For each Census Block containing a sample site, there was a trend of higher outdoor air concentrations of AZM and CPF (ng/m^3) with increasing tree fruit ($\rho_{tree\text{-}fruit}$) acreage density (See Figure 6.7). For example, substantially higher concentrations AZM and CPF were reported in Census blocks A and B, which had tree fruit densities of 40 and 22%, respectively. However, this trend was not observed in all cases, as Census Block E reported higher outdoor air concentrations of CPF and AZM than expected. The trend was non-informative for outdoor air concentrations of oxygen analogs.

Figure 6.6A/ Average Log of Outdoor Monthly Air Concentrations (ng/m^3) of CPF by Residential Proximity to Tree Fruit Fields (m). The dotted line represented 95% C.I. Slope and R^2 values are for linear regression using log-transformed air concentration values for CPF (ng/m^3).

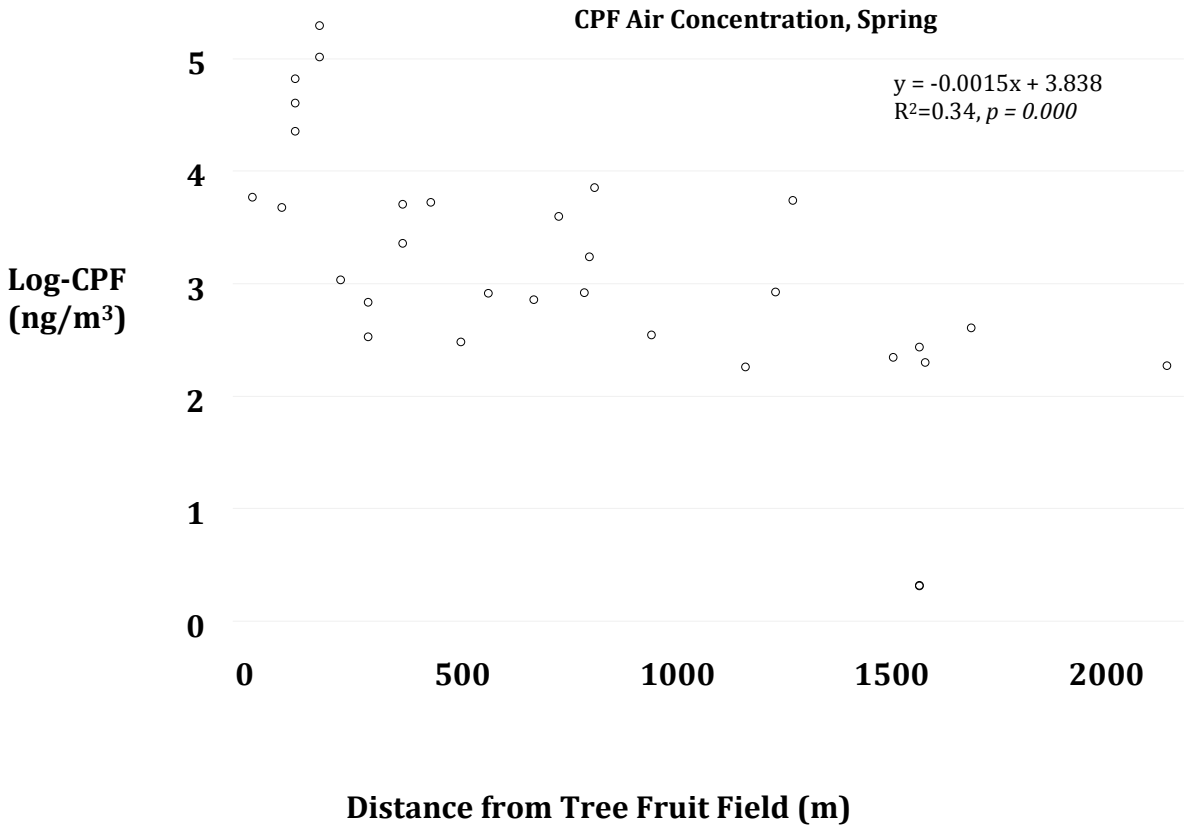


Figure 6.6B/ Average Log of Outdoor Monthly Air Concentrations (ng/m^3) of CPF-0 by Residential Proximity to Tree Fruit Fields (m). The dotted line represented 95% C.I. Slope and R^2 values are for linear regression using log-transformed air concentration values for CPF-O (ng/m^3).

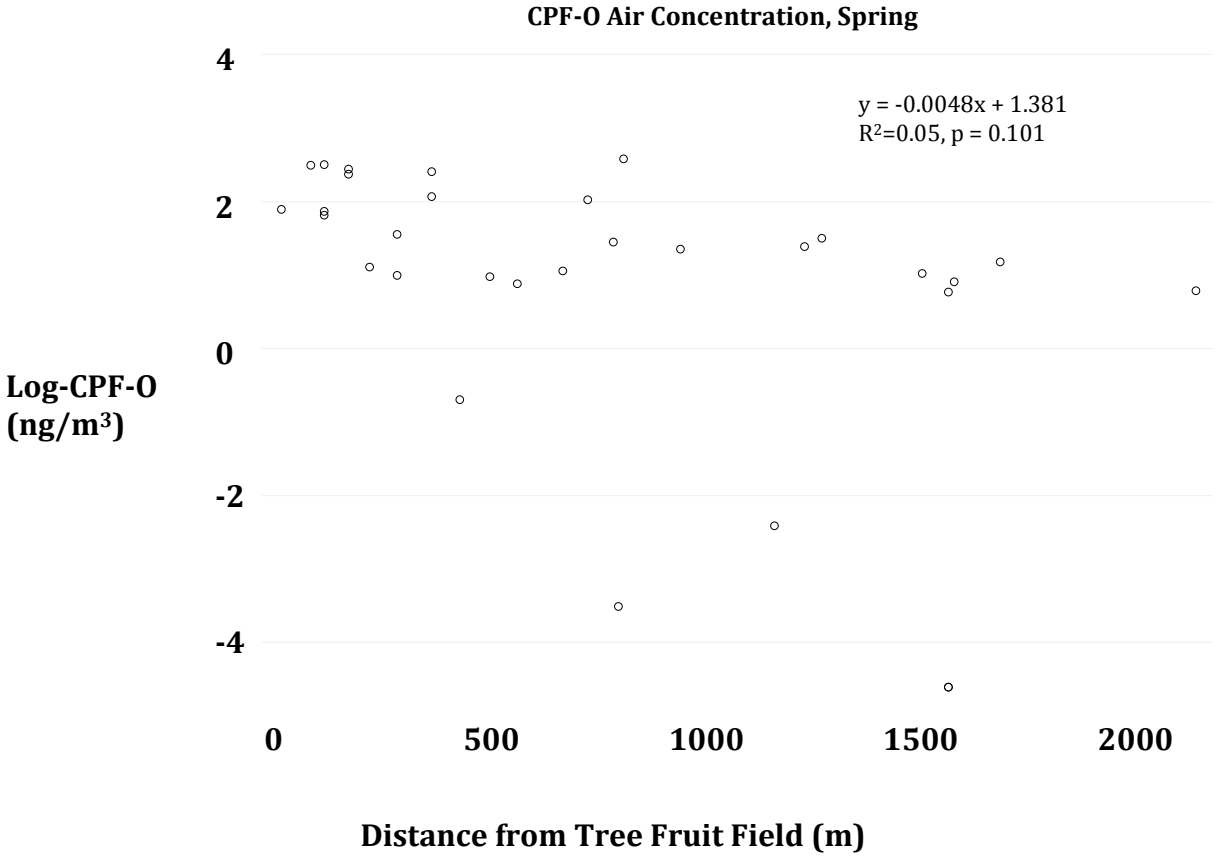


Figure 6.6C/ Average Log of Outdoor Monthly Air Concentrations (ng/m^3) of AZM by Residential Proximity to Tree Fruit Fields (m). The dotted line represented 95% C.I. Slope and R^2 values are for linear regression using log-transformed air concentration values for AZM (ng/m^3).

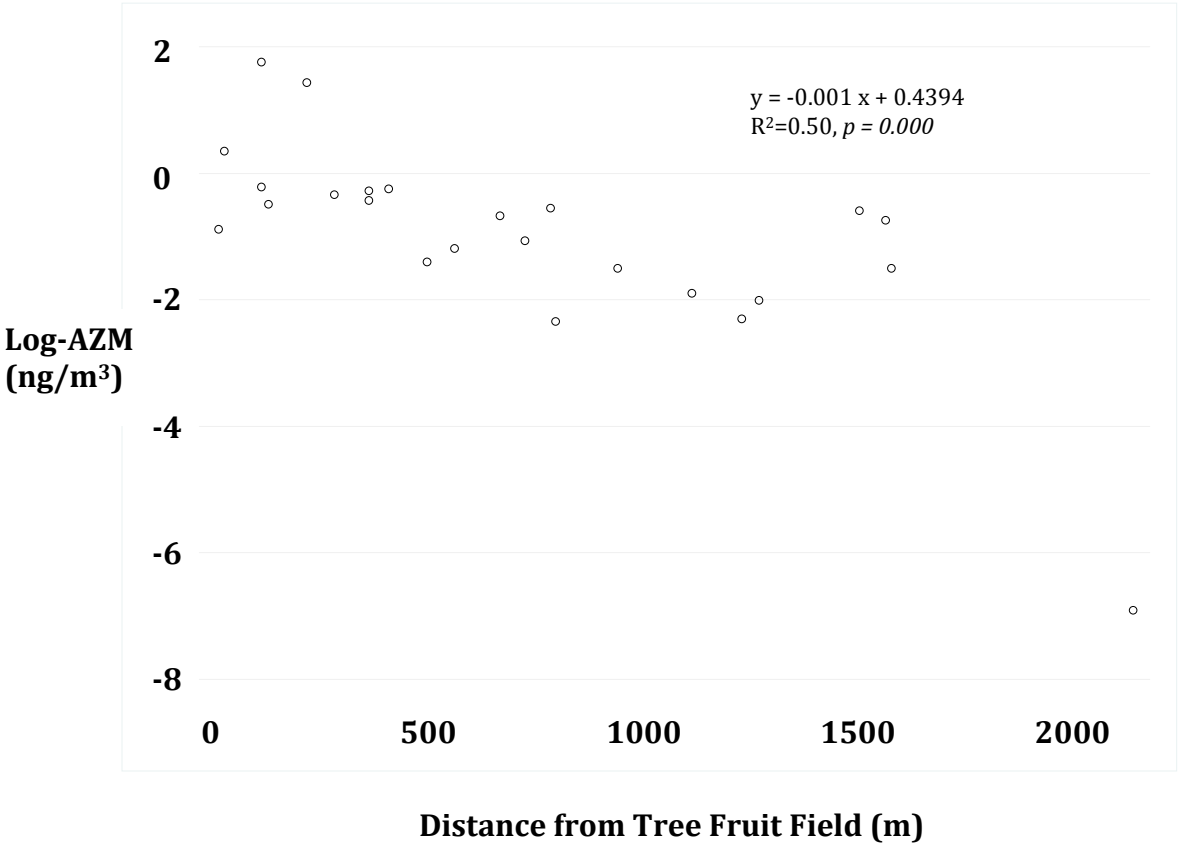


Figure 6.6D/ Average Log of Outdoor Monthly Air Concentrations (ng/m^3) of AZM-O by Residential Proximity to Tree Fruit Fields (m). The dotted line represented 95% C.I. Slope and R^2 values are for linear regression using log-transformed air concentration values for AZM-O (ng/m^3).

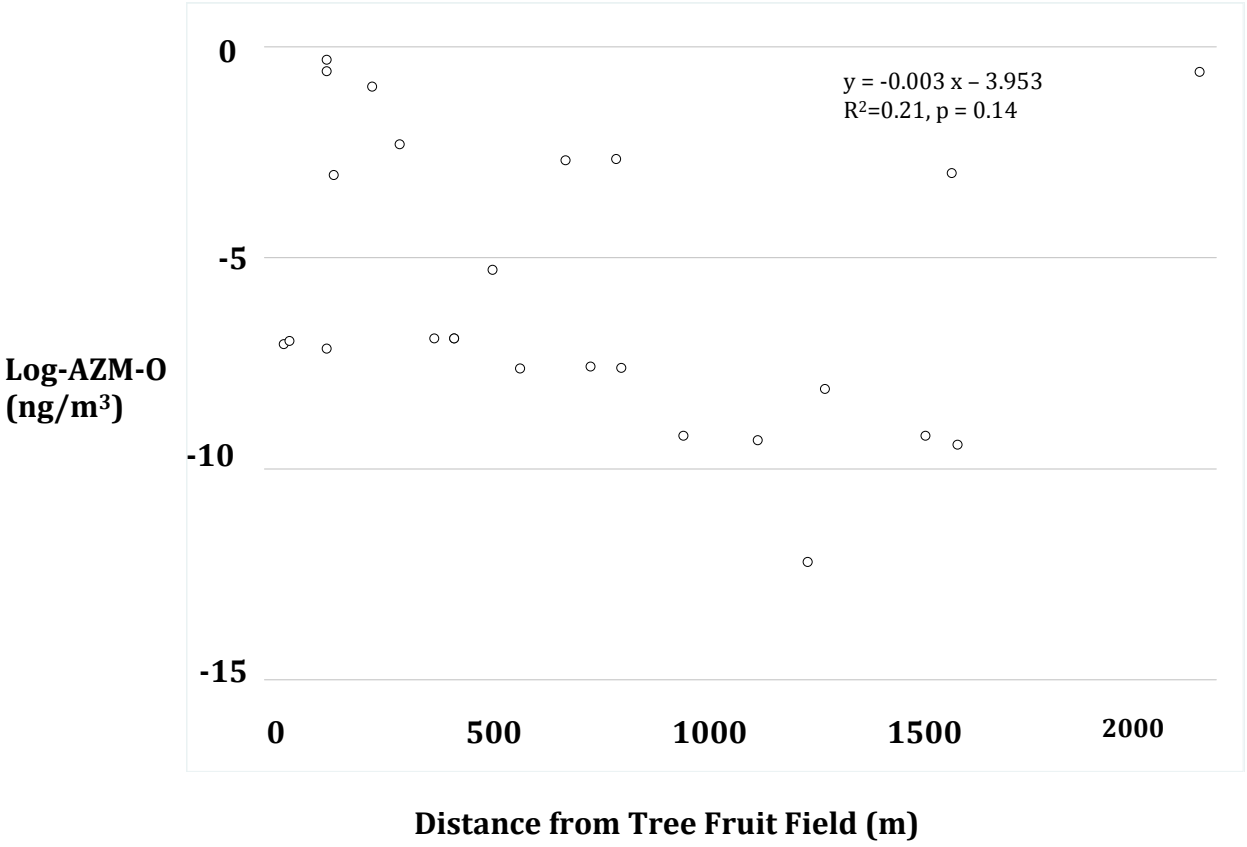
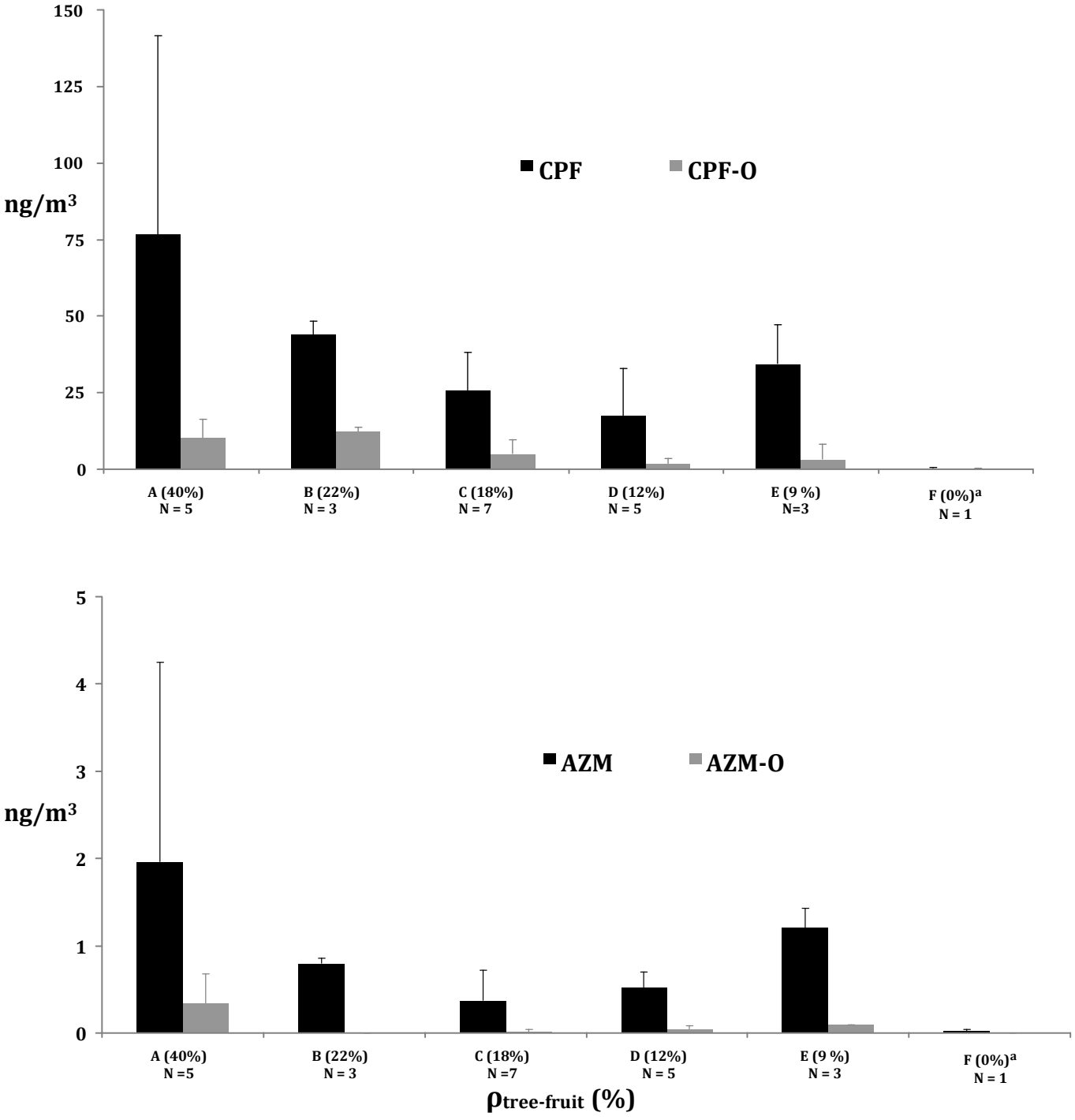


Figure 6.7/ Cumulative Monthly Air Concentrations (ng/m^3) of CPF, CPF-O, AZM, AZM-O by Tree Fruit Acreage Density, $\rho_{tree\text{-}fruit}$ (%). The y-axes are scaled according to reported concentrations of CPF and AZM. N= number of sample site locations.

