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Development of a passive air sampler to measure airborne organophosphorus pesticides and oxygen analogs in an agricultural community

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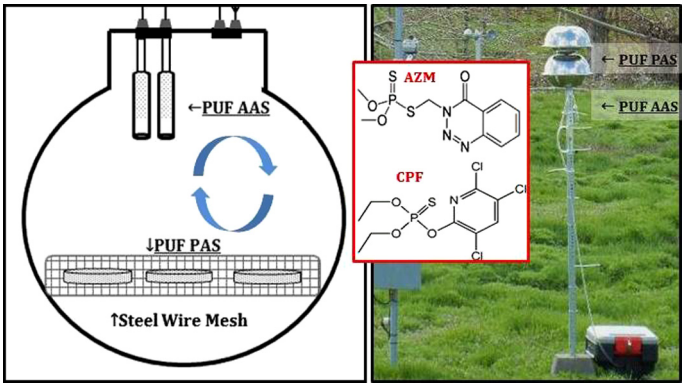
HIGHLIGHTS

- We can passively air sample OPs and oxygen analogs without false transformation.
- Oxygen analogs were detected in outdoor passive air samples.
- Indoor passive air sampling rates for OPs and analogs were lower than outdoors.
- Outdoor passive air sampling rates were greatly influenced by wind velocity.
- Outdoor passive air sampling rates were somewhat influenced by humidity.

GRAPHICAL ABSTRACT



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ABSTRACT

Organophosphorus pesticides are some of the most widely used insecticides in the US, and spray drift may result in human exposures. We investigate sampling methodologies using the polyurethane foam passive air sampling device to measure cumulative monthly airborne concentrations of OP pesticides chlorpyrifos, azinphos-methyl, and oxygen analogs. Passive sampling rates ($m^3\ d^{-1}$) were determined using calculations using chemical properties, loss of depuration compounds, and calibration with side-by-side active air sampling in a dynamic laboratory exposure chamber and in the field. The effects of temperature, relative humidity, and wind velocity on outdoor sampling rates were examined at 23 sites in Yakima Valley, Washington. Indoor sampling rates were significantly lower than outdoors. Outdoor rates significantly increased with average wind velocity, with high rates (>4 $m^3\ d^{-1}$) observed above 8 $m\ s^{-1}$. In exposure chamber studies, very little oxygen analog was observed on the PUF-PAS, yet substantial amounts chlorpyrifos-oxon and azinphos methyl oxon were measured in outdoor samples. PUF-PAS is a practical and useful alternative to AAS because it results in little artificial transformation to the oxygen analog during sampling, it provides cumulative exposure estimates, and the measured sampling rates were comparable to rates for other SVOCs. It is ideal for community based participatory research due to low subject burden and simple deployment in remote areas.

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1. Introduction

1.1. Organophosphorus pesticides and oxygen analogs

Organophosphorus (OP) pesticides are some of the most widely used insecticides in the United States, and spray applications are a concern due to potential human exposures from off target volatilization and drift. Exposures to OP pesticides in air usually occur through inhalation or dermal pathways and can be occupational or residential. Airborne exposures are a concern in Washington State because >95% of OP pesticides are applied with an air-blast spray tank pulled behind a tractor (Brunner et al., 2003). The presence of the oxygen analog transformation product in airborne mixtures also is important, as *in vivo* toxicity studies have demonstrated that the toxicity of the analog may be 5–100 times higher than the parent OP (Chambers and Carr, 1993; Cole et al., 2005, 2011; Timchalk et al., 2007; Armstrong et al., 2013a,b). The analogs may occur in the atmosphere through OH-initiated photooxidation (as described by Zhou et al. (2009)).

In 2008, the FIFRA Scientific Advisory Panel called for improved measurement of OP pesticide drift and distribution of chemical phases in residential environments (EPA, 2008). Current methods employing active air sampling (AAS) for OP pesticides rely on collection and sorption onto polyurethane foam (PUF) or XAD-2 (styrene–divinylbenzene) resins (NIOSH, 1994; EPA, 1999; ASTM, 2011). Although the NIOSH Method 5600 recommends the use of XAD-2 in OSHA Versatile Sampling (OVS) tubes (NIOSH, 1994), we found that OVS tubes artificially transform substantial amounts of OP pesticides to their oxygen analogs (Armstrong et al., 2013a). If laboratory analyses focus solely on the OP parent compound, then air concentrations and exposures are underestimated. This can also lead to underestimation of health risks, given the greater toxicity of the analogs. In a recent study we demonstrated that the PUF matrix is a good alternative to prevent artificial transformation (Armstrong et al., 2013b).