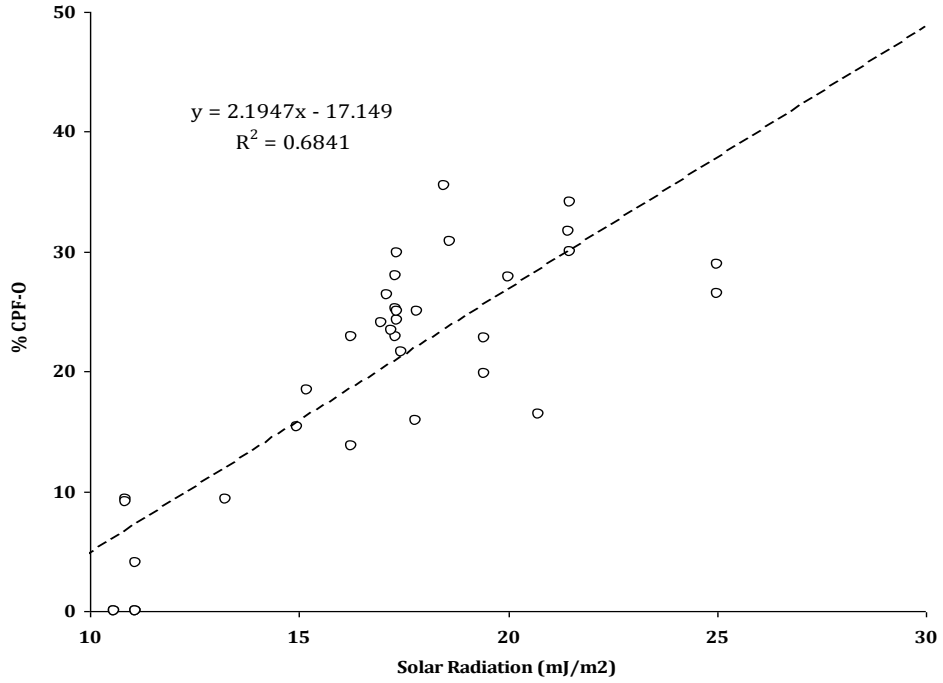


6.5.2 Outdoor Oxygen Analogs

Outdoor measured proportions CPF-O (%CPF-O) was associated with increases in monthly solar radiation (MJ/m^2) (R^2=0.6841, p=0.0001, Figure 6.8); but not with temperature or relative humidity. There was small increase in %CPF-O with higher average wind velocity (m/s), but this was not significant (R^2=0.10, p=0.070). There was increased proportions AZM-O (% AZM-O) with increases solar radiation, but not as significant (R^2=0.3302, p=0.051) and attributable to the low amounts of AZM-O detected in air relative to CPF-O. Based on previous findings (see Chapter 3), we would expect a significant increase in %CPF-O with further residential proximity to tree fruit fields. There was a small increase in %CPF-O with further distance to tree fruit fields (m), but the effect was not significant and the variability was high. This was not attempted for % AZM-O due to low amounts of AZM-O in the atmosphere.

Figure 6.8/ Higher proportions CPF-O and AZM-O (%) by Average Monthly Solar Radiation (MJ/m²).

Overall levels of AZM-O were low and >60% of AZM-O samples were >LOD. There was no observed association by temperature or relative humidity.



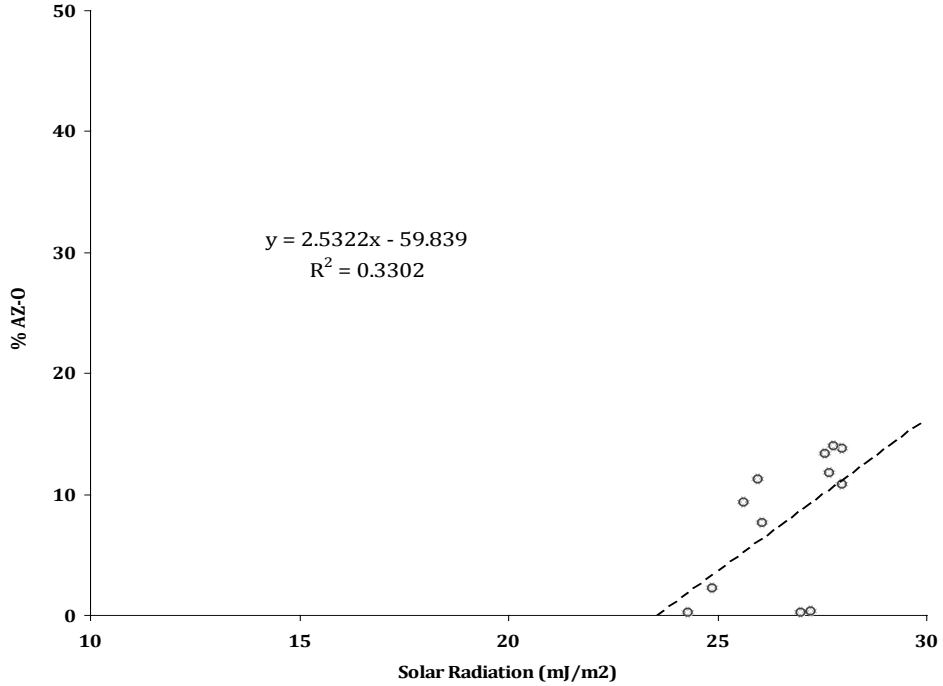
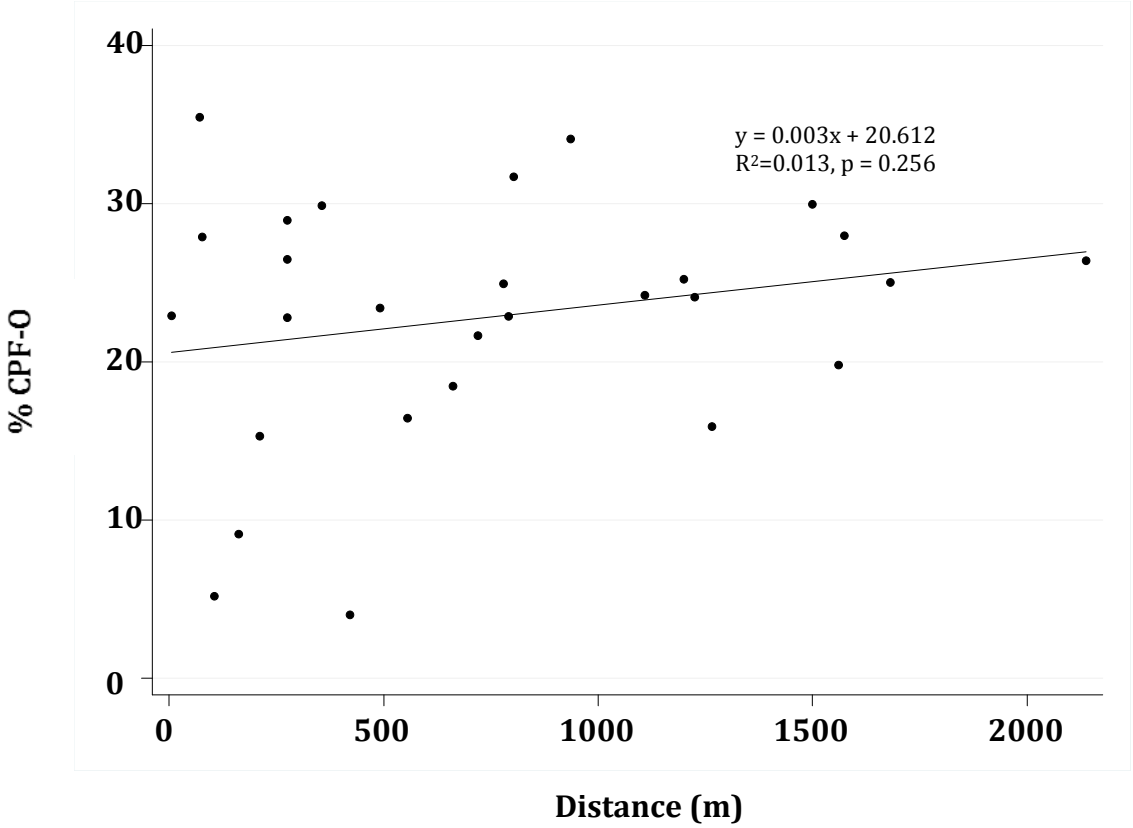


Figure 6.9/ Proportion CPF-O (%) by Residential Proximity to Tree Fruit Fields (m). There was no statistically significant change in proportion of CPF-O (%CPF-O) by distance.



6.5.3 Indoor Air Concentrations

Measured air concentration values indoors were much lower than outdoors. During the spring, 79% of air samples were >LOD for CPF (0.02 ng/cm^3), concentrations ranged from 0.56 to 17.5 ng/m^3. During the summer, only 55% of air samples were >LOD (0.01 ng/cm^3) for AZM, with concentrations ranging from 0.02 to 1.02 ng/m^3. Very few samples detected oxygen analogs, only 5 samples yielded detectable CPF-O and 4 samples yielded detectable AZM-O; all of these were <1ng/m^3 (See Table 6.2). During the winter non-application season, two households reported indoor concentrations of CPF ranging from 0.02 to 0.1 ng/m^3; and all samples were <LOD for CPF-O, AZ, and AZ-O.

There was little difference in indoor air concentrations between proximal and non-proximal households. There were slightly higher levels of AZ in proximal households, but this difference was <1 ng/m^3. However, farmworker households reported indoor air concentrations of CPF that were significantly higher than reported in non-farmworker households (p=0.009) and mean air concentrations of AZM that were slightly higher, but not statistically significant (p=0.270) (Figure 6.3). This trend was seen in CPF-O and AZM-O, but not significant and most likely due to low numbers of detection.

6.5.4 Indoor Surface Deposition

On average, proximal households reported indoor surface deposition CPF that were higher than non-proximal households and this was statistically significant (p=0.03) (Table 2). This was not true for AZM, and there was none to very low amounts of oxygen analog detected in deposition samples (<0.1 ng/m^2). During the winter non-application season all deposition samples were <LOD.

During the application seasons, simple linear regression demonstrated a correlation between reported surface deposition (ng/m^2) and air concentrations (ng/m^3) of CPF and AZM inside the home (See Figure 6.7). The relationship was slightly stronger for indoor CPF (R^2= 0.8661) than for AZM (R^2=0.7932), but both were statistically significant (p < 0.001). This regression was not completed for oxygen analogs since most samples were <LOD.

Figure 6.10A/ Average Log Monthly Indoor Air Concentrations (ng/m^3) of CPF and Log Monthly Indoor Surface Deposition (ng/cm^2) CPF.

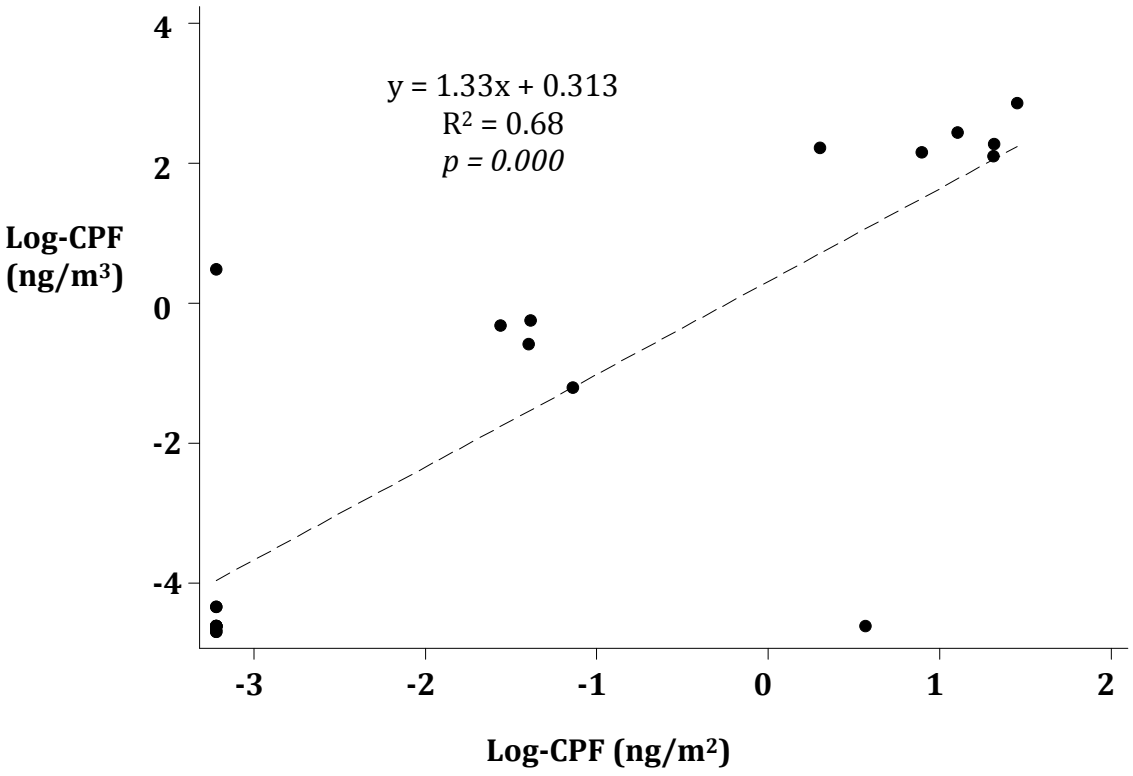
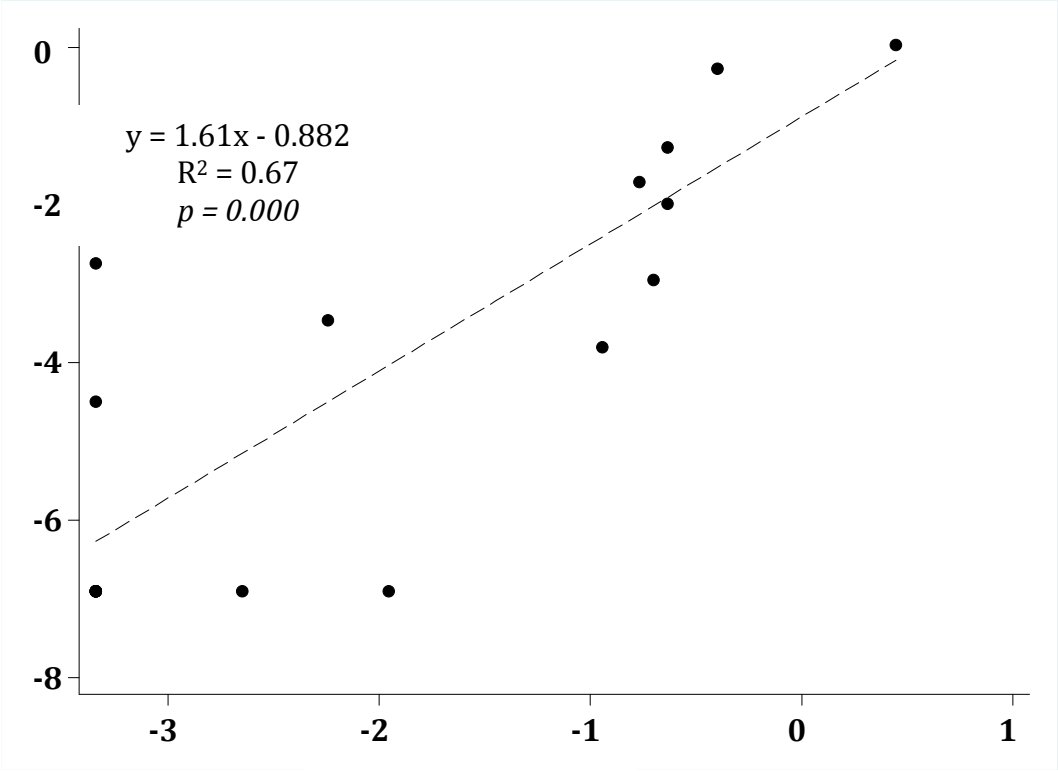


Figure 6.10B/ Average Log Monthly Indoor Air Concentrations (ng/m³) of AZM and Log Monthly Indoor Surface Deposition (ng/cm²) AZM.



6.6 Discussion

6.6.1 Outdoor Air Concentrations

This study is the first of its kind to use two passive air sampling methods, PUF-PAS devices and polypropylene (PP) deposition plates, to measure for airborne and surface exposures to OP pesticides and oxygen analogs in a residential setting. Both methods are beneficial for capturing longer term cumulative monthly exposure estimates with minimal invasiveness and good research participant acceptability.

All reported outdoor air concentrations were within the range of concentrations reported in previous studies in California and Washington states (CARB 1999; CDPR 2006, 2009; Fenske et al. 2009). Some air samples in these previous studies reported levels that were much higher than what was determined with the PUF-PAS devices-- but this was expected because the PUF-PAS yields monthly averages instead of 24 hour samples. For example, the highest average outdoor air sample for CPF in this study was 199 ng/m^3. In the Washington State Department of Health study, there were some samples >600 ng/m^3.

Outdoors, *a priori* classified as proximal (≤ 250 m) households reported significantly higher mean outdoor air concentrations of CPF, CPF-O, and AZM than non-proximal households (>250 m) and there was a noted relationship between outdoor concentrations of CPF and AZM with proximity to tree fruit fields (Figures 1, 2). This is expected, as many other studies have demonstrated associations between proximity and higher residential OP pesticide levels in air, dust, and in biomarkers of near-by residents (Loewenherz et al. 1997, Lu et al. 2000, Fenske et al. 2002). The proximity relationship was not clear for the oxygen analogs, although using linear regression with log transformed concentrations (ng/m^3) showed significantly lower CPF-O with increased log-distance (m) ($p=0.05$). The log-log transformation results are available in the Appendix, Figures S.6.1-S.6.4. These results show potential exponential decay

occurring as the distance from the nearest field (m) increases. Theoretically, the higher vapor pressures and longer half-life in air of the oxygen analogs may influence their greater dispersion into upper air and subsequent further transport; this may be interfering with the potential observable relationship between proximity and airborne levels in Figures 6.6 and 6.9. These findings are similar to the study in Chapter 3 that measured higher concentrations of CPF-O at community locations farther away 24 hours post-application than near the field perimeter during the actual application.