1.2. Passive sampling

In order to deploy AAS devices, researchers need to know the timing of pesticide applications. Although feasible in an occupational setting, it may difficult to obtain for community studies. Under these conditions, community air monitoring studies that rely on AAS monitoring often have to cover several months to capture peak exposures and cumulative exposure levels, as completed in a previous study (Fenske et al., 2009).

In contrast, passive air sampling (PAS) is ideal for remote agricultural areas where OP pesticides are commonly used because it is better suited when electrical power is difficult to obtain. AAS requires frequently changes of the sampling matrix (e.g., hourly/daily), and PAS matrices may be changed over longer periods of time (e.g., weekly/monthly). Although the general advantages and disadvantages of general passive air sampling for semi volatile organic compounds (SVOCs) are well documented (Shoeib and Harner, 2002a,b; Harner et al., 2006a,b; Bohlin et al., 2008), we have compared the advantages and disadvantages of PAS and AAS specific to measuring airborne pesticides in Supplemental Material (Table 1).

Passive air samplers like the polyurethane foam sampler (PUF-PAS) rely on atmospheric diffusion to collect contaminants without the use of a pump, as the rate of uptake is controlled by the air boundary layer. This process of accumulation is understood mathematically using simple chemical models (Bartkow et al., 2005). In the past couple decades, passive sampling with a PUF-PAS has been used to study seasonal and spatial trends of polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) (Shoeib and Harner, 2002a,b; Harner et al., 2004; Wilford et al., 2004; Gouin et al., 2005), polycyclic aromatic hydrocarbons (PAHs) (Bohlin et al., 2008; Bohlin, 2010), and organochlorine (OC) pesticides (Harner et al., 2004; Gouin et al., 2008; Hayward et al., 2010). In addition, polyurethane foam has been identified as a sorbent reservoir for the accumulation of OP pesticides in homes [in furniture and toys (Gurunathan et al., 1998)].

This article reports on use of PUF-PAS to measure the airborne OP pesticides chlorpyrifos (CPF), azinphos-methyl (AZM), and their oxygen analogs chlorpyrifos-oxon (CPF-O) and azinphos-methyl-oxon (AZM-O). The research involved sampling in both a laboratory exposure chamber and outdoors in the field. Specific aims were to quantify passive sampling rates, or $R_{PUF\text{-}PAS}$ (in $m^3\ d^{-1}$), and examine OP pesticide recoverability and potential conversion to the oxygen analog on the PAS matrix. Sample rates were determined three ways: (1) using theoretical calculations based on chemical properties, (2) measuring the loss of labeled depuration compounds, and (3) calibration with side-by-side AAS in a dynamic laboratory exposure chamber and in the field.

Past studies have found that outdoor meteorological factors like temperature, relative humidity, and wind velocity may affect sampling rates, causing them to differ from those determined in the laboratory (Soderstrom and Bergqvist, 2004; Tuduri et al., 2006; Hazrati and Harrad, 2007; Hayward et al., 2010). We examined the effects of these factors on sampling rates with labeled depuration compounds using linear regression. All experiments were conducted for time periods ranging from 0 to 30 d in order to simulate pesticide application seasons in Washington State.

2. Experimental

2.1. Calculation of sampling rates

The theory of passive sampling and mass transfer across the PUF-PAS disk interface has been explained in numerous past studies (Shoeib and Harner, 2002a,b; Harner et al., 2004, 2006a,b). Data are reported as the mass collected per unit time, and can be converted to estimated air concentration ($ng\ m^{-3}$) using uptake rates from side-by-side calibration studies.

Table 1 presents the equations used to calculate theoretical and actual sampling rates ($R_{PUF\text{-}PAS}$). It is possible to estimate K_{oa} from the octanol–water partition coefficient (K_{ow}), Henry's Law Constant (H), the ideal gas constant (R), and absolute temperature (K) is the absolute temperature (Eq. (1)). Similar to Shoeib and Harner (2002a,b), we calculated sampler partition coefficients (K_{PUF}) by using octanol–air partition coefficients [K_{oa}] (Noble, 1993; Eq. (2)) and the average of effective passive sampling rates (K_A) for similar semi-volatile pesticides (Eq. (3)) (Gouin et al., 2008; Hayward et al., 2010). Our computed log K_{oa} values (unitless) for CPF and AZM were 8.36 and 11.33, respectively. There are no data on octanol–air partition coefficients for the oxygen analogs, so the sampling rates for CPF-O and AZM-O were assumed to be similar to parent compounds. The theoretical sample air volume (V_{air}) was calculated using the dimensionless K_{PUF} (K'_{PUF}), K_A, and passive sampling media characteristics like PUF-PAS volume and thickness (Eq. (3)).

To model expected sampling volumes (m^3) for time periods representative of pesticide application seasons, we used time periods (t_{days}) ranging 0–30 d and sampling volumes were modeled in STATA™ 11.2 (StataCorp LP College Station, Texas). For CPF and AZM at room temperature (25 °C), the expected air sampling rates were calculated to be 3.37 and $3.69\ m^3\ d^{-1}$, respectively. These rates were similar to measured rates for other SVOCs such as PBDEs and OC pesticides, which range from 1 to $8\ m^3\ d^{-1}$ (Shoeib and Harner, 2002a,b; Harner et al., 2004, 2006a,b; Wilford et al., 2004; Gouin et al., 2005, 2008; Hayward et al., 2010).

Table 1
Equations for theoretical and actual passive sampling rates. Equation variables are explained in the text.

	Equation	Estimate	References
Theoretical sampling rates			
(1)	$K_{oa} = K_{ow}$ (RT)/H	Octanol/air partition coefficient	Shoeib and Harner (2002a,b) and Meylan and Howard (2005)
(2)	$\log K_{PUF} = 0.6366\ X_{\log}\ K_{oa} - 3.1774$	PUF/air partition coefficient	Shoeib and Harner (2002a,b)
(3)	$V_{air} = K'_{PUF} \times (0.0002^{a}) \times \{1 - \exp[-(t_{days}) \times (K_A)/(K'_{PUF})/(0.0013^{b})]\}$	Air volume	Shoeib and Harner (2002), Gouin et al. (2008) and Hayward et al. (2010)
(4)	$R_{PUF\text{-}PAS} = V_{air}/t_{days}$	Sampling rate	–
Measured sampling rates			
(5)	$R_{PUF\text{-}PAS} = M_{PUF\text{-}PAS}/(C_{PUF\text{-}AAS} \times t_{days})$	Sampling rate (side-by-side)	–
(6)	$R_{PUF\text{-}PAS} = \ln(C/C_o)^{c}$	Sampling rate (depuration compounds)	Gouin et al. (2005) and Harner et al. (2006a,b)

(–) = No reference required.
[a] Volume of PUF-PAS (m^3).
[b] Effect film thickness (m).
[c] C = final concentration of depuration compound, C_o = initial concentration of depuration compound.

2.2. Laboratory sampling rates

2.2.1. Materials

The PUF-PAS disks (14 cm in diameter, 1.3 cm thick; Tisch Environmental, Cleves OH) were pre-cleaned by soxhlet extraction with ethyl acetate at 77 °C for 1 h (~20 cycles) or rinsed with acetone and ultrasonicated for 1.5 h (2 cycles). Two cleaning methods were used to examine potential variability, but no differences were observed. The disks were dried and stored in sealed glass petri dishes. Each disk was sectioned (92.5 cm^2 surface area) to fit inside the exposure chamber.

The dynamic exposure chamber was constructed of chemically inert materials including polytetrafluoroethylene (PTFE) tubes, rubber caps, and glass inlets. The chamber was a cylindrical glass mixing container (volume = 549 cm^3) with outlets for inlet carrier/dilution flow of dry laboratory air, outlet flow, and two connections for AAS (Fig. 1). The chamber was placed in a ventilated hood and temperatures ranged from 21 to 23 °C.