The measured proportions of oxygen analogs in outdoor air increased with average solar radiation (MJ/m^2), but not with temperature or relative humidity. There was a small increase in % CPF-O with higher average wind velocity (m/s), although it was not statistically significant. These effects were more observable for CPF-O than AZM-O.

There was an observable trend of higher outdoor air concentrations with increasing tree fruit acreage land-use, but this was not the case for all census block groups. For example, air monitoring sites in census block E reported higher average outdoor air concentrations of both AZM and CPF than expected, even though only 9% land-mass was used for tree fruit crops. This may reflect limitations in land use data which do not differentiate pesticide usage, and it does not distinguish organic vs. conventional tree fruit fields.

During the spring, air concentrations indoors and outdoors reached levels 5-10x higher for CPF and CPF-O than summer concentrations of AZM and AZM-O. A very small amount of CPF and CPF-O was detected in the air during the winter non-application season ($<6ng/m^3$), and small amounts of CPF,CPF-O, and AZM also were detected at the Seattle urban site ($<1ng/^3$).

6.6.2 Indoor Air Concentrations and Surface Deposition

Reported indoor air concentrations for CPF were within the range of concentrations reported in another 2004-2005 residential study conducted by Columbia University. However, the Columbia study took place in New York City (Whyatt et al. 2007) and aimed to capture levels CPF stemming from past residential use. For example, levels of detected CPF indoors ranged from 0.30-17.53 ng/m^3 in the Yakima Valley study, as compared to 0.4-177 ng/m^3 in the Columbia study. This is good news, given the fact that residential levels in an agricultural community were found to be even lower than past studies in urban communities.

Air concentration values indoors were much lower than outdoors, and farmworker/non farmworker status was more influential than proximity for indoor levels. Farmworker households reported slightly higher indoor mean air concentrations and surface depositions (ng/cm^2) of CPF than non-farmworker households. These findings are similar to other studies that have identified farming households as more being consistently more contaminated (Curwin et al, 2005, Simcox et al. 1995, Bradman et al. 1997). The trend was similar for AZM but not statistically significant.

Two households reported indoor air concentrations of CPF during the winter non-application season, yet there was no reported surface deposition. This suggests the source of detected airborne CPF may not be due to newly settled particulate. It may reflect the continued volatilization over time once it had been brought indoors on dust, clothes, or objects during previous seasons.

In contrast to outdoor samples, there was very little oxygen analogs detected inside the home. This is expected, as less photolysis takes place indoors and leads to longer degradation time. During both application seasons, there was good correlation between surface deposition measurements (ng/m^2) and air concentrations indoors, suggesting that deposition may be a good surrogate exposure measurement if air monitoring is not feasible. For future studies, a time period ≥30 days is recommended to increase changes of deposition detection indoors since the study was limited by the large amount of non-detect

samples. Indoor/outdoor air concentration ratios (I/O) were not calculated due to a large amount of indoor air samples <LOD.

Notes to Chapter 6

1. ASTM. 2011. Standard Practice for Sampling and Selection of Analytical Techniques for Pesticides and Polychlorinated Biphenyls in Air. ASTM D4861-11. 2011 Annual Book of ASTM Standards: Volume 11.07, Atmospheric Analysis. (ASTM formerly known as American Society for Testing and Materials).
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Chapter 7: Discussion and Conclusions

List of Figures:

7.1 Performance of Current Air Sampling Methods

The first aim of this dissertation was to test performance of current recommended air sampling methods. In chapters 2-3, we found that the oxygen analogs may be formed artificially during air sampling with matrices containing XAD-2, but not with PUF. PUF was identified as the superior matrix for sampling OP pesticides and oxygen analogs in a mixture. Artificial transformation is a major concern because a number of federal agencies (USEPA and NIOSH) currently recommend the use of XAD-2 resin air sampling matrices. Researchers will underestimate air concentrations by 5-35% if they continue to rely on methods that call for analysis without measurement of oxygen analogs. Overall health risk assessment may be underestimated to an even greater extent given the increased contribution to toxicity attributable to the more potent oxon.

Currently, the acute and sub-chronic screening levels for CPF in air are 1,200 and 850 ng/m^3, respectively. The acute and sub-chronic screening levels for AZM in air are 5,000 and 3,500 ng/m^3 (USEPA 2006, 2008). These values were used to describe the inhalation exposure to CPF based on the No Observable Adverse Effect Levels (NOAELs) in rat inhalation studies of CPF and AZM (CDPR, 2000). The levels are determined using the following equation (EPA Exposure Factors Handbook, 2008):

$$\textbf{Screening Level (ng/m}^3\textbf{) = (RfD x BW x AT) / (IR x ET)} \qquad \textit{(Eq. 7.1)}$$

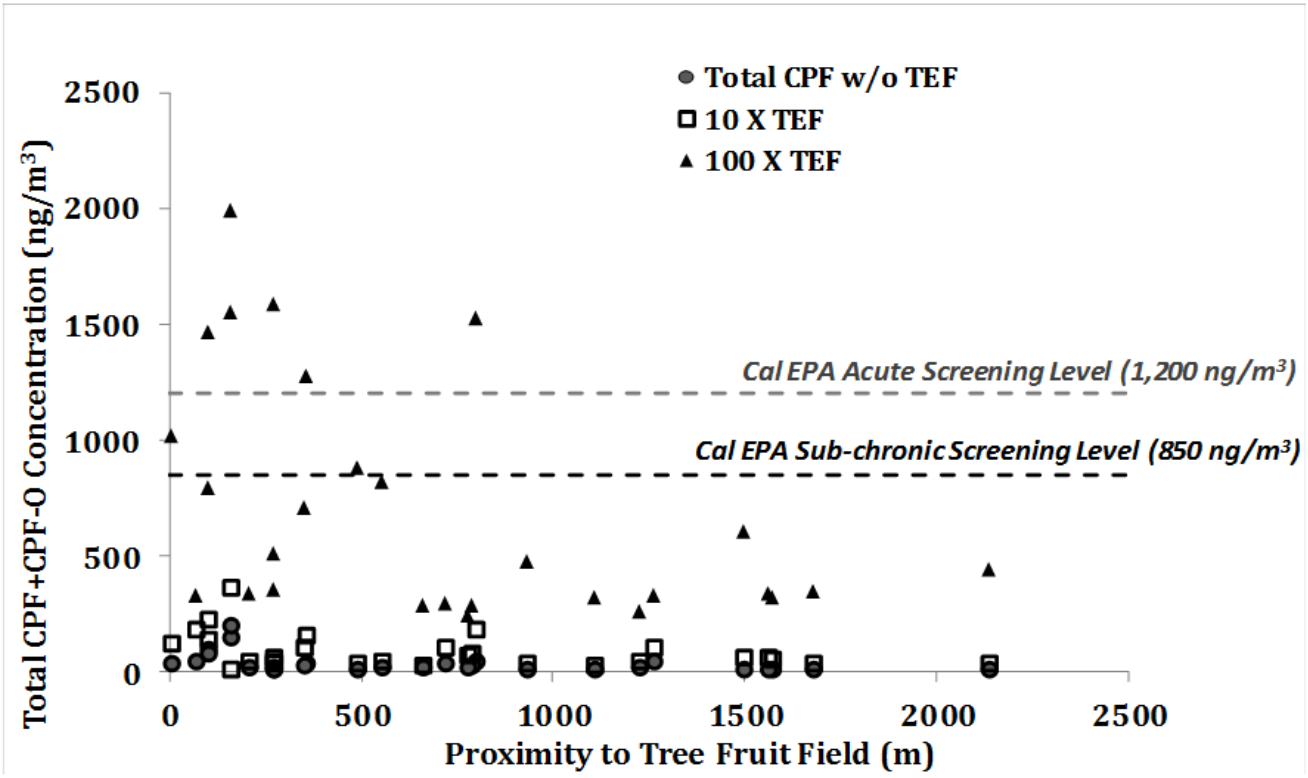
where RfD-Reference dose (ng/kg/day); BW=body weight (kg); AT=averaging time (hours or days); IR=inhalation rate (m^3/day). These screening levels may also include uncertainty factors for animal-to-human and within-human variability or database deficiencies. Acute and sub-chronic levels are adjusted for differences in averaging time of exposure. The acute screening level is for exposure levels manifested

within a relatively short time period, such as 24 hours (CDPR 2006). The sub-chronic screening level, the period of exposure is generally 30-90 days, and at least 20 days as defined by the USEPA (1998). This sub-chronic time period is optimal for incorporating the use of passive sampling devices.

These screening level values are consistent with those used by the California Air Resources Board (CARB) and are stated to be a guideline for evaluating sample detection limits are not intended for use in risk assessments. Currently, there are not clearly defined screening levels in air for these compounds. In addition, regulatory agencies currently do not provide any guidance on screening levels for oxygen analogs or they recommend the analogs are to be treated like the parent compound. This is a concern, given that the oxon is environmentally present in air and is much more potent than the parent compound.

Figure 7.1 combines the community passive air monitoring results from Chapter 6 and toxicity equivalent factors for CPF-O from Chapter 2. If CPF-O had not been measured, all reported cumulative airborne levels in the agricultural community would fall below EPA recommended exposure limits (REL). However, if we account for two toxicity equivalence factors (T.E.F.) as stated by Cole et al., there are 4 sites reporting cumulative monthly measurements exceeding the acute REL (1,200 ng/m^3) and 7 sites report measurements surpassing the sub-chronic REL (850 ng/m^3). This suggests that previous studies reporting levels just below the recommended exposure limits (REL) in air should be interpreted with caution and re-examination including the presence of the oxygen analog would be prudent. The potential for exceeding recommended toxicity thresholds is of concern if oxon was present in ranges which we have observed. These findings in Chapter 6 indicate this is particularly important for CPF and CPF-O.

Figure 7.1/ Toxicity Equivalent Total CPF/CPF-O mixtures in air, accounting for increased potency of CPF-O.



7.2 Passive Air Sampling Method Development

The second aim of the research was to develop new passive air sampling methods, which involved theoretical estimates, testing in a laboratory exposure chamber, side-by-side sampling with the traditional AAS method, and field performance. The original goal of passive sampling development was to be able to minimize inconvenience to research participants in community health studies. The largest achievement with the passive methods was that they provided minimal invasiveness and good participant acceptability in the *Para Niños Saludables* community based participatory research project. In a primarily Hispanic agricultural community, over 95% of the approached households in the project agreed to participate in the air monitoring. It was simple to describe the "flying saucer" design to participants, and 3 participant households had positive comments on the modest design. The deposition plates were also easy to deploy in the field. Since they were situated in a baking tray, the researchers could simply consult with the family on the best location to locate the tray.

The device is easy to deploy and can be explained to an untrained lay-person. For example, one participant had a rental property and was concerned about informing the landlord of the air monitoring study equipment. After viewing the outdoor PUF-PAS device, he was convinced it was not a concern. Another family changed addresses during the air monitoring study period. The PUF-PAS device was simply re-located and the disks were replaced. Unlike large volume active air samplers, the PUF-PAS disks and cylinders are small enough to be shipped from remote locations. Throughout the study, field research staff checked on PUF-PAS housing and masts following wind and rain storms, and they remained sturdy. Only two PUF-PAS devices had to be checked for water damage after a strong storm loosened the joints on the stainless steel encasements.

The passive methods are a good option for capturing longer term exposure estimates because air concentrations are integrated over a time weighted average (TWA). Although this is an improved design

for collecting exposure data on the seasonal use of OP pesticides, it is not appropriate for estimates of acute exposure. For example, if the aim is to collect data to provide local health warnings on specific days of high exposures, the PUF-PAS is not as effective as other instruments. Another limitation of the passive air monitoring study in Chapter 6 is that it only occurred for 1-2 months during three seasons. A more complete air monitoring study may include 12 monthly samples in tandem throughout the course of a year.

As expected, the passive air sampling rates for OPs are similar to other semi-volatile organic compounds (SVOCs). Outdoor sampling rates were highly variable because they were strongly affected by wind velocity. A few samples had recoveries of depurations compounds <15%. Therefore, sample periods > 30 days are not recommended outdoors. A future PUF-PAS sampling device may be modified to deal with these high wind velocities, especially when sampling in rural regions like Yakima Valley—where high wind speeds are common. One possible solution to dampen wind speeds within the PUF-PAS housing would be to place a protective PFTE circular "shield" over the 1.5 cm gap between the stainless steel chamber encasements. In this study, the gaps were left open for rapid air movement. The PFTE shield could have small, 1-2mm diameter holes (i.e. a "screen") to allow the air to flow over the PUF disks and be passively sampled, while lessening the effects of strong wind speeds. The other benefit to this design would be the additional protection against larger particles settling on the sample as a result of wind.

We expected to find differences in sampling rate with temperature because it may affect gas-particle partitioning, in turn affecting uptake on PUF (Jayward et al. 2004). This was not observed, and it may have been due to the little variation in monthly cumulative temperatures across sampling sites. For example, temperatures only ranged from 8-13 °C during the spring (pre-thinning) sample collection. If future studies are conducted, the collection of wind velocity, relative humidity, and temperature data is important.

Although the PUF-PAS devices were able to accurately detect OPs and oxygen analogs indoors as well as outdoors, many of the indoor samples were below the limits of detection. Since indoor sampling rates were

lower than outdoors and wind velocity was not a factor, future indoor studies could involve longer indoor deployment times of ≥2 months. Another limitation was that indoor concentrations are approximate because depuration compounds could not be used inside the homes without an increased risk of exposure to research participants. Therefore, all sample rates indoors were determined using average sampling rates ($R_{PUF\text{-}PAS}$) from the laboratory chamber studies. The exposure chamber may not be a truly representative of the indoor home environment.

Passive sampling results were enhanced with the use of LC-MS/MS chemical analysis (Chapter 4). All compounds were identified based on retention time and ratio of analyte to internal standard, allowing for the use of large extraction volumes from the PUF disks and low limits of detection, ranging from 0.5-5 ng/sample. Since PUF-PAS devices are deployed for long periods of time, they have large air sampling volumes (e.g. 60-120 m^3) and subsequent lower levels of quantifications (0.02-0.1 ng/m^3). This sensitive analysis from a passive device was a major achievement. However, it does not rule out a potential matrix effect on the larger PUF matrix stemming from other related air contaminants. During this study, additional procedures were taken during extraction to filter out visible particles. Some difficulties arose when small amounts (0.1-0.25 mL) of oil was identified in the extract solution. During the application seasons, horticultural oils (usually a petroleum or vegetable oil) are diluted with water may help to combat pests. The timing and amount of horticultural oil use is not well known.

7.3 Measurement of Exposure to Airborne Pesticide and Oxygen Analogs

7.3.1 Outdoors

The final aim of the research was to use new methods to estimate airborne exposure pathway of OP pesticides for the children's health study in a subset of residential locations from the *Para Niños Saludables* community based participatory research project. Outdoors, households closer in proximity tree fruit fields may be at risk for higher airborne exposures to CPF and AZM. There was an observable trend of higher outdoor air concentrations at sites located in areas of higher tree fruit acreage land-use, but this was not the case for all census block groups. There are a growing number of tree fruit farmers relying on integrated pest management (IPM) practices instead of conventional pesticide applications, and not all conventional farms rely on CPF and AZM specifically. If the tree fruit acreage measurement is used for future exposure assessments, more data on applied/non-applied orchards and pesticide use patterns should be obtained.

The cumulative monthly air concentrations of CPF during pre-thinning season were 5-10x higher than AZM during thinning season. There have been a number of restrictions placed on the annual amounts and on re-entry intervals for AZM and such actions have contributed to reduced usage. From 1989 to 2000, the % usage AZM on tree fruit orchards dropped by more than 40% for AZM and increased slightly (12%) for CPF (Beers and Brunner 1991, Brunner et al. 2011). In 2006, the U.S. Environmental Protection Agency (EPA) declared that AZM cannot be used in apple production after September 2012 (EPA 2009). This was recently extended to September 2013 due to difficult meteorological conditions. It is possible that these changes in OP pesticide usage are being reflected in measured air concentrations.

In contrast to the parent compounds, the proximity and farmworker relationships for CPF-O and AZM-O are not clear. Although both CPF and CPF-O were present at substantial concentrations in community air, there was little to no AZM-O. In chapters 3 and 6, we detected some larger proportions of

CPF-O further from fields and found that higher levels were reported during periods of high solar radiation (mJ/m^2). There was a trend between increased proportions of CPF-O during periods of high wind turbulence, but it was not statistically significant. No relationships were observed for temperature or relative humidity. This study was limited due to low variability in meteorological factors; all samples were taken within the same month. Sampling over the course of many seasons will generate data with increased variability in temperatures (e.g. up to 30 °C) may yield different results when examining the relationship between temperature and transformation of CPF to CPF-O.

Over time, increased distance of transport of CPF and continued volatilization allows for atmospheric interactions with oxidizing compounds, photolysis, and wind erosion long after application (MacCollom et al. 1986). For example, concentrations of CPF-O ≥20ng/m^3 were identified as far as 1.5 kilometers away from the nearest tree fruit field. This data support Van den Burg's theory that oxygen analogs may have higher vapor pressures and longer half-life in air than their parent compounds (1999). As researchers learn more about the formation of CPF-O, they may be able to use the ratio of masses (ng) CPF-O and CPF [CPF-O/CPF] to determine the "aging" process of the parent compound if pesticide application data (e.g. time, amount, location) is unavailable. For example, the half-life of CPF in is 2-4 hours and 1-9 days in air and on foliage respectively outdoors; and we may hypothesize that outdoor air samples with high proportions of CPF-O were applied some time ago (e.g. ≥ 9 days) as compared to air samples with low proportions of CPF-O, which may have been applied recently (e.g. ≤9 days). It will become difficult to estimate the time of application from indoor air samples, as the residence times of CPF indoors in dust and carpeting may be up to 7 years (Shin et al. 2012).

There is greater concern for outdoor CPF-O than AZM-O. Even though passive sampling corrected for artificial transformation, more than 95% of outdoor samples were positive for CPF-O (ranging 4-35% of the total OP mixture) and only 31% of samples were >LOD for AZM-O (ranging 2-14% of total mixture).

These results are expected if the oxygen analogs behave similarly to parent compounds; CPF has a slightly higher vapor pressure (10^{-5} mmHg at 20 °C) and Henry's Constant (10^{-5} atm m^3/mole) than AZM (10^{-5} mmHg and 10^{-8} atm m^3/mole, respectively) (Lyman et al. 1990, Racke 1993, Rice et al. 1997). Compounds with higher H constant values will have longer atmospheric residence times with they are less removed by water or particle deposition, and lower H values will be more effectively washed out by rain or humidity (Sanusi et al 1999).