A temperature-controlled DynaCalibrator (Model 230, VICI Inc, 2011) was used to deliver gas phase concentrations of OP pesticides (range 10–50 ng m^{-3}) into the exposure chamber to replicate past background community levels recently measured in central Washington State in a previous study (Fenske et al., 2009). The permeation tube was made by capping CPF (99.5%, solid, ChemService, West Chester PA, N11459) inside a PTFE tube with 10.7 cm active length. The ends were plugged with packed glass fiber and PTFE caps. The permeation tube was placed in the DynaCalibrator and weighed daily for one month to calculate an emission rate of 5.5 ng CPF min^{-1} at 35 °C. AZM was not generated in the chamber due to difficulty achieving consistent volatilization rates from the permeation device at low concentrations. This may be attributable to the lower volatility of AZM (4.7×10^{-9} mmHg at 20–25 °C) in comparison to CPF (1.9×10^{-5} mmHg at 20–25 °C).

A range of carrier and dilution flow rates were calculated for the generation of CPF in the chamber (VICI, 2011), and the final carrier flow was 10 L min^{-1} paired with a dilution flow rate of 5 L min^{-1}.

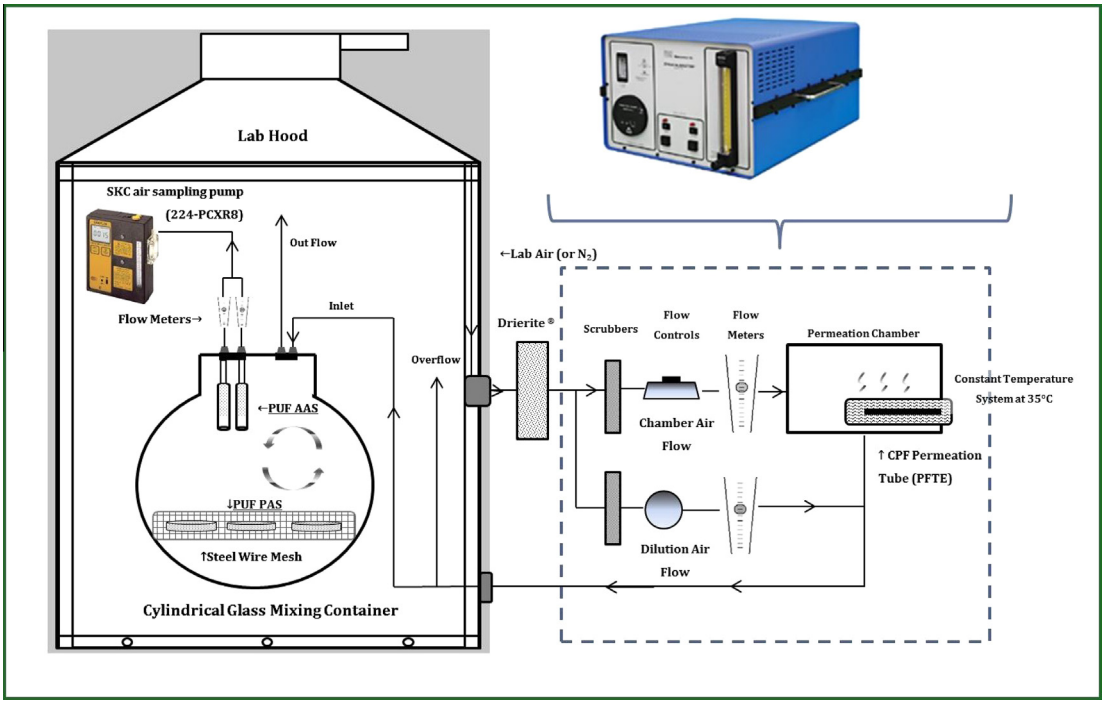

Fig. 1. Schematic of laboratory dynamic exposure chamber for PUF-PAS method development. A temperature-controlled DynaCalibrator (VICI, 2011) was used to deliver gas phase concentrations of CPF.

The DynaCalibrator was operated for 8 h prior to experiments for a well-mixed atmosphere.

2.2.2. Methods

To examine retention on the PUF disk, we deployed spiked triplicate air matrices of CPF (99.5%, 1000 μg mL^{-1} in acetonitrile, ChemService, West Chester PA, PS-674) and AZM (99.5%, 100 μg mL^{-1} in MeOH, ChemService, F2055S) in acetone of 0 and 400 ng using a 50 μl Hamilton syringe and spiking into the center of the matrix. For CPF, we also deployed spiked triplicates at a mass of 25 ng. The PUF matrix was allowed to equilibrate at room temperature for 30 min. Next, the disks were laid on steel mesh wire inside the chamber, 3 cm apart with an aluminum lid to simulate PUF-PAS conditions. They were deployed in the chamber for 0, 5, 15, and 30 d.

In the same fashion, we deployed triplicate samples spiked with 210 ng of CPF-methyl-D_6 (CPFM- D_6, 99%, 100 μg mL^{-1} in acetonitrile, EQ Laboratories, Atlanta GA) and 450 ng of azinphos ethyl D_{10} (AZE-D_{10}, 98.5%, 1000 μg mL^{-1} in toluene, EQ Laboratories) for 30 d in the chamber. Spike levels were determined by using the predicted mass from previous monitoring results in Washington State [concentration (ng m^{-3}) × t_{days} = expected mass (ng)] (Fenske et al., 2009). The theory of using depuration compounds to calculate sampling rates states that the steady loss of compounds should occur at similar rates as uptake of target compounds. This has been described in detail, as the loss from the PUF matrix has been used to calculate passive sampling rates in m^3 d^{-1} (Table 1, Eq. (6)) (Wilford et al., 2004; Harner et al., 2006a,b).

Three sets of duplicate PUF active air sampling tubes (22 × 100 mm, outer diameter × length, SKC) and PUF-PAS disks (70 mm × 13 mm, inner diameter × width, Tisch Environmental) drew air for a 24 h sample period inside the chamber. The PUF matrices were pre-cleaned with acetone by the supplier prior to purchase. The active PUF tubes were hung inside the chamber and connected to air sampling pumps (SKC, 224-PCXR8) with PFTE tubing. The pumps operated at a flow rate of 2 l per minute (LPM) and were pre- and post-calibrated with a DryCal. Eq. (5) (Table 1) was used to estimate $R_{PUF\text{-}PAS}$ from active sampling air concentrations ($C_{PUF\text{-}AAS}$). Laboratory sampling rates obtained from depuration compounds and side-by-side calibration were compared using two sample *t*-tests. Laboratory sampling rates were compared to theoretical rates using a one-sample *t*-test.

2.3. Outdoor sampling rates

A total of 66 PUF-PAS air samplers were deployed at 23 air monitor site locations across Yakima Valley, WA during the spring (March–April 2011) pre-thinning season and summer (June–August 2011) thinning season. The sample sites were scheduled in collaboration with the *Para Niños Saludables* community-based research project at twenty participant homes and three community monitoring sites (Strong et al., 2009). One community site was operated by the Washington State Department of Ecology, and two sites by Washington State University. Each PUF-PAS sampler was deployed in stainless steel housing at 1.5 m in height (Fig. 2). Inside the housing, a LogTag recorder (#TRIX-8) measured temperature (°C) in 15 min intervals. All sites were ⩽5 km to the nearest Agricultural Weather Net 2.0 station recording relative humidity and wind velocity at hourly intervals (AgWeatherNet, 2011). Each PUF-PAS was spiked with depuration compounds (CPFM-D_6 or AZE-D_{10}) for time periods of 5–30 d.

In addition, side-by-side calibration with AAS methods was conducted outdoors for 5 d at the community sites with a meteorological station. After collection, the samples were stored in sealed petri dishes, stored in a −20 °C freezer, and transported to the University of Washington Environmental Health Laboratory on dry ice.

Observed outdoor sampling rates from depuration compounds and side-by-side calibration were compared using two sample *t*-tests. Sampling rates were plotted with environmental factors (e.g., average temperature, wind speed, and humidity) using linear and exponential regression. Calculations were performed in STATA 11.2 (StataCorp LP, College Station, TX).