7.3.2 Indoors

Indoor airborne levels were reduced when compared to outdoors, and many indoor samples were <LOD. In the future, indoor samples may have longer collection time periods (e.g. 2-3 months) to increase the detection. Since wind speed is not a major concern inside the home, it is estimated that the time to equilibrium indoors will be longer than on outdoor samples. There was little to no detected CPF-O of AZM-O inside the home in air or deposition samples. This was expected, as chemical transformation or degradation by photolysis has little effect on removal when sunlight is not present. Past studies have demonstrated the remaining presence of organophosphate pesticides like chlorpyrifos indoor for years following the ban for household use in 2000 (Quiros-Alcala et al. 2011).

Results from Chapters 3 and 6 demonstrate that higher levels of CPF-O may be present in air vapors than in deposited particulate. In addition to proximity, the status of farmworker/non-farmworker may also be important factor influencing indoor air concentrations. There are a number of potential differences among farmworker vs. non-farmworker homes. For example, a survey conducted in Oregon State found that the majority (94%) of farmworking families do not have air-conditioning in their homes (McCauley et al. 2001). In fact, 98% of these families indicated that they left their doors and windows open for ventilation during the summer. The farmworking households also had higher residential density (average 6 persons/home) than the national average and the majority of the farmworker homes in the survey had

carpeting. Although these factors were not examined for this dissertation, future research will involve collaboration with the *Para Niños Saludables* project to examine other potential household characteristics (e.g. air conditioning, vacuuming, household density, cleaning frequency) in the Yakima Valley cohort that may be linked to elevated airborne pesticide exposures. Linear regression showed that indoor levels of settled particulate/dust collected with surface deposition (ng/cm^2) were related to indoor levels of airborne CPF and AZM. However, this relationship may have been improved with greater numbers of samples (n) >LOD achieved with longer sampling periods.

7.4 Conclusions

This work has highlighted some of the complexities of currently recommended active air sampling guidelines for OP pesticides and oxygen analogs. It has demonstrated that passive sampling methods (including PUF-PAS and deposition) combined with sensitive analysis (LC/MS-MS) may be used to improve our understanding of the continued fate and transport of these OP pesticides in residential communities. Further methods testing that meet the requirements of the American Society for Testing and Materials (ASTM) may lead to international methods for the sampling of these compounds. The methods are ideal for community based participatory research due to low subject burden and simple deployment. The EPA should examine these passive methods as it continues to develop standard methodologies and guidance to evaluate exposures from spray-drift and from residues brought into households. The PUF-PAS has been previously used in regional and global surveys (Bohlin et al. 2008), and is ideal for sampling in remote areas where active sampling is not ideal.

In the future, the determination of OP and oxygen analogs in the airborne environment will be critical given that the effects of climate change are being demonstrated in some agricultural areas. Some regions are expected to have increased ultraviolet radiation, temperatures, concentrations of oxidizing compounds

in the atmosphere (e.g. ozone), and changing pest lifecycles that could result additional pesticide application (Boxall et al. 2008).

In the United States, the regulatory definition of pesticide spray drift limits pesticide movement to occur during a time period during and soon after spraying (US OPP/EPA, 2010). However, this dissertation has demonstrated there is continued movement into residential environments and volatilization long after application. This was the first major study to demonstrate larger proportions of oxygen analogs in air during periods of increased solar radiation (MJ/m^2). Although proximity to fields is a major consideration concerning total outdoor air concentrations, the more potent CPF-O and AZM-O may be a concern at locations up to 1500 km away, particularly on sunny days with high wind turbulence. If the intent of FIFRA is to consider the cumulative and aggregate effects of exposure to OP pesticides in order to protect the unique health needs of infants and children, inclusion of the oxygen analogs in airborne assessments is necessary.

Notes to Chapter 7

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List of Figures:

8.1 PUF and XAD-2 Resin Active Air Sampling

Most standard operating procedures for this experiment were developed by M. Tsai (2007) and Fenske et al. (2009) adopted from NIOSH method 5600 and EPA Method TO-10A.

8.1.1. Field Procedures

GENERAL REQUIREMENTS:

To evaluate exposures via airborne pesticides during applications, it is necessary to collect air samples before, during, and after application. Data sheets should include: date/time, sampling duration, volumetric flow rate [in Liters per Minute (LPM)], and description of work conditions, temperature, pressure, ozone, and any other pertinent information.

PRE-CALIBRATION OF ROTAMETERS:

- Calibrate personal sampling pumps, rotameters before entering the field using a DryCal DC-Lite.

BEFORE SAMPLING:

- Cut Tygon tubing to appropriate length for sampling. Total length should be over 1 meter long.

- Attach reducing connectors (Cole Parmer RY4-6HDPE, Highdensity polyethelyene ¼“ ID, 3/8” ID) to one end of large Tygon tubing (VWR 63010-133, 3/8 inx 9/16 in) and two ends smaller Tygon tubing (VWR 63010-64, ¼ in x 3/8 in).
- Cover both types of sampling tubes with aluminum foil to hinder reactivity with sunlight.

AIR PUMP AND SAMPLE SET UP

- Place all SKC air pumps inside protective Rubbermaid or other weather-safe storage container to prevent dust and precipitation from depositing on the air pumps. Hook up to electrical outlets or generator.
- Connect the end of large Tygon tubing with reducing connectors and small tubing attached to the inlet of the pump.
- Connect Rotameters to smaller end of Tygon tubing and attach to rebar of sampling mast using plastic cable ties (see Figure 8.1).
- Attach tubes and Tygon tubing to Rotameters and hang from top of mast. Use duct tape to stabilize. See Figure 8.2.
- Remove both sets of sampling tubes from containers and fasten to Tygon tubing. Check sampling ID number label on the glass tube and record on the data sheet.

Figure 8.1/ Connected rotameters to sample mast.

Figure 8.2/ Hanging OVS/PUF Tubes.

- Remove PUF or XAD-2 Resin sampler from jar or caps, and connect to outlet of small Tygon tubing. Do not do this until air sampling is about to start. The sampler should be placed vertically with the large end down.
- Place XAD-2 caps in snack size Ziploc bag.
- Turn on Pump and record the start time and flow rate on data collection sheet.

DURING SAMPLING:

- Conduct 1-2 flow rate checks. Make note of any flow rate changes.

AFTER SAMPLING:

- After collection time (e.g. 8 hours for occupational and 24 hours for community exposures) is over, turn off the pump and record on the data collection sheet the stop time, flow rate, and other comments on datasheet.
- Wearing a new pair of disposable nitrile gloves for each sample, remove the sampling tube from the end of the Tygon Tubing.
- Replace caps on XAD-2 tubes or cover PUF tubes with aluminum foil.

- Place all tubes in invididual Ziploc bags. Immediately place the PUF tubes in the glass jar. Immediately place all samples into cold storage (e.g. freezer with dry ice).
- Remove and dispose the tubing connected to the air pumps and rotameters.
- After sampling is complete, break down masts and remove air pumps from Rubbermaid containers.

POST-CALIBRATION:

- After sampling, post calibrate all of the air pumps and rotameters with a DryCal DC-Lite.
- Calculate and record flow rate and time on calibration data sheet. The average of pre and post-calibrations will be used to calculate total air sampling volume.

8.1.2. Field Packing List

Storage

Cooler (with ice)

1 box small snack bags (enough for PUF and XAD2 tubes post sampling)

Quart size Ziploc bags

Calibration Materials

Dry Cal DC-Lite Defender 520 and Plug In

8 SKC hi-lite air sampler and 9 electric cords

Two boxes small tygon tubing, 63010-64, ¼ in x 3/8 in, 50 feet

One box large tygon tubing, 63010-133, 3/8 inx 9/16 in, 50 feet

Cole-Parmer Reducing Connectors (RY4-6HDPE, Highdensity polyethelyene ¼ " ID, 3/8" ID)

On-site Preparation Materials

Four Mast Poles, stands

Four Rubbermaid Storage Containers

Four Concrete Blocks

Extension cords and electric cord splitters

8 1-foot high stands

Dry Ice (for storage)

MSDS for chemicals, storage

Sampling

13 PUF sampling tubes (labeled) in glass containers Lot No 6238 ST PUF PLUG, 226-92

13 XAD sampling tubes (labeled) in baggies Lot no. 4501, 226-58

18 Calibrated Rotameters

Extra rotameter fittings, Cole Parmer Pipe Adapter 1/8 in NPT x ¼ in ID

17 Pre-cleaned Deposition PUF disks, Tisch Environmental TE-1014, ½ in x 5.5 in polyurethane collection substrates in glass Petri dishes

Tape (for Petri dishes)

Plastic wrap (for Petri Dishes

Rubber bands

Scissors

3 Extra glass Petri dishes (empty)

2 Rolls Duct Tape

20 field data sheets and clip board

Standard Operating Procedures and Sampling Information Binder

Pens

Sharpies

Screwdrivers

Plastic ties (to hold up rotameters)

Extension cords and electric cord splitters

2 generators

Double stick velcro

2 boxes nitrile gloves

Large binder clips

Aluminum Foil

Trip Spikes

50 uL Syringe

12 VWR underpads

2 vials known concen. CPF (kept cold) for Trip Spikes *(one at ~350 ng, one at 20 ug)*

8.1.3. Extraction and Chemical Analysis

All extractions and chemical analysis were performed according to NIOSH Method 5600 for XAD-2 Resins and EPA Method TO-10A for PUF tubes. These methods are available in published literature.

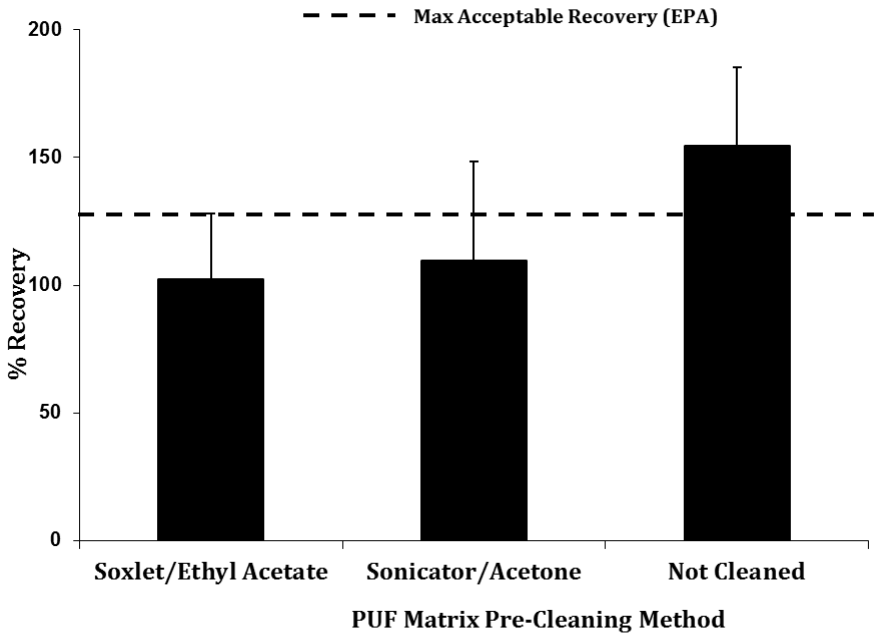
8.2 Outdoor Passive Air Sampling With PUF-PAS Devices

8.2.1. Pre-cleaning Procedures (Two Options)

Prior to sampling, it is important that that the encasements and PUF disks are properly cleaned. There are a number of ways to clean the PUF disks, and the usual cleaning method is Soxhlet, with the same solvents used for extraction (e.g. acetone or ethylene acetate). Other cleaning solvents include petroleum ether. The PUF disks may then be dried in a 60°C oven or in a vacuum desiccator at about 40◦C and stored in clean aluminum foil and ziplock bags. If stored in aluminum foil, the disks should be then placed in air tight ziplock bags.

Extraction is a fundamental part of this process to remove pesticides from the sampling material. If the filters pick up a large amount of other compounds or are not properly cleaned before analysis, it will become difficult to identify the compound of interest. To examine the best pre-cleaning method, the cleaned PUFs were be spiked with a low level (20 ng) of CPF and AZ to observe potential widening of the peak in the LC/MS-MS stemming from a matrix effect. The data on this test is available in Figure 8.3.

Figure 8.3 Experimental % Recoveries from pre-cleaned and non-pre-cleaned PUF matrices at spike masses of 25ng. Un cleaned PUF-Disks require cleaning in Soxlet or Sonicator to achieve EPA defined acceptable % recoveries.

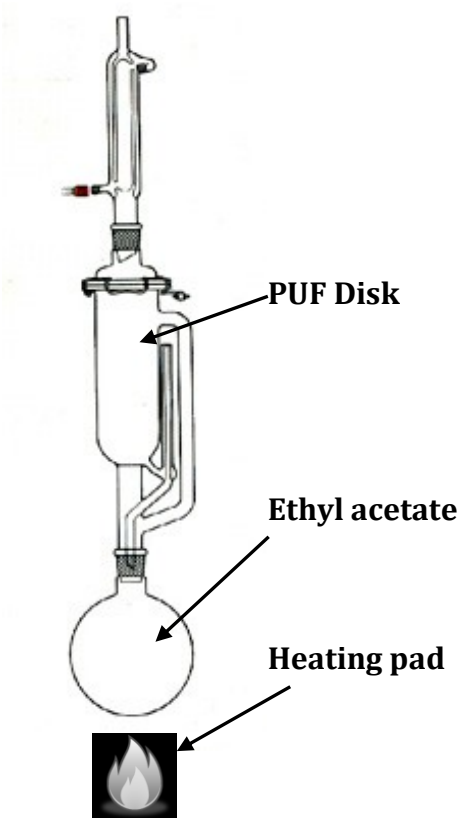


Option 1: Sonicator Extraction (For recoveries, see Figure 7.3)

1. Put on gloves, lab coat, and protective glasses.
2. Lay PUF disks in glass tray, turn on water (slow speed), rinse with hot water for 2 minutes.
3. Lay PUF disks in glass tray, rinse with 50-100 ml of acetone, or until disks have been coated.
4. Place PUF disks in sonicator, using tweezers.
5. Sonicate at 60° C for ~45 minutes.
6. Remove PUF disks and lay to dry in a clean fume hood for at least 10 hours.
7. Rinse and clean glass trays before next use.
8. After ≥10 hours, remove PUF disks with tweezers, wrap in clean aluminum foil and place in a ziplock bag.
9. Send for chemical analysis or deploy for field use.

Option 2: Soxhlet Extractions (For recoveries, see Figure 8.3)

Figure 8.4 Soxhlet Extractor, Cole Parmer®, www.coleparmer.com



Setup Soxhlet Extractor using appropriate glassware, tygon tubing, ring stand and Powerstat temperature control in a fume hood.

Put on gloves, lab coat, protective glasses.

Pour 300 ml of ethyl acetate in a 1 L boiling flash condenser with 3-4 PTFE boiling chips.

Leave on current setting marked with black pen on Powerstat temperature control. The boiling point of ethyl acetate is 77 C (141 F), and this is equivalent to the voltage of 50.

Place 1 large PUF disk (or 4 small quarters) using tweezers in the extractor per batch. These should be submerged in solvent when extractor is full.

Turn water on (slow speed)

Flip the extractor switch to turn it on

Allow extraction cycles to run for 6-8 hours per sample batch. Each cycle should take approximately 30 minutes (12-16 cycles total).

At end of the last cycle, turn off the extractor and water

Allow the PUF disks to cool, and then remove them from Soxhlet extractor and allow them to air dry in the fume hood on a pan lined with clean aluminum foil (for ~ 24 hours)

Wrap in clean aluminum foil that has been rinsed with acetone.

Place in zip lock bag and store in a cool, dry location for future use.

To turn off the soxhlet, turn off the heat (voltage) and allow stopping boiling. Wait for vapors to condense.

In ~10 minutes, turn off water flow after everything has cooled. Shut down.

8.2.2. Field Procedures

Most standard operating procedures for this experiment were developed new and specifically for this project, but I relied strongly on guidelines introduced by Harner et a.l (2002, 2006) at Environmental Health Canada and Bohlin (2007) at the University of Gotenburg, Sweden.

GENERAL REQUIREMENTS:

Data sheets should include: date/time, sampling duration, estimated passive sampling rate, and description of work conditions, including temperature, pressure, and any other relevant information.

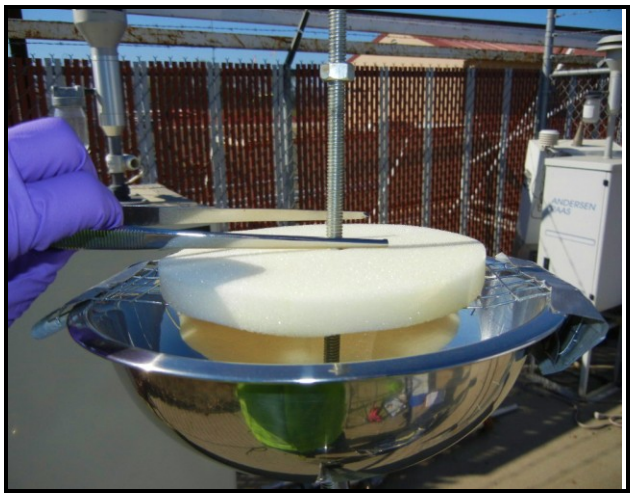
PRE-CLEAN OF SAMPLER ENCASEMENT AND PUF DISK:

1. After pre-cleaning, wrap in aluminum foil and place in labeled ziplock bags.
2. Clean PUF-PUS sampling device with acetone and gauze, allow drying before field deployment.
3. Pre-clean 50 uL Syringe with acetone.

BEFORE SAMPLING:

4. In the field, check the passive sampling device and clean again with acetone if needed.
5. Attach with Velcro and turn on mini-Hobo Pendant Data loggers on the inside of 2 sampling devices (TBD).
6. Put on nitrile gloves. Remove PUF disk from aluminum foil wrap, place on top of stainless steel grated mesh holder (see Figure 8.5).
7. Screw and tighten the sampling device onto the sampling mast, using a wrench. More than one passive sampling device can go on one mast (see Figure 8.5 for an example of a duplicate sample).

Figure 8.5. Placing PUF Disk inside PUF-PAS housing.




8. Seal top screw of sampling device with water proof tape.
9. Using hammer, nail in sampling mast ~15-25 cm into the ground.
10. Place concrete block near one side of the mast to stabilize.