2.4. Extraction and analysis

PUF-PAS matrices were placed in 50 μL Corning® centrifuge tubes, with internal standard (ISTD) solutions (100 ng mL^{-1} CPF-diethyl-D_{10} in acetone, Cambridge Isotope Labs, Andover MA DLM-4360; 100 ng mL^{-1} $^{13}C_2$, ^{15}N-CPF-O in acetone, donated by Dow Agro Sciences, Indianapolis IN; 4000 ng mL^{-1} AZM-D_6 in toluene, EQ Laboratories, Atlanta GA; 1000 ng mL^{-1} AZM-OD_6 in acetone, Bayer Crop Science, Research Triangle Park, NC, K-176) and ISTD solution for depuration compounds chlorpyrifos-methyl (100 μg ml^{-1} in Acetonitrile, ChemService Inc, S-11460A1-1ML) and azinphos-ethyl (100 μg ml^{-1} in Acetonitrile, SigmaAldrich 45332-250MG). Four samples were analyzed without chlorpyrifos-methyl and azinphos-ethyl to check for their presence in ambient air and neither was detected. The ISTD were added to 10–50 mL acetonitrile and sonicated for 1.5 h at room temperature (20–23 °C), followed by evaporation at 60 °C to 1.5 mL. If particulate was present, the extract was transferred to a leur-lock 3 mL polypropylene syringe, and filtered with a PTFE syringe filter (13 mm, 0.2 μm porosity). Laboratory controls included matrix blanks and reagent blanks with acetonitrile and ISTD but no air sampling matrix.

Sample analysis was conducted using a published liquid chromatography tandem mass spectrometry (LC–MS/MS) method (Armstrong et al., 2014). Stable isotope-dilution quantification was performed on an Agilent (Santa Clara, CA) 6410 liquid chromatography tandem mass spectrometer. Electrospray ionization was used in multiple reaction mode. Reagents were acetonitrile, acetone, deionized water, and formic acid.

The limits of detection for CPF and AZM were 1 and 5 ng $sample^{-1}$, respectively; for CPF-O and AZM-O 1 and 5 ng $sample^{-1}$; and for CPF-methyl-D_6 and azinphos-ethyl D_{10}, 1 ng $sample^{-1}$. Samples were divided by $\sqrt{2}$ if below limits of detection (LOD) (Hornung and Reed, 1990).

2.5. Quality assurance

Fortification spike recoveries were a mean of 89% for CPF, 82% for CPF-O, 89% for AZM, and 78% for AZM-O from the PUF-PAS (Supplemental Material, Table 2). The final concentration, *C*, was corrected for spike recovery of CPFM-D_6 and AZE-D_{10} after sample period t_{days} = 0 [C/C_0 (Corrected)]. The mean spike recoveries for depuration compounds were 82% for CPFM-D_6; and 87%, for AZE-D_{10}. No laboratory blanks, field blanks, or reagent blanks contained measurable amounts of OP pesticides or oxygen analogs. All laboratory experiments were conducted with duplicate or triplicate samples. In the field, duplicate samples were deployed as 20% of samples.

3. Results

3.1. Recovery of OP pesticides and transformation to oxygen analogs

After 5–30 d in the exposure chamber, the percent recoveries for CPF from the PUF-PAS disk ranged from 61% to 100% for high spike masses (400 ng) and from 63% to 116% for low spike masses

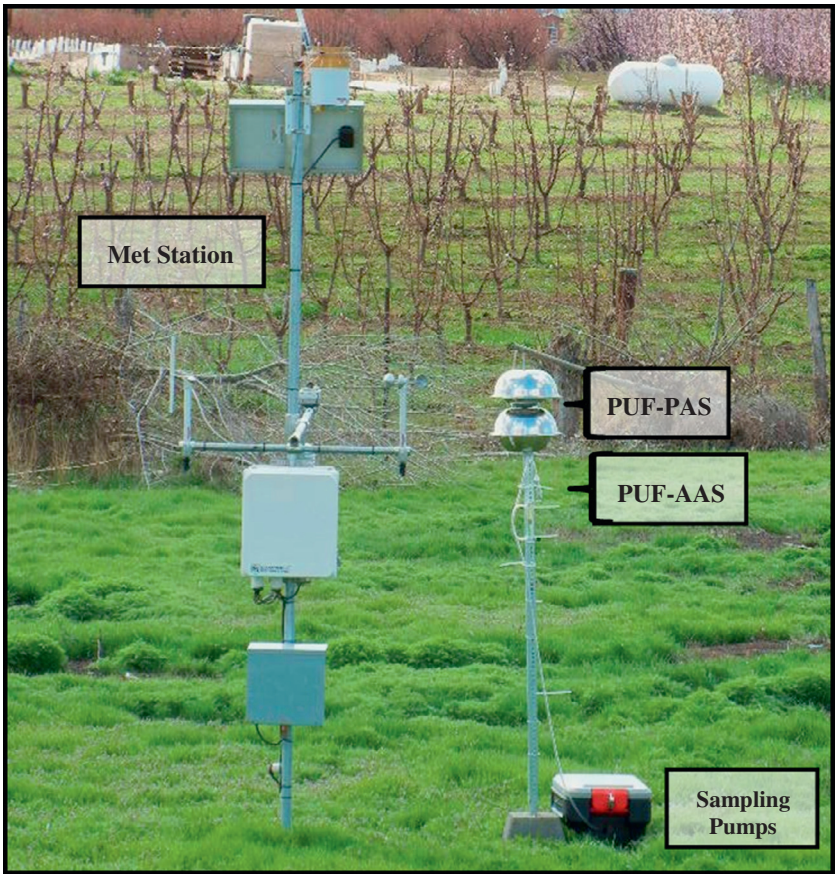

Fig. 2. Outdoor PUF-PAS testing location in Yakima Valley, WA. The PUF-PAS devices are located side-by-side with PUF-AAS tubes near an orchard and meteorological station.

(25 ng). Percent recoveries for AZM ranged from 71% to 105% for high spike masses (400 ng) (see Fig. 3A–C, Supplemental Table 3).

There was little to no conversion to the oxygen analog on the PUF-PAS after prolonged deployment in the chamber up to 30 d. Only 2 of 30 CPF-spiked samples had a CPF-O level of 1 ng (<2%) after the longest time period (30 d) and no spiked samples of AZM had detectable AZM-O.

3.2. Exposure chamber and outdoor air sampling rates

After 30 d in the exposure chamber, the percent recoveries for CPF-D_6 and AZE-D_{10} were lower than the parent compounds, at 33–50% and 87–89% respectively. We expect the loss of the depuration compounds to be comparable to the loss of parent compounds. Optimal depuration compound recoveries should be >20% to ensure that the PUF-PAS is not reaching equilibrium (Soderstrom and Bergqvist, 2004).

Overall, sampling rates in the exposure chamber were lower than outdoors. For CPF, the loss of depuration compound corresponded to a mean indoor $R_{PUF\text{-}PAS}$, of 2.25 $m^3\ d^{-1}$ in the exposure chamber, which was not significantly different from the outdoor mean of 3.12 $m^3\ d^{-1}$ (Table 2). For AZM, the loss of depuration compound corresponded to a $R_{PUF\text{-}PAS}$ of 3.04 $m^3\ d^{-1}$ in the exposure chamber, which was significantly lower than the outdoor mean of 4.72 $m^3\ d^{-1}$ ($p < 0.05$).

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 2. For CPF, all observed $R_{PUF\text{-}PAS}$ were similar to the expected rate of 3.37 $m^3\ d^{-1}$. The mean exposure chamber $R_{PUF\text{-}PAS}$ was not statistically different from the mean $R_{PUF\text{-}PAS}$ determined by side-by-side calibration, and the mean outdoor $R_{PUF\text{-}PAS}$ was not statistically different from the mean $R_{PUF\text{-}PAS}$ determined by side-by-side calibration. An outdoor 4 weeks sample period for CPF corresponded to air sample volumes ranging from 63 to 225 m^3.

For AZM, the mean exposure chamber $R_{PUF\text{-}PAS}$ of 3.04 $m^3\ d^{-1}$ was near the theoretical value of 3.69 $m^3\ d^{-1}$. Side-by-side calibration was not conducted in the exposure chamber due to difficulties in achieving steady, low concentrations of AZM. The mean outdoor $R_{PUF\text{-}PAS}$ determined by depuration compounds was 4.72 $m^3\ d^{-1}$, and was not significantly different from the mean $R_{PUF\text{-}PAS}$ determined by side-by-side calibration (4.92 $m^3\ d^{-1}$). Therefore, an outdoor 4 weeks sample period for AZM corresponded to an air sample volume ranging from 69 to 252 m^3. The outdoor air volumes for both CPF and AZM had large ranges, and were likely influenced by meteorological factors. These factors are explored in the following section.