START SAMPLING:

5. Check mast stability and record the start time and estimated passive sampling rate on data collection sheet (See Figure 8.6).

Figure 8.6. Checking Mast stability.


6. Remove one PUF disk, leaving it wrapped and in plastic ziplock bag, and place in a small, shoe box size Rubbermaid storage container. Place weight on top of container. This is the field blank.

TRIP SPIKES:

3. Lay down a VWR underpad on a stable surface (e.g. outdoor table or SUV trunk).
4. Put on nitrile gloves.
5. Remove two clean PUF disks. Place them on the underpad on top of an aluminum foil sheet.
6. Clean the inside of a 50 uL Syringe with acetone.
7. Spike one PUF with a large concentration (TBD) and small concentration (TBD).
8. Use tweezers and minimal glove contact to remove the PUF disk from the sampler. Place in large VWR glass Petri dish, wrap in aluminum foil.
9. Immediately place all dishes in a quart size plastic bag and put all samples into cold storage (e.g. freezer with dry ice).

DURING SAMPLING:

10. Return onsite to conduct 1-2 checks on sampling mast stability and make sure the device is clear of debris and has not been tampered with. High wind speeds may loosen the housing encasement and the housing may need to be tightened. The outdoor PUF-PAS will be deployed for time periods ranging from 5 days to 1 month.

AFTER SAMPLING:

11. After collection time is over, record on the data collection sheet the stop time and other comments (e.g. debris in the sampler, mast was twisted).
12. Loosen nuts with the wrench and remove washers and the top half of the sampler.
13. Turn off and remove mini-Hobo Pendant Data logger.
14. Wearing a new pair of disposable nitrile gloves for each sample, use tweezers and minimal glove contact to remove the PUF dik from the sampler (See Figure 8.7). Place in large VWR glass Petri dish, wrap in aluminum foil (See Figure 8.8).

Figure 8.7. Removing PUF disk from the sampling device.

Figure 8.8. Placing PUF disk in the glass petri dish. The disk on the left is a field blank and the disk on the right was deployed.

15. Clean tweezers with acetone and chemwipes between each PUF disk removal, and put on new nitrile gloves.

16. Immediately place all glass Petri dishes in a quart size plastic bag and put all samples into cold storage (e.g. freezer with dry ice).

17. Remove the masts, or clean the sampling devices with gauze and acetone if replacing with a new PUF sampling disk. Wait a few minutes for the acetone to dry before deploying a new PUF disk.

18. After sampling is complete, break down masts.

POST-CALIBRATION:

19. Send all samples to be analyzed at the UW Environmental Health Laboratory.

20. Wipe down the stainless steel PUF-PAS housing with rubbing alcohol and hot water before and after each use.

8.2.2. Field Packing List

Storage

Cooler (with ice)

1 box large Ziplock bags (enough for PUF disks post sampling)

Quart size Ziploc bags

One Rubbermaid Storage Containers (to store all supplies)

On-site Preparation Materials

2 Mast Poles, stands (for outside) (≥ 1 m)

4 PUF-PAS sampling devices

2 Concrete Blocks (to hold masts in place)

One small, shoe box size Rubbermaid storage container (for field blanks)

Hammer

1 squirt bottle of Acetone, gauze pads (for additional cleaning of the sampler)

Dry Ice (for storage)

MSDS for chemicals, storage

Sampling

10 PUF sampling disks (labeled) in glass containers or ziplock bags, Lot No 6238 ST PUF PLUG, 226-92 (4 sampling, 2 trip spikes, 1 field blank, 2 extra)

7 cleaned VWR Glass Petri Dishes

2 mini-Hobo Pendant Data loggers (weather sampling devices)

2 rolls water proof tape

20 field data sheets and clip board

Pens

Sharpies

Screwdriver, wrench (to tighten passive sampling device)

2 boxes nitrile gloves

Aluminum Foil

Tweezers

Trip Spikes

2 50 uL Syringes

12 VWR underpads

1 vial known concen. CPF (kept cold) for Trip Spikes *(one at ~50 ng)*

1 vial known concen. DCs

8.2.4. Extraction and Chemical Analysis

See Section 8.4.3.

8.3 Indoor Passive Deposition Sampling With PP and Glass Deposition Plates

8.3.1 Field Procedures

PRE-CLEAN OF SAMPLER TRAY AND DESPOSITION PLATES:

1. Wash all baking pans with phosphate free detergent and dry in a dishwasher or air-dry in a laboratory hood.
2. Wash all petri dishes with phosphate free detergent. (This step can be skipped for petri dishes for microscope slides but the two types can't be mixed up)
3. Rinse three times petri dishes with acetone and dry in hood.
4. Solvent washing microscope slides followed by acetone rinse, wipe with chemwipes, and dry in laboratory hood. This step is unnecessary if the slides are pre-ordered and have been cleaned and sanitized.

BEFORE SAMPLING:

5. Place a clean lab pad down on the work surface and wear clean nitrile gloves without and flocking or powder.
6. Put two overlapping strips of household double stick tape on the bot bottom of the petri dish near the side.
7. For the glass slide deposition plate, hold the slide on the ground glass portion with the ground glass portion right-side up. Put the non-ground glass end on the tape, leaving the middle half untouched. Seal petri dishes with ½ width parafilm wrapped twice around the outside (side) and store in clean boxes or bags.
8. For the polypropelyene filter paper, use clean forceps to place filter paper inside of petri dish. Seal petri dishes with ½ width parafilm wrapped twice around the outside (side) and store in clean boxes or bags.

9. Store all in individual clean & sealed plastic bags.

START SAMPLING:

10. Find a location in the home, that is in a living area, about 1-1.5m from the floor and out of reach or not in directly in children's play areas. These can be on top of bookshelves, media centers, refrigerators. These should not be surfaces that are commonly used in the home such as tables.
11. Handle petri dishes with clean nitrile gloves. Put a label on the bottom of the petri dish.
12. Remove Petri dish cover and parafilm. Place petri dish back in the labeled bag and store until sample collection.
13. Record start time, date, and location.

DURING SAMPLING:

None.

AFTER SAMPLING:

14. Wear clean nitrile gloves. Place petri dish cover back on appropriately labeled dish.
15. Seal dish with parafilm.
16. Record collection time and date.

TRANSPORT AND STORAGE:

17. During transport, do not tip or dislodge petri dishes from baking pan.
18. Up arrival at storage location, remove petri dishes with glass slides from baking pan and store upright in a clean, dry location at 20-25 °C. Do not place in the freezer.
19. Remove PP filter petri dishes from baking pan and store in a cold storage (on dry ice, cooler).

8.3.2 Field Packing List

Storage

Cooler (with ice)

Box (for glass deposition plates)

1 box medium Ziplock bags (enough for all small petri dishes post sampling)

One Rubbermaid Storage Containers (to store all supplies)

On site Preparation Materials

8x8 in baking pans

Aluminum foil

Deposition petri plates

1 squirt bottle of Acetone, gauze pads

Dry Ice (for storage)

Extra PP filters and glass slides

Sampling

Extra small VWR Glass Petri Dishes

2 rolls double sided tape

20 field data sheets and clip board

Pens

Sharpies

2 boxes nitrile gloves

Aluminum Foil

Tweezers

Parafilm

Extra labels

8.3.4. Extraction and Chemical Analysis

See Section 7.4.3.

8.4 Indoor Passive Air Sampling With PUF-PAS Devices

8.4.1 Field Procedures

PRE-CLEAN OF SAMPLER and PUF:

1. The PUF-cylinder is cleaned as in section 7.2.1.
2. After pre-cleaning, attach cylinder to an eyelet hook with thin steel wiring.
3. Clean small aluminum square (covering) with acetone and gauze, allow drying before field deployment.
4. Label aluminum cover with ID.
5. Wrap entire PUF-PAS device in aluminum foil and place in labeled ziplock bags.

BEFORE SAMPLING:

6. In the field, check the passive sampling device and clean again with acetone if needed.
7. Begin to consult with participants about optimal sample location.

START SAMPLING:

8. Place near deposition plates (see step 10 for deposition plates).
9. Handle PUF-PAS cylinder with clean nitrile gloves. Hang from a free standing hook with the eyelet hook.
10. Record start time, date, and location.

DURING SAMPLING:

None.

AFTER SAMPLING:

19. After collection time is over, record on the data collection sheet the stop time and other comments.
20. Wearing a new pair of disposable nitrile gloves for each sample, remove the PUF cylinder from the sampler. Wrap in aluminum foil and place in a labeled ziplock bag.
21. Immediately place all bags dishes into cold storage (e.g. freezer with dry ice).

8.4.2 Field Packing List

Storage

Cooler (with dry ice)

1 box large Ziplock bags

One Rubbermaid Storage Containers (to store all supplies)

On-site Preparation Materials

Free-standing ornament hangers(8-9 in height)

Steel Wire (0.25 in)

Extra aluminum coverings (4x4in)

One small, shoe box size Rubbermaid storage container (for field blanks)

1 squirt bottle of Acetone, gauze pads (for additional cleaning of the sampler)

Sampling

PUF sampling cylinders (labeled) in ziplock bag. (1 sampling (2 if duplicate), 1 field blank, 2 extra)

Free-standing ornament hangers(8-9 in height)

2 rolls water proof tape

20 field data sheets and clip board

Pens

Sharpies

2 boxes nitrile gloves

Aluminum Foil

Tweezers

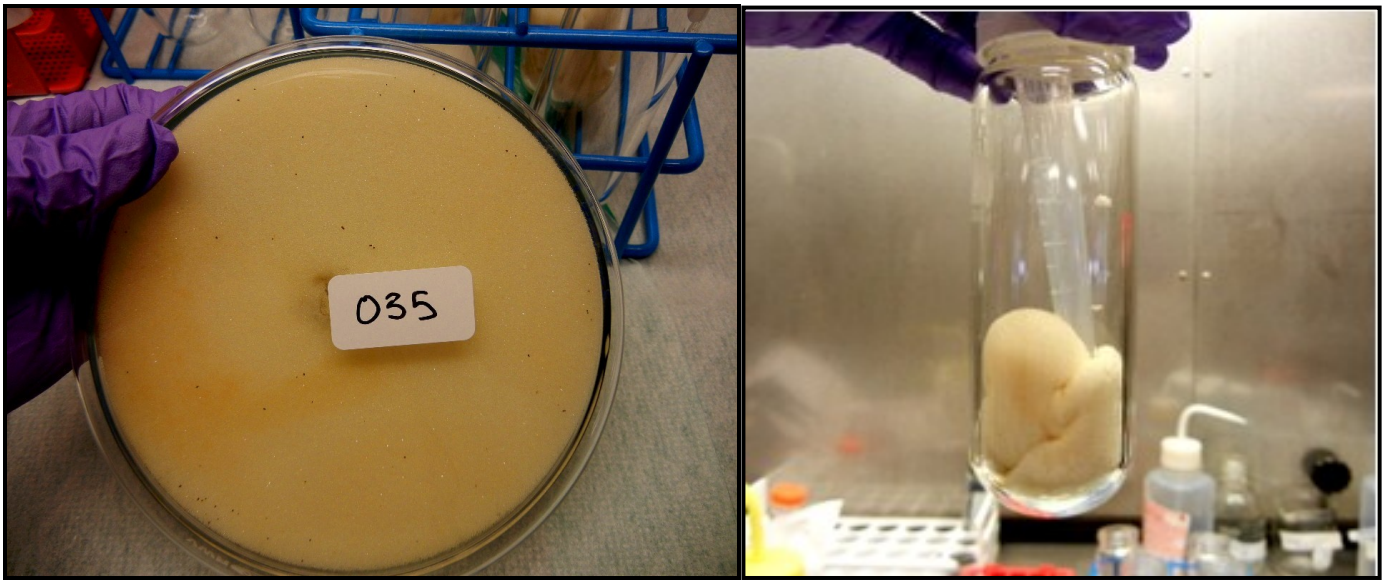
8.4.3 Extraction and Chemical Analysis

Preparation:

1. Use nitrile gloves for all procedures. First, clean scissors and tweezers with acetone.

2. Use tweezers to remove PUF foam disk from glass petri dish, and place in 100 ml Pyrex ® glass jar. (or, If PUF cylinder, remove with twezers and place in a 50ml Corning® Tube.) Condense to the bottom of the jar with tweezers (See Figure 8.9). This is a challenging step, as the tweezers will need to be rinsed afterwards.

Figure 8.9 Receiving the PUF-disk and condensing to the bottom of a Pyrex® jar.



3. Rinse PUF glass disk collector and tweezers with 20 ml acetone solution. If PUF cylinder, only rinse tweezers.

4. Use pasture pipettes to extract acetone from glass dish and pour over PUF in 100 mL glass jar.

Extraction for CPF, CPF-O, CPF-MD$_6$ (Depuration Compound):

5. Use 100 ml pipette to pour 80 ml acetone into glass jar (total of 100 ml). The PUF disk should be pressed to the bottom of the vial so that acetone solution covers the top portion. For PUF cylinder, pour only 30 ml acetone into tube (total of 50 ml).

6. For all analysis, two laboratory blanks with acetone solution only (no PUF) should also be included, and laboratory blanks with high, low spikes of CPF should be included.

7. Add 1 ml acetonitrile with internal standard for CPF and CPF-O to all samples.

8. Add 25 ul of CPF-Methyl solution (1.603 ug/mL) to all samples. Leave 2 samples *without* addition of CPF methyl, in order to test if CPF methyl is present in the field.

106.3ug/ml Add 100 ml Acetonitrile (1.603 ug/ml) to make Large Spike Solution

 Spike with25 ul = 26.575 ng

9. Let stand for 10 minutes.

10. Place in sonicator bath for 1.5 hours at room temperature. Remove and let stand for another 10 minutes.

11. Remove all solution liquid by using 25 ml pipette. Place in labeled 200 mL TurboVap glass containers. Seal tops with Parafilm®.

12. Place in ≤-20°C freezer and allow to sit for 8-24 hours. This is to let particulate settle overnight and is critical for outdoor PUF disks. In addition, cooking oil or agricultural oils can settle on the matrix. Freezing the sample will separate the oil from solution.

Extraction for AZ, AZ-O, AZ-ethyl-D_{10} (Depuration Compound)

13. Use 100 ml pipette to pour 80 ml acetone into glass jar (total of 100 ml). The PUF disk should be pressed to the bottom of the vial so that acetone solution covers the top portion. For PUF cylinder, pour only 30 ml acetone into tube (total of 50 ml).

14. For all analysis, two laboratory blanks with acetone solution only (no PUF) should also be included, and laboratory blanks with high, low spikes of AZ should be included.

15. Add 1 ml acetonitrile with internal standard of AZ (AZ-MD_6, 100 ng/µl, 1.1 ml, EQ Laboratories Inc.) and AZ-O (AZ-OD_6 Bayer K-176, 99.3%, solid in vial) to all samples.

16. Add 25 ul of azinphos ethyl P-201N (10 mg solution, Accustandard) to all samples.

17. Let stand for 10 minutes.

18. Place in sonicator bath for 1.5 hours at room temperature. Remove and let stand for another 10 minutes.

19. Remove all 100 ml liquid by using 25 ml pipette and squeezing PUF. Place in labeled 200 mL TurboVap glass containers. Seal tops with Parafilm®.

20. Place in ≤-20°C freezer and allow to sit for 8-24 hours.

Evaporation and Clean-Up

21. Remove all samples from freezer.

22. If oil droplets are floating on the surface, remove oil with pasteur pipette and discard into polar organic waste. This is expected if oil mists were used in the field.

23. Place in TurboVap for 25 minutes @ 40◦C, or until solution is evaporated down to 1 ml.

24. If particulate is present: quantitatively transfer extract to a leur-lock 3 mL all polypropylene syringe fitted with a PTFE syringe filter (13 mm, 0.2 µm porosity). Filter into labeled LC-MS vial.

25. If particulate is not present: quantitatively transfer extract to labeled LC-MS vial.

26. Load in vial tray (Figure 8.10), begin analysis or place in freezer.

27. Full LC/MS-MS analysis is described in Chapter 3.

Figure 8.10 Loading LC-MS extraction vials for analysis.

Appendix

List of Tables:

List of Figures:

Supplementary Material, Chapter 1

Table S.1.1/ Vapor Pressures in 10^x (mmHg at 20 °C), Kow, and Henry's Constant (atm m^3/mole) of Some Common-Use Pesticides, Herbicidess, and Fumigants.

Pesticide/Herbicide	Vapor Pressure (mmHg at 20 °C)	Kow	Henry's Constant (atm m^3/mole)	Predicted Airborne Phase[a]
Metsulfuron Methyl, Aminopyralid	10^{-11} to 10^{-12}	10^{-2}	10^{-16} to 10^{-17}	**Particulate**
Pyrethroids, Type II	10^{-9} to 10^{-10}	10^{5} to 10^{7}	10^{-4}	**Particulate**
Atrazine, Simazine	10^{-9}	10^{2}	10^{-9}	**Particulate**
Neonicotinoids (e.g Imidacloprid)	10^{-7} to 10^{-10}	10^{0} to 10^{1}	10^{-11}	**Particulate to Semi-Volatile**
Pyrethrins, Phosmet	10^{-6} to 10^{-8}	10^{2} to 10^{4}	10^{-5} to 10^{-9}	**Particulate to Semi-Volatile**
Hexazinone	10^{-7}	10^{1}	10^{-12}	**Particulate to Semi-Volatile**
Pyrethroids, Type I	10^{-6}	10^{3}	10^{-3} to 10^{-7}	**Semi-Volatile**
Methyl Parathion	10^{-6}	10^{3} to 10^{4}	10^{-8}	**Semi-Volatile**
Azinphos-Methyl[b]	10^{-6}	10^{2}	10^{-8}	**Semi-Volatile**
Azinphos-Methyl Oxon	10^{-5} to 10^{-6}	NA	NA	**Semi-Volatile**
Chlorpyrifos[b]	10^{-5}	10^{4}	10^{-6}	**Semi-Volatile**
Chlorpyrifos-Oxon	10^{-4} t o 10^{-5}	NA	NA	**Semi-Volatile**
Diazanon, Malathion	10^{-5}	10^{2} to 10^{3}	10^{-2} to 10^{-3}	**Semi-Volatile to Volatile**
2,4D	10^{0}	10^{2}	10^{-8}	**Volatile**
Fumigants (e.g. Metam Sodium)	10^{3}	10^{1}	10^{-4}	**Volatile**
Methyl Bromide	10^{3}	10^{1}	10^{-1} to 10^{0}	**Volatile**

[a]Predictions based on theory similar to Harner et al. 1998.

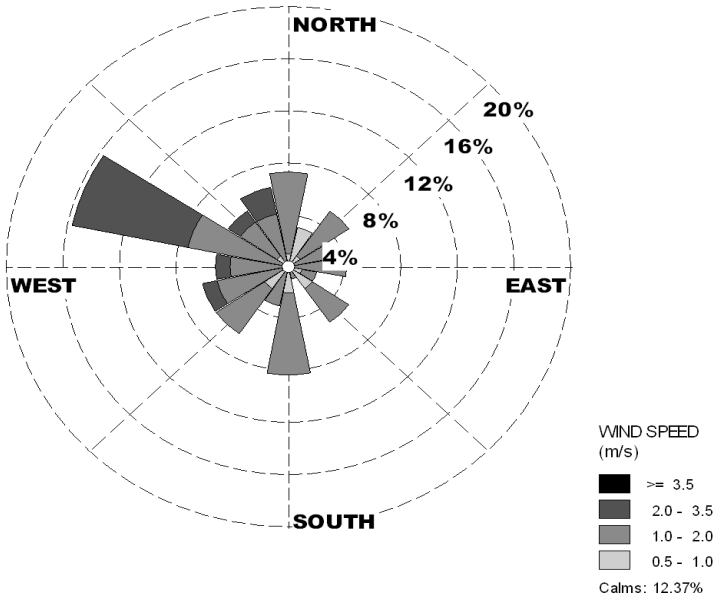
[b] Low solubility of CPF (1.12 mg/L 20 °C) and AZM (28 mg/L 20 °C) indicate dry deposition rather than wet deposition. (Bowman et al 1983, CDPR 1997-2006, Felsot and Dahm 1979, Lyman et al. 1990, Racke 1993, Rice et al 1997, TOXNET Toxicology Data Network, Van den Berg et al. 1999)

Supplementary Material, Chapter 3

Figure S.3.1/ Wind Roses during and following application. During pesticide application, wind speeds were calm and primarily from the northwest. Following application, outdoor temperatures and wind speeds were similar, but wind directions became more variable.

Wind Data, Orchard Sampling (<8 m from Perimeter)

(6 hours during spray) March 18th, 2010. 7:30am



Wind Data, Community Sampling (>150m from Perimeter)

(24 hours post spray) March 18th - 19th, 2010

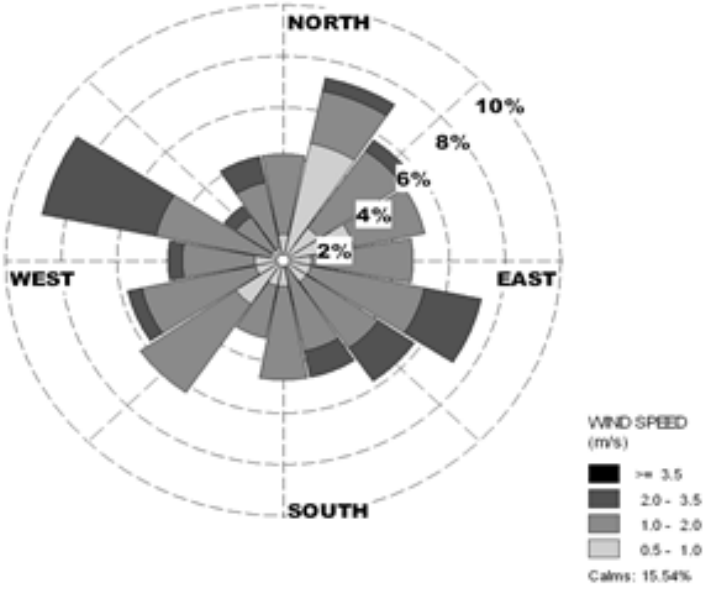
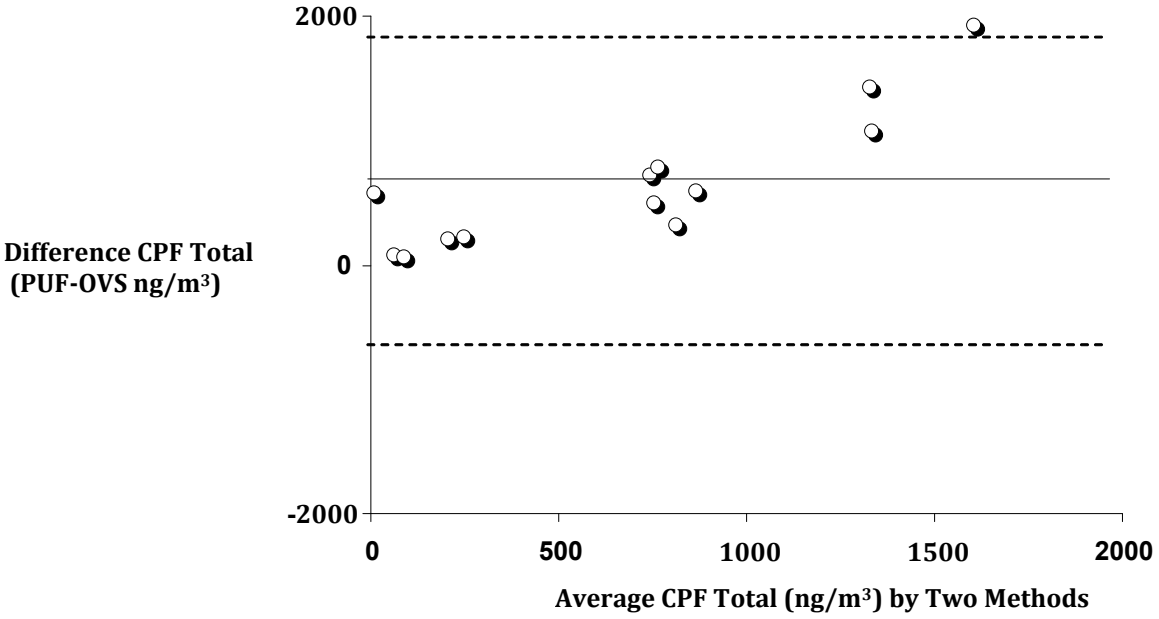


Figure S.3.2/ Bland-Altman plots of PUF vs. OVS tubes for sampling during March 2010. The solid line is the mean difference between sampling matrices, and the dashed lines are 95% CI (α=0.05). These plots are used to compare two sampling methods. PUF matrices tended to report higher levels of total CPF (ng/m3) and lower % oxon.



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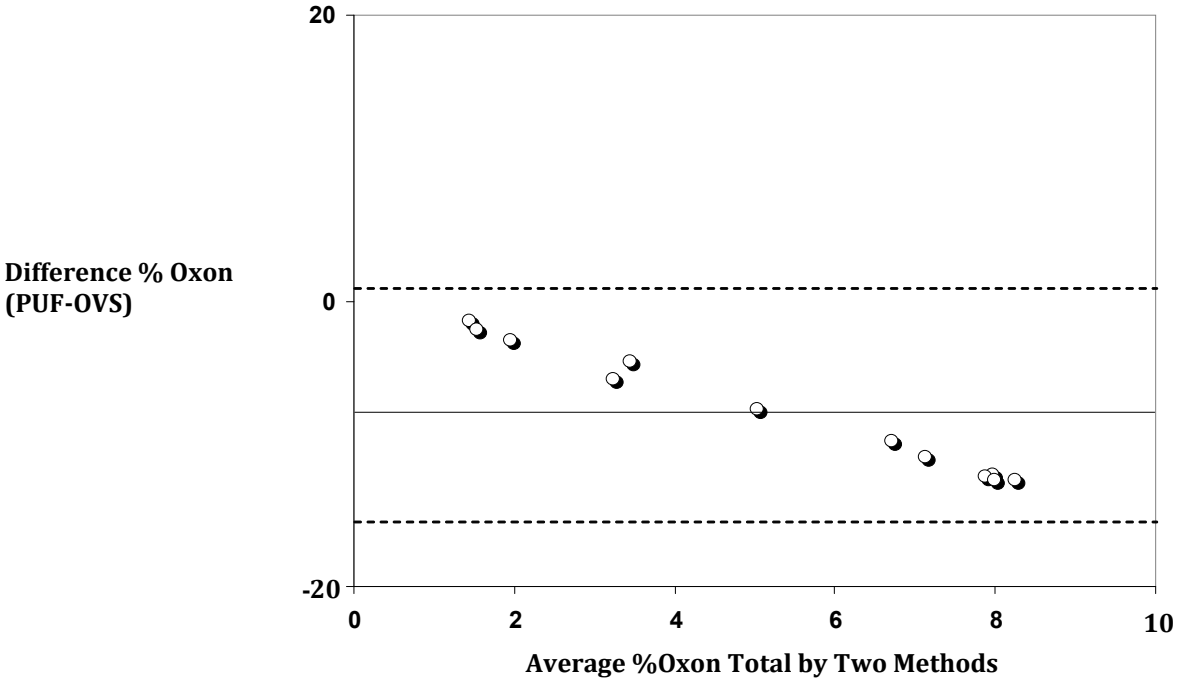


Supplementary Material, Chapter 4

Instrumental Analysis (Co-Author, Russell Dills, PhD, EH Laboratory)

Stable isotope-dilution quantification was performed on an Agilent (Santa Clara, CA) 6410 liquid chromatography tandem mass spectrometer using a C_{18} reverse-phase column (Gemini, 3µ, 150 x 2.0 mm with 4 x 2.0 mm guard column; Phenomenex, Torrance, CA). Electrospray ionization (positive polarity; nebulizer gas, N_2, 350° C, 9 L/min, 40 psi; capillary voltage 4,000) was used in multiple reaction mode (MRM; N_2 collision gas). MRMs and optimized acquisition parameters are listed in Table 1.

Isocratic elution (Agilent G1312A binary pump; mobile phase A, 0.1% formic acid/deionized water; B, 0.1% formic acid/acetonitrile; 0.2 ml/min flow) was used for both groups of compounds but with different % composition for the separate analyses (CPF-related, 25% A, 75% B, runtime 12 min; AZ-related, 45% A, 55% B, runtime 13 min). An Agilent G1313A auto-sampler was used for injections (5 uL volume). Since we report aggregate results from two recent air monitoring studies conducted in Washington State, two separate isocratic methods were used for CPF/CPF-O and AZM/AZM-O. However, this may be also accomplished with a single method.

Calibrants were prepared in internal standard solution (CPF-D_{10} 260 ng/mL, CPF-$^{13}C_2$-^{15}N-Oxon 27 ng/mL, AZM-D_6 100 ng/mL, and AZM-O-D_6 25 ng/mL). Calibration ranges were for 1–1000 ng/mL CPF and AZM, 0.5–1000 ng/mL for CPF-O and 0.1–1000 ng/mL for AZM-O. Depending on sample loading, the upper calibration was lowered to 200–250 ng/mL. Weighted (1/concentration) linear regression was used with 6-10 calibrants depending on the range needed for analysis. Samples with analytes above the upper calibrant were diluted in acetonitrile and rerun. The lowest calibration observed valued was within 25% of nominal.

Table S.4.1/ Multiple Reaction Monitoring Table (MRM). Acquisition Parameters.

Compound	Precursor Ion (m/z)	Product Ion (m/z)	Fragmentation (V)	Collision Energy (V)	Retention Time (min)
CPF-D_{10}	362	201	90	20	8.28
CPF Quantifier	352	200	90	20	8.49
CPF Qualifier	352	97	90	20	
CPF-$^{13}C_2$-^{15}N-Oxon	339	283	90	10	4.02
CPF-O Quantifier	336	280	90	10	4.02
CPF-O Qualifier	336	308	90	10	
AZ-D_6	324	131	90	10	9.70
AZ Quantifier	318	125	90	10	9.81
AZ Qualifier	318	132	90	10	
AZ-Oxon-methyl-D_6	308	132	70	5	4.00
AZ-O Quantifier	302	132	70	5	4.01
AZ-O Qualifier	302	245	70	5	

Table S.5.1/ Example Calculation of Effective Sampling Rate for PUF Disks Based on Depuration Compounds: Some equations were obtained with supplementary materials from Environment Canada Hazardous Air Pollutants (HAPs) Laboratory.

INPUT:		
Sampling Period:		
	Deployment Time (days)	**30**
	Average Temperature (°C)	**18**

Formula for calculation of sampling rate, R:

Sampling Rate, R (m^3/day) = k_A (m/day) × Surface Area of PUF (m^2)

(*from Shoeib and Harner, Environ. Sci. Technol. 2002, 36, 4142-4151.*)

Characteristics of Passive Sampling Media (PUF):		
	Effective film thickness, Dfilm (m)	**1.30E-03**
	Density (g/m^3)	**2.10E+04**
	Surface Area (m^2)	**1.54E-02**

OUTPUT:

Chemical	**log K_{OA}****	**log $K_{puf\text{-}air}$**	**$K'_{puf\text{-}air}$ (no dim.)**	**C/Co (Corrected)**	**k_A (m/d)**	**R (m^3/day)**
Chlorpyrifos	8.34	2.13	2.86E+06	0.500	63.33	**1.44**
AZ-Methyl	11.31	4.03	2.24E+08	0.950	49.40	**3.66**
Chlorpyrifos -oxon	*See CPF*	*See CPF*	*See CPF*	*See CPF*	*See CPF*	**NA**

** for log K_{OA} calculations:
OPs: **log K_{OA} = Kow (RT)/(H)** (Meylan and Howard, 2005)

Table S.5.2/ Example of a PUF Disk Air Volume Calculation for Target Organophosphates (using an estimated sampling rate). Some equations were obtained with supplementary materials from Environment Canada Hazardous Air Pollutants (HAPs) Laboratory.

INPUT:

Sampling Period:	
Deployment Time (days)	30
Average Temperature (°C) during Sampling Period	14
Effective Sampling Rate (for mild weather), R (m^3/day)	3.12
Note: The "effective sampling rate" is subject to change. "3" is example after depuration spiking tests for CPF.	

Formula for calculation of PUF disk effective air volume, V_{air}:

Expected Air Volume (m^3) = $(K'_{PUF\text{-}PAS}) \times (PUF\text{-}PAS_{volume}) \times \{1 - \exp[-(t_{days}) \times (k_A)/(K'_{PUF\text{-}PAS})/(D_{film})]\}$

Where $K'_{PUF\text{-}PAS} = K_{PUF\text{-}PAS} \times (PUF\text{-}PAS_{density})$ (dimensionless)

For PUF disk, $\log K_{puf\text{-}a} = 0.6366 \times \log K_{OA} - 3.1774$ (*from Shoeib and Harner, Environ. Sci. Technol. 2002, 36, 4142-4151.*)

Characteristics of Passive Sampling Media (PUF):	
Volume of PUF=PAS (m^3)	2.00E-04
Effective film thickness, Dfilm (m)	1.30E-02
Density (g/m^3)	2.10E+04
Surface Area (m^2)	1.54E-02

(Data from Rice et al J. Agric. Food Chem. 1997, 45, 2291-2298)

Characteristics of Compounds Organophosphate Pesticides (OPs)	at 20-25 C	Kow	Henry's Constant	Vapor Pressure mmHg	Phase	Passive Sampling
Chlorpyrifos		6.31E+04	6.76E-01	1.87*10^-5	Vapor	Yes
Azinphos Methyl		5.01E+02	5.70E-06	2.2*10^-7	Vapor/ Particulate	Yes

OUTPUT:

Air-side MTC, k_A (m/day) [calculated from sampling rate, R]	203

k_A = R/ (Surface Area of PSM)

Organophosphate Pesticides (OPs) OP	log Kow	Henry's Constant	log K_{OA}	K'puf$_{air}$ (no dim.)	V_{air} (m^3)
Chlorpyrifos	4.80	6.76E-01	8.3472	2.9E+06	**86.4**
Chlorpyrifos-oxon	NA	NA	NA	NA	**NA**
AZ Methyl	2.70	5.70E-06	11.3212	2.3E+08	**93.5**
AZ Methyl	NA	NA	NA	NA	**NA**

log K_{OA} = KOW(RT)/H where T is in Kelvin, Oxons are estimated with sampling rates similar to parent compounds. There is little to no chemical information on the oxons.

NOTE ABOUT VOLUME: THIS VALUE SHOULD BE ESTIMATED USING THE EFFECTIVE SAMPLING RATE

Figure S.5.1/ Dilution and Carrier Flow Rate Calculations for a range of potential chlorpyrifos concentrations at a permeation rate of 5.5ng/min at 35°C in a dynamic exposure chamber. Calculated using $F_d = [(P \times K_m)/C)] - Fc$, where F_d = dilution flow rate (cc/min), P= permeation rate (5.5 ng/min at 35 °C), K_m= molar constant of device gas (dry air = 28.96 g/mol), C= concentration (ppm), and F*c* = carrier flow rate. Potential carrier and dilution flow rates were converted to liters per minute (LPM).

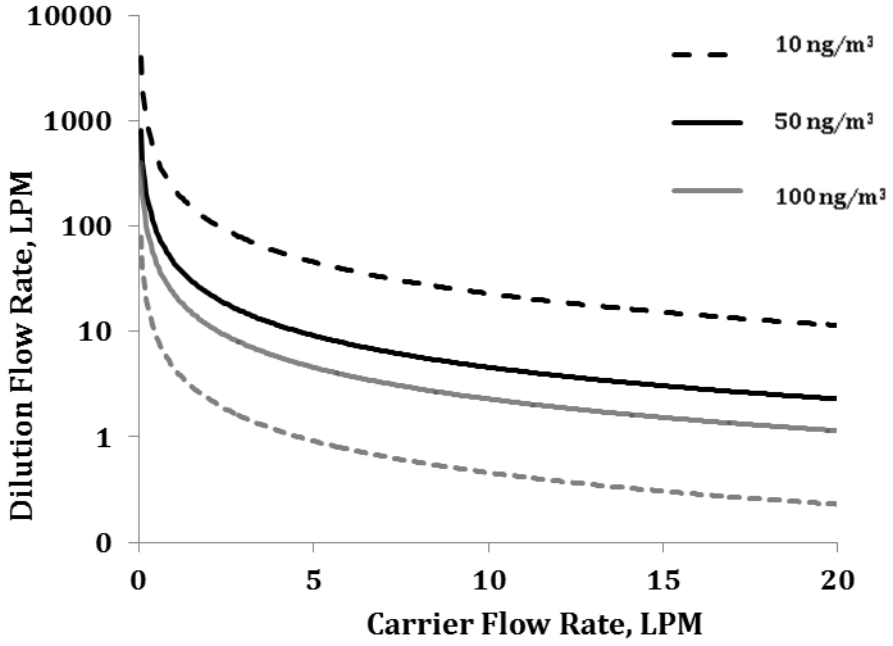


Figure S.5.2/ Measured loss of mass (g) from CPF permeation tube at 35°C in a dynamic exposure chamber. The rate of 5.5 ng/min was determined only during the experimental period.

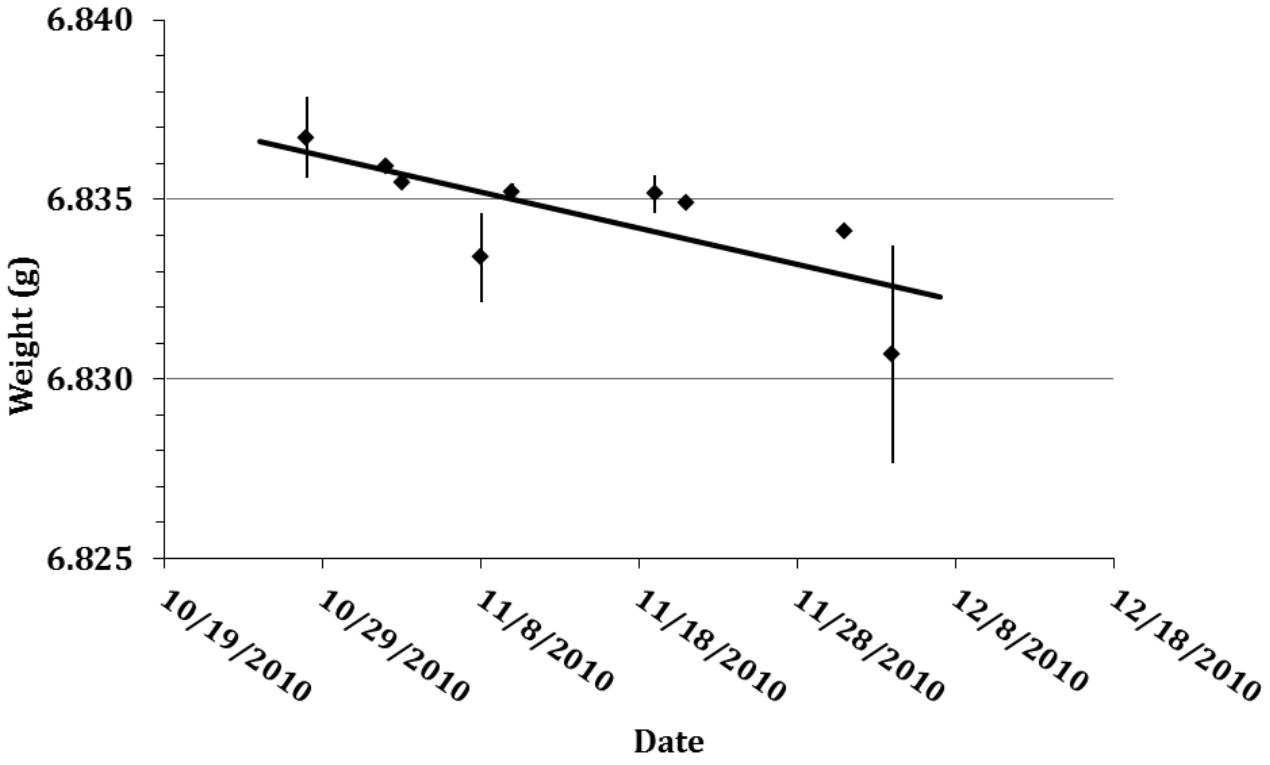
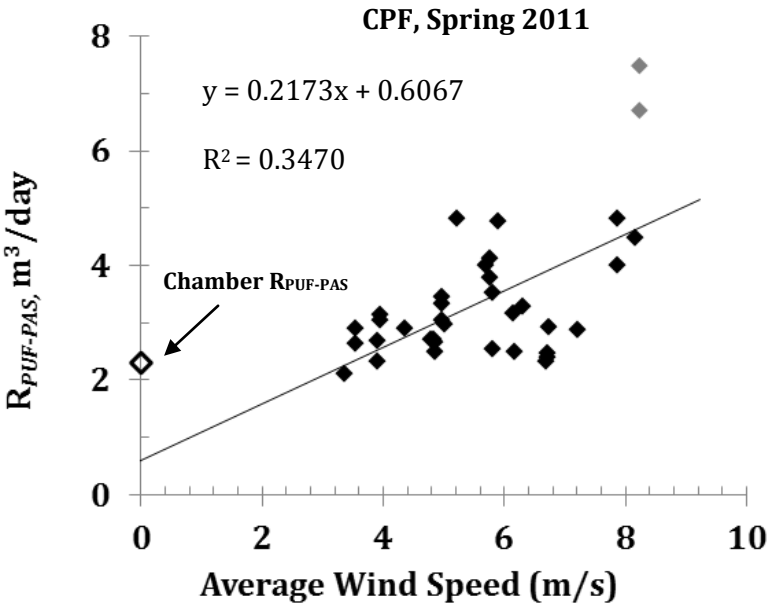
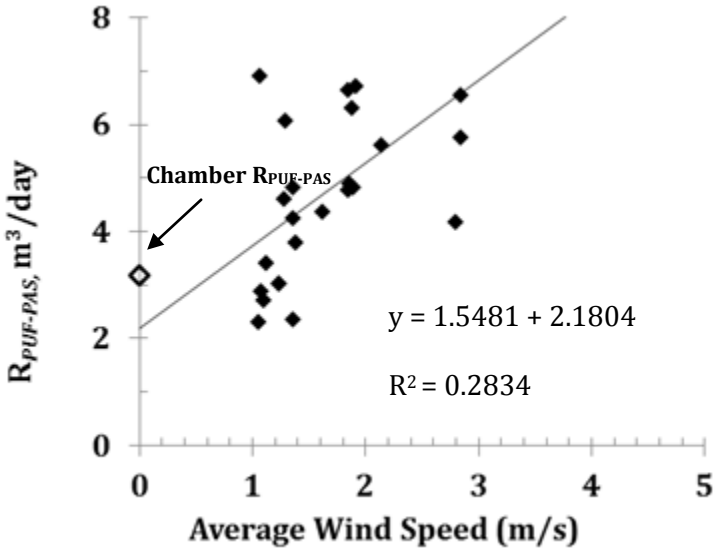


Figure S.5.3/ Linear regression demonstrating the effects of average wind speeds (t_{days}=30) and measured sampling rates, R_{PUF_PAS} with depuration compounds. Average monthly spring wind velocities were greater than summer wind velocities. For comparison, the average sample rate determined in the exposure chamber is in the clear diagonal box and was assumed to be representative of wind speeds near 0 m/s.





The two grey data points had recoveries of depuration chlopyrifos-methyl-D_6 <15%. For CPF, there was a small increase in $R_{PUF\text{-}PAS}$ (0.22 m^3/day, 95% C.I. 0.11- 0.32, p≤0.005) with each 1 m/s increase in wind speed (R^2=0.3470). For AZM, there was an increase in $R_{PUF\text{-}PAS}$ (1.548 m^3/day, 95% C.I. 0.48- 2.61, p≤0.005) with each 1 m/s increase in wind speed (R^2=0.2834). For both CPF and AZM, the reported $R_{PUF\text{-}PAS}$ in the chamber was higher than expected from the linear relationship. At a wind speed of 0 m/s, sampling rates of 0.61 and 2.18 were expected for CPF and AZM, respectively. These linear relationships did not fit the data as well as exponential regression.

Supplementary Material, Chapter 6

Figure S.6.1/ Average Log of Outdoor Monthly Air Concentrations (ng/m^3) of CPF by Log of Residential Proximity to Tree Fruit Fields (m). The dotted line represented 95% C.I. Slope and R^2 values are for linear regression using log-transformed air concentration values for CPF (ng/m^3) and distance (m).

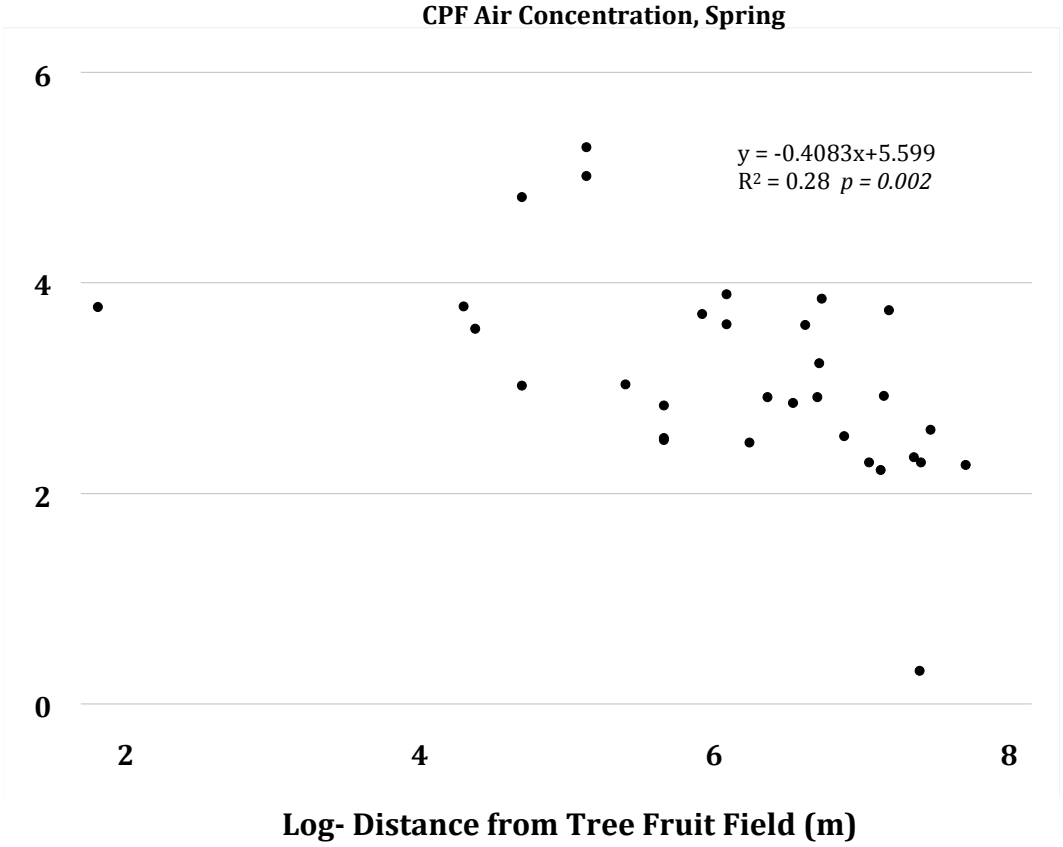


Figure S.6.2/ Average Log of Outdoor Monthly Air Concentrations (ng/m^3) of CPF-0 by Log of Residential Proximity to Tree Fruit Fields (m). The dotted line represented 95% C.I. Slope and R^2 values are for linear regression using log-transformed air concentration values for CPF-O (ng/m^3) and distance (m).

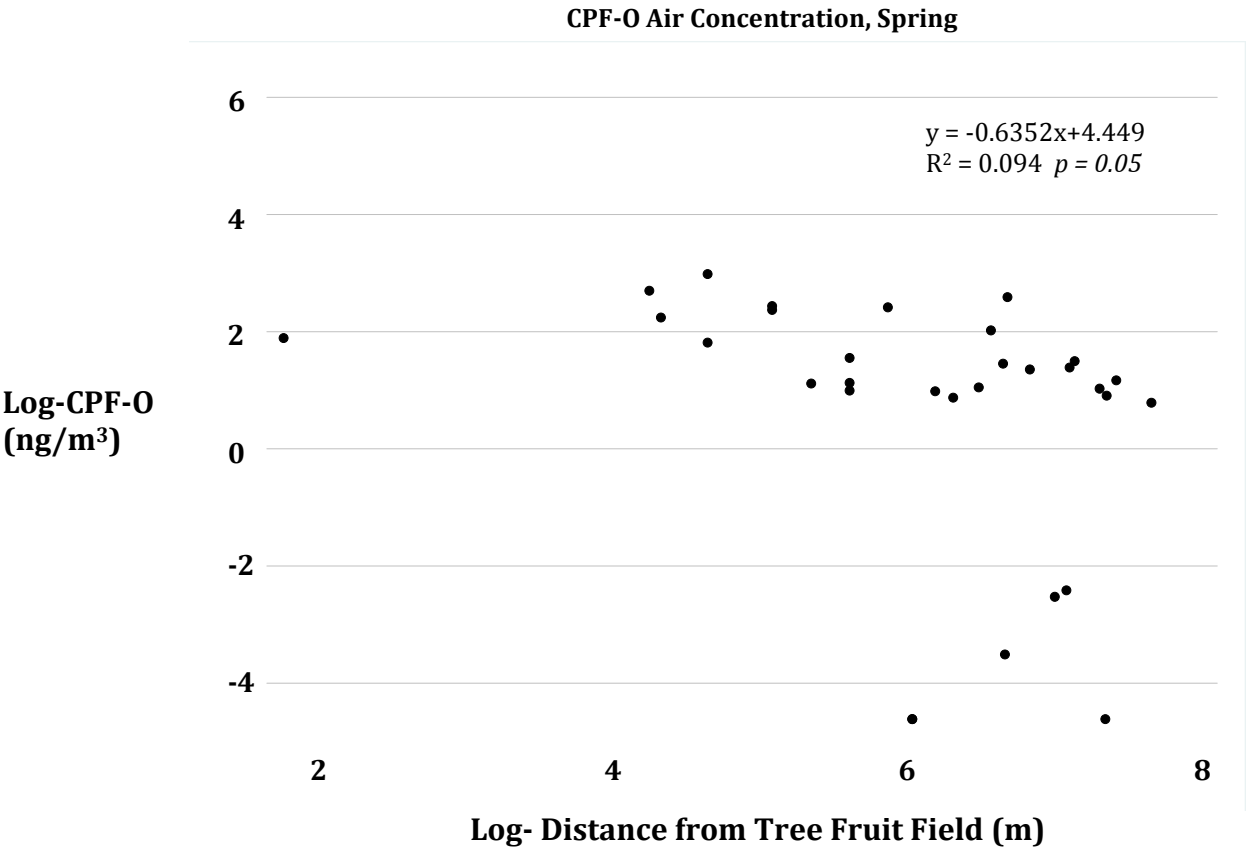


Figure S.6.3/ Average Log of Outdoor Monthly Air Concentrations (ng/m^3) of AZM by Log of Residential Proximity to Tree Fruit Fields (m). The dotted line represented 95% C.I. Slope and R^2 values are for linear regression using log-transformed air concentration values for AZM (ng/m^3) and distance (m).

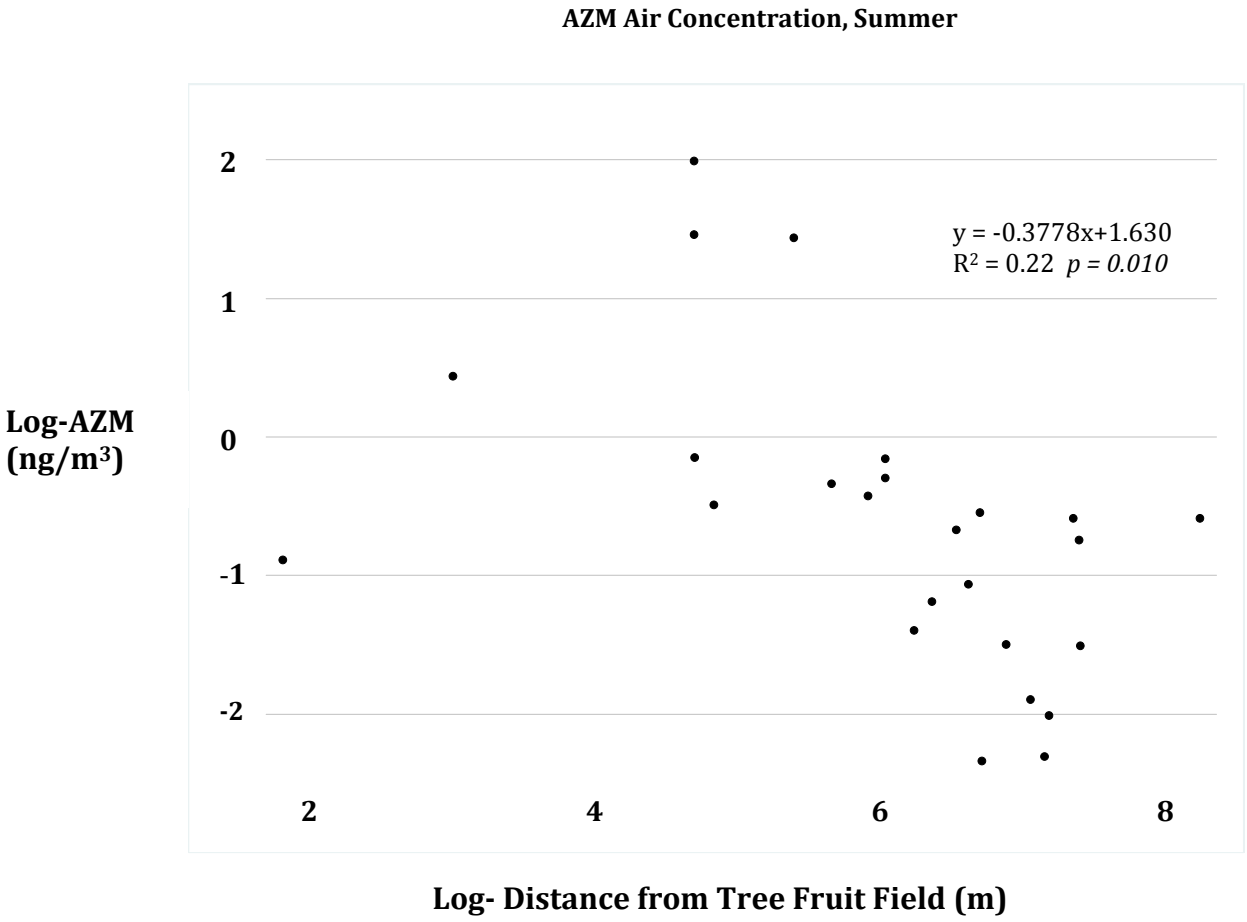
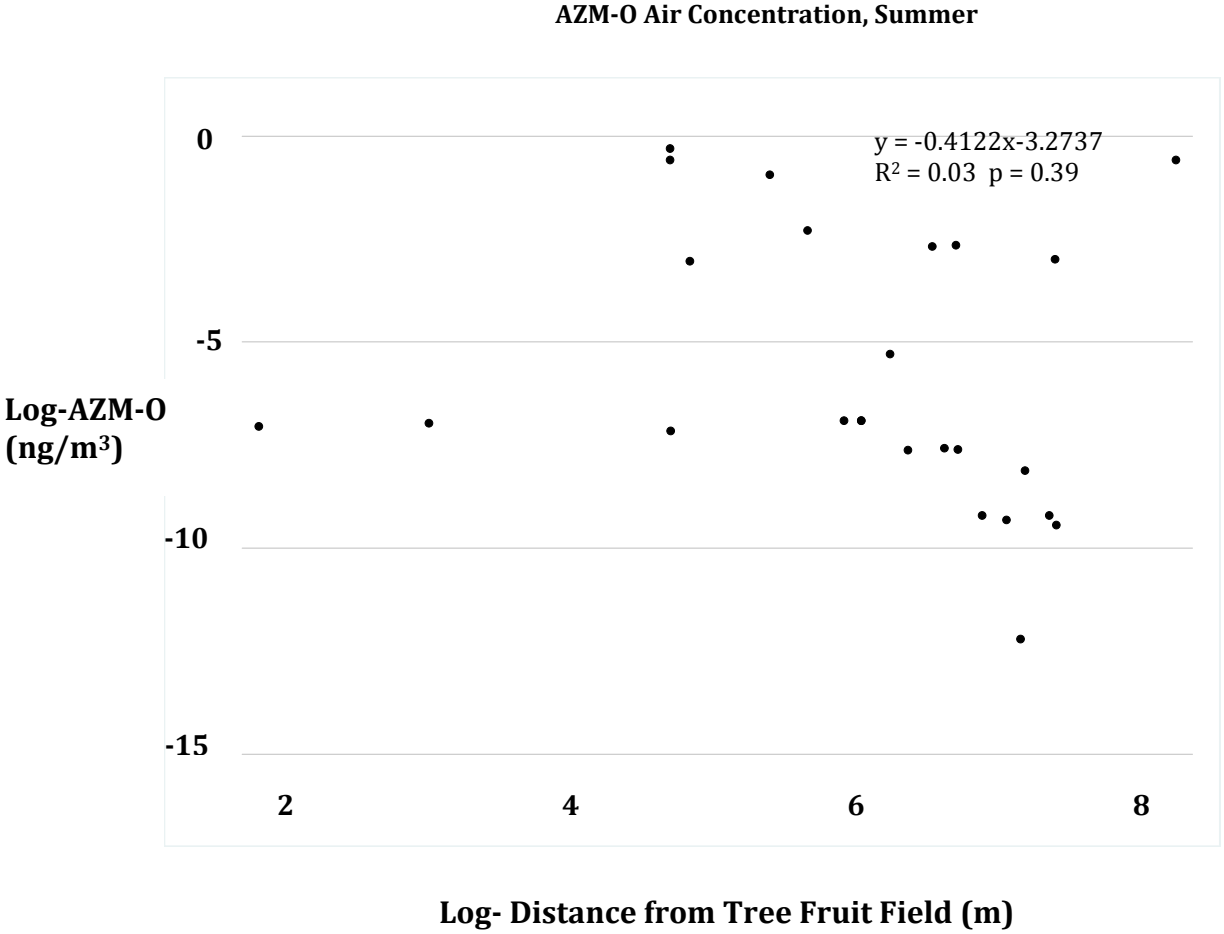


Figure S.6.4/ Average Log of Outdoor Monthly Air Concentrations (ng/m^3) of AZM-O by Log of Residential Proximity to Tree Fruit Fields (m). The dotted line represented 95% C.I. Slope and R^2 values are for linear regression using log-transformed air concentration values for AZM-O (ng/m^3) and distance (m).



Biography

Jenna L. Armstrong is a current PhD candidate at the University of Washington in Seattle and has an MPH in Global Health and BA in Biology from the University of Iowa. For the past three years, she has been investigating routes of airborne pesticide exposures in the agricultural region of central Washington State as part of the Children's Health Center *"Para Ninos Saludables"* Child Health Center project using economical passive air sampling methods. In addition, she has been working as a field and laboratory technician for the AFARE (Aggravating Factors of Asthma in a Rural Environmental), a project examining the factors (ammonia, endotoxin, pollen, particulate, pesticides) of asthma as part of a community-academic partnership project in the Yakima Valley. She will be continuing research in air quality and respiratory illnesses in a position as Senior Industrial Hygienist Research Fellow on the CDC/NIOSH Field Studies Branch Research Team (Division of Respiratory Disease Studies) in Morgantown, WV. Her contribution will focus on airborne exposure assessments for epidemiologic investigations and strategic planning of sampling in worksites, field data collection, data reduction, and epidemiologic analysis of exposures in relation to health outcomes among workers.

Jenna has been an active member in the International Society of Exposure Sciences (ISES) Student/New Researcher committee and the Student Public Health Association (SPHA) for the past two years. She was on the University of Iowa women's basketball team been an active member of the University of Iowa Alumni Association and served on the UW Graduate and Professional Student Senate for two years. She also received training in Project Management and Decision Making Analysis at the University of Washington Industrial Engineering Program.

Curriculum vitae

EDUCATION

PhD, Environmental and Occupational Hygiene, Risk Assessment Emphasis Program
University of Washington, Seattle expected Fall 2012.

Engineering Leadership Certificate, Industrial Engineering
University of Washington, Seattle expected Fall 2012.

MPH, Global Health
University of Iowa, Iowa City IA, 2008

BA, Biology
University of Iowa, Iowa City IA, 2006

RESEARCH EXPERIENCE

Associate Research Fellow, Senior Industrial Hygienist, US Centers for Disease Control and Prevention (CDC), National Institute of Occupational Safety and Health (NIOSH), Morgantown, WV. ***December 2012 start.***

Research Technician, "*Proyecto Bienestar*" (NIEHS) Aggravating Factors of Asthma in a Rural Environment (AFARE), University of Washington, Seattle, WA, ***September 2011 to Present.***

- Coordinating lab analysis for novel air samplers at 14 rural sites to be used to determine ambient environmental factors (ammonia, endotoxin, pollen, particulate, pesticides) of asthma exacerbations in a community-academic partnership project.
- Performed extrapolation and gravimetric filter analysis for PM 2.5, PM 10, and organophosphate pesticides.

Research Assistant, University of Washington Children's Health Center (CHC) ***"Para Ninos Saludables"*** **(NIEHS/EPA) Pacific Northwest Agricultural Safety and Health Center, University of Washington, and Fred Hutchinson Cancer Research Center, Seattle, WA,** ***September 2010 to Present.***

- Conducted field air monitoring at local residences of Hispanic migrant farmworkers for pesticide and oxygen analog atmospheric drift in Yakima Valley, Washington.
- Performed chemical extraction/analysis of organophosphate pesticides at UW Environmental Health Laboratory using LC-MS-MS. Analyzed environmental sampling data of pilot studies and 2008 Department of Health pesticide study results using SPSS, STATA.
- Arranged final report for local community on study outcomes and recommendations for exposure measurement.

Research Scientist, Ministry of Social and Economic Inclusion. Quito, Ecuador ***May-August 2008***

- Used ARCGIS to map results from the National Food Supply and Nutrition Assessment Survey in 5 different provinces. Compiled "best practices" report regarding an international Fruit and Vegetable campaign.
- Assisted Zone Technicians with community meetings with locally engaged stakeholders about environmental health concerns and food access.

Research Assistant, Department of Geography, University of Iowa, Iowa City, IA *January – June 2008.*

- Designed novel outdoor/indoor air pollution sampling device and monitored residential indoor/outdoor air pollution levels of PM 2.5, PM 10, and NO_x emissions at10 Iowa City homes, including biological FEV data on residents and children.

Undergraduate Research Assistant, University of Iowa School of Public Health and College of Medicine, August 2005 – March 2006.

- Conducted baseline interviews with college student athletes on *Perceived Social Support on Athlete's Resilience Following Athletic Injuries*.
- Conducted literature review on psycho-social support following athletic injury and database entry.

TEACHING EXPERIENCE

Teaching Assistant, *Food and Health 110*, College of the Environment, University of Washington, Seattle, WA, September *2011 to December 2011.*

- Presented class lectures on environmental health topics, including agricultural chemical use, climate change, and human health outcomes.
- Lead discussion facilitator, organized and led computer simulation lab sections.
- Developed exam and homework questions, website, graded weekly assignments and managed grade database.

Student Mentor, Department of Environmental and Occupational Health, Summer Undergraduate Program (NIEHS), Seattle WA, *Summers 2011-present.*

- Mentored undergraduate students in the laboratory research setting, assisted with poster presentations, and managed student's regular hourly schedules.

Teaching Assistant, *Environmental Health 111*, Department of Environmental and Occupational Health Sciences, University of Washington, Seattle, WA, September *2010 to December 2010.*

- Presented 3 class lectures on environmental health topics, including pesticide use, GMOs, food-borne illness, and environmental policy.
- Lead facilitator during discussions, posted and maintained office hours bi-weekly. Worked one-on-one with undergraduate students to read articles and revise papers.
- Developed exam and homework questions, website, graded weekly assignments and managed grade database.

Workshop Leader, *TA/RA Conference on Teaching, Learning, and Research*, Graduate School, University of Washington, Seattle, WA, Summer *2011 and 2012.*

English Conversation Teacher, *Hyundai Heavy Industries,* UW Foster School of Business Executive Education Program, Seattle, WA, Summer *2011 and 2012.*

Teaching Assistant, Global Health and Global Food 152, Department of Global Health Studies, University of Iowa, Iowa City, IA, September *2007 to December 2007.*

PROFESSIONAL EXPERIENCE

Toxicology and Risk Assessment Intern and Industrial Hygienist, Chevron, Richmond Refinery, California, ***June-September 2009***

- Conducted toxicological lit review to compile a database (ToxNet) of safer-use chemicals and generated proper MSDS information for materials handling.
- Monitored potential industrial exposures to hydrofluoric acid, VOCs, and noise on site at the refinery. Conducted on-job exposure assessments.

Social Entrepreneur, Hand in Hand Non-Profit, Tamil Nadu, India, ***December – January 2008.***

- Developed an interdisciplinary occupational and environmental health training program for "self-help" microfinance consortium using current ILO guidelines.
- Aided self-help group meetings in non-profit atmosphere and worked closely with local informal farm and textile workers to discuss health concerns.

Student Intern, Center for Human Rights, University of Iowa International Programs, Iowa City, IA January 2007- October 2008.

- Organized Human Rights Library and Resources onsite and via web development into a Reworks database.
- Liaison for two Global Health Conferences (Global Health Inequalities and Global Climate Change). Contacted speakers and organized travel and fundraisers.
- Prepared student-lead networking and fund raising events (e.g. Earth Day Concert).

Student Intern, Office of Environmental Health and Sustainable Development, Pan American Health Organization (Regional Office of WHO), Washington, D.C. August 2006 – January 2007.

- Prepared two policy review papers regarding health care worker brain drain and child labor issues in developing countries.
- Worked as a student intern liaison for four international PAHO, ILO, and OAS (Organization of American States) conferences held in Washington, D.C. Organized travel and managed itineraries for traveling health administrators, researchers, and ministers of health from all across the Americas.

PUBLICATIONS

Scientific Journals

1. Presence of organophosphorus pesticide oxygen analogs in air samples. Jenna L. Armstrong, Richard A. Fenske, Michael G. Yost, Kit Galvin, Maria Tchong-French, Jianbo Yu. *(Atmospheric Environment,* IN PRESS, *2012).*
2. Comparision of polyurethane foam and XAD-2 sampling matrices to measure airborne organophosphorus pesticides and their oxygen analogs in an agricultural community. Jenna Armstrong, Richard A. Fenske, Michael G. Yost, Kit Galvin, Jianbo Yu. *(Chemosphere, IN REVIEW).*
3. Development of a unique multi-contaminant air sampler for a rural asthma cohort. Jenna L. Armstrong, Cole F. Fitzpatrick, Michael G. Yost, Maria Tchong-French, Catherine Karr. *(to be submitted to Journal of Exposure Science and Environmental Epidemiology October 2012).*
4. A sensitive LC-MS-MS method for measurement of organophosphorus pesticides and their oxygen analogs in community air samples. Jenna Armstrong, Richard A. Fenske, Michael G. Yost, Russel Dills, Jianbo Yu *Journal of Journal of Agricultural and Food Chemistry, IN REVIEW).*

Reports and Commentary

5. "Field Based Study and Integration of Passive Air Sampling Methods." *Environmental Health Sciences Bulletin Quarterly*, Environmental Protection Agency (EPA), Fall 2011.
6. "New Findings Related to Air Monitoring for Organophosphorus Pesticides and Related Compounds in Washington State." *Migrant Clinician's Network, Streamline Newsletter. May 2010.*
7. Potential Chlorpyrifos-oxon Generation Sub-Study. Organophosphate Air Monitoring in Yakima Valley and North Central Washington. Washington State Department of Health, 2008.

CONFERENCES/PRESENTATIONS

1. "Airborne Total Dust, PM 2.5, and NH_3 and Residential Proximity to Confined Animal Feeding Operations (CAFOs) and Rural Roadways" Lilian Turcios, Jenna Armstrong, Michael Yost, Catherine Karr. "Passive air sampling for indoor and outdoor exposures to OP pesticides and oxygen analogs in an agricultural children's health study." Jenna Armstrong, Michael Yost, Maria Negrete, Ilda Islas, Richard Fenske. *International Society of Exposure Scientists, Seattle 2012.*
2. "Novel Air Sampling Methods for Organophosphorus Pesticides in a Community-Based Project in Yakima Valley, Washington." *X2012, Edinburgh, 2012.*
3. "Airborne Pesticide Exposures and Aggravating Factors for Asthma in Rural Environments." *EPA Region 10 Air Toxics, Seattle, 2012.*
4. "Integration of Passive Air Sampling Methods with Community Based Participatory Research in Yakima Valley." *Children's Environmental Health Research Matters Conference, Seattle 2012.*
5. "Children and Air Quality in Agricultural Communities." Jenna Armstrong, MPH, PhDc. *University of Washington Board of Regents Meeting, Children's Environmental Health Journal Club, 2011*

6. "Unique Air Sampling Strategies for Pesticides." *Semiahmoo Conference, 2010*
7. "Method comparison of polyurethane foam and XAD-2 resin sampling matrices to measure airborne organophosphate pesticides and oxygen analogs." Jenna Armstrong, Richard A. Fenske, Michael G. Yost, Kit Galvin, Maria Tchong-French, Jianbo Yu. *International Society of Exposure Science, Seoul, Korea 2010*
8. Potential Chlorpyrifos-oxon Generation Sub-Study. Appendix H, Organophosphate Air Monitoring in Yakima Valley and North Central Washington. Washington State Department of Health, 2008.
9. "Organophosphorus Pesticide Oxygen Analogs in Air Samples: Are they present in air or an artifact of sampling?" Jenna Armstrong, Richard A. Fenske, Michael G. Yost, Kit Galvin, Maria Tchong-French, Jianbo Yu. *International Society of Exposure Scientists, Minneapolis 2009*
10. "Oxon Formation During Sampling for Chlorpyrifos." *Semiahmoo Conference, 2010*
11. "Organophosphorus Pesticide Oxygen Analogs in Air Samples." *ERC Interdisciplinary Program Research Presentation, 2010*
12. "Method Development for Sampling of Organophosphorus Pesticides and Oxygen Analogs in Yakima Valley, WA." Jenna Armstrong, Richard A. Fenske, Michael G. Yost, Kit Galvin, Maria Tchong-French, Jianbo Yu. *Northwestern Migrant Stream Forum, 2010*
13. "Microfinance Partnerships in Occupational and Environmental Health." *Social Entrepreneurship: Learning by Sharing Conference, Anandha Hotel, Pondicherry India. 2008*

LEADERSHIP POSITIONS

University of Iowa Women's Basketball Team (Varsity) 2001-2005
University of Washington Student Public Health Association (SPHA Co Chair), 2011-12
AIHA, American Industrial Hygiene Association, 2009-present
ISES, International Society of Exposure Scientists, 2009- present
ISES Board Student Representative, Student and New Researchers Committee, 2010-2011
University of Iowa Alumni Association and I-Club, 2008- present
DEOHS Student Faculty Representative, 2009-2011
DEOHS Curriculum Committee Representative, 2010-2011
Exposure Sciences Representative of DEOHS Student Advisory Committee, 2009- present
Social Activities Coordinator, DEOHS 2009-10
University of Washington Disability Resources for Students Classroom Volunteer 2009-2010
Graduate and Professional Student Senator, 2010- present
Graduate and Professional Student Executive Councilor, 2010-2012
Graduate Department Review Committee Member, 2010- 2011
Universit of Washington Department of Environmental and Occupational Health Faculty Search Committee, 2012-2013.
UW Farm, 2010-2012

SKILLS, CERTIFICATIONS

Spanish, 5 years. 40 hr course Spanish and Culture Center, Intercambio Cultural, Ecuador
OSHA Certificate, 30 hours Standards for the General Industry
OSHA Certificate 510, 30 hours Standards for the Construction Industry
Knowledge of statistical analysis software packages such as STATA, SPSS, SAS/STAT, R, Excel, and geographical monitoring systems such as AERMOD and ArcGIS.
Knowledge of project management software, including Microsoft Project and GanttProject.

Knowledge of Decision Analysis software, including Monte Carlo, Decision Tree Analysis, Linear Programing, and AHP.
Technical and Policy Writing
Biological and Chemical Laboratory Training
Blood Borne Pathogens and Laboratory Safety Training, University of Washington 2009, 2010
CITI Certification, University of Washington and University of Iowa Courses in Protection of Human Research Subjects

AWARDS

Outstanding Doctoral Student- Environmental and Occupational Health, UW School of Public Health, 2012.

Academic All-Big Ten (GPA > 3.0), 2001-2005
University of Washington SPH Gilbert S. Omenn Award for Academic Excellence Nominee, 2010 & 2012
University of Iowa International Programs Student Travel Award, Tamil Nadu India 2008
ERC Trainee Grant Recipient, 10 students/year 2009-2010
Northwest Center for Occupational Health (NIOSH) Pilot Study Award, 2 awarded/year 2009-2010
Northwest Occupational Health Conference Poster Presentation, Honorable Mention, 2010.
George Washington Carver Award in Outstanding Education Achievement, 2001