3.3. Outdoor factors influencing air sampling rates

During the spring and summer application seasons, wind velocity, temperature, and relative humidity were examined for their potential effects on sampling rates using exponential and linear regression. For CPF, there was no statistically significant relationship between $R_{PUF\text{-}PAS}$ and average temperature or humidity, although there were slight trends of increased sampling rates with increased temperature (°C) and relative humidity (%) (Supplemental Fig. 1A and B). However, there was an exponential relationship between wind velocity and sampling rate (Fig. 4A and B). In Fig. 4A, two samples had very large air sampling rates with recoveries of CPF-methyl-D_6 < 15%. The low recovery of depuration compound indicated these two samples were approaching equilibrium.

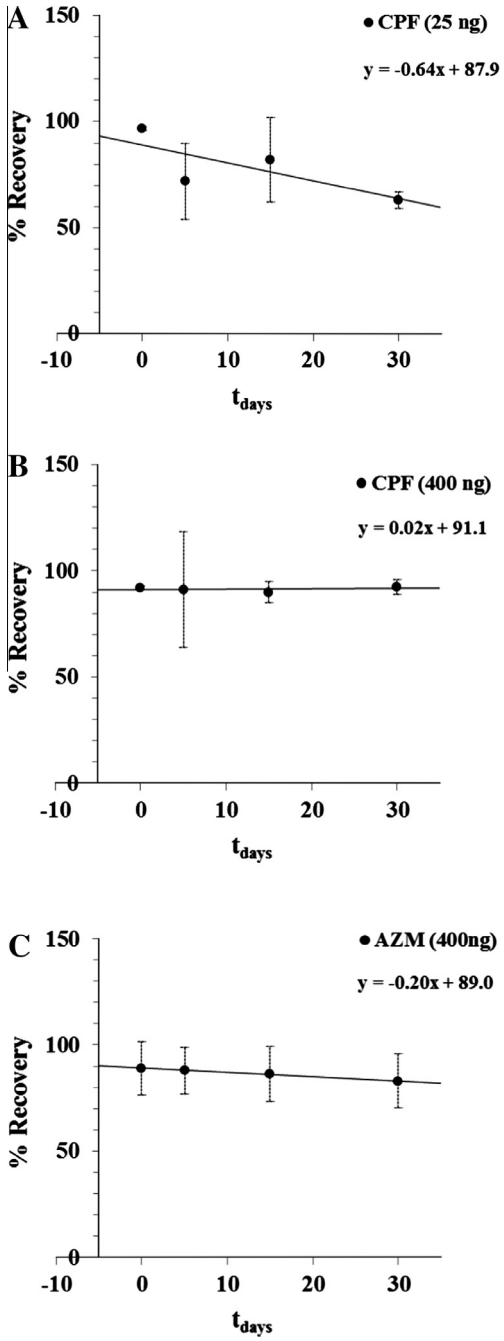

Fig. 3. (A–C) Percent recoveries CPF and AZM from PUF-PAS after 0, 5, 15, and 30 d in an exposure chamber.

For AZM, there was no statistically significant relationship between air sampling rates and average temperature ($R^2 = 0.05$). There was a linear trend toward small increases in $R_{PUF\text{-}PAS}$ (0.12 $m^3\ d^{-1}$, 95% C.I. 0.01–0.23) with each percent increase in relative humidity ($R^2 = 0.17$), but this was not significant ($p = 0.17$) (Supplemental Fig. 1C and D). AZM has a slightly lower octanol/water partition coefficient and is slightly more hydrophilic than CPF, which may have affected the partitioning from to the PUF-matrix (Noble, 1993; Rice et al., 1997). Similar to CPF, there was an exponential relationship between wind speed and sampling rate for AZM (Fig. 4B).

3.4. Discussion

This study included theoretical calculation, laboratory and field performance tests, and side-by-side comparisons with traditional AAS methods to test PUF-PAS for measurement of airborne OP pesticides. Although airborne exposure measurements with AAS can help identify peak exposures, we have found the PUF-PAS to be a useful option for measuring cumulative concentrations of both OP pesticides and their oxygen analogs. It should be noted that the PUF-PAS will not respond to large fluctuations in air concentrations and is not appropriate for estimating short-term concentrations. However, there are many well-known benefits to using the PUF-PAS in remote and agricultural communities (Supplemental Material, Table 1). To avoid issues with LOD, researchers will need to have an idea of expected airborne concentrations prior to pursuing passive sampling.

Most of the initial tests on PUF-PAS in the laboratory yielded acceptable percent recoveries and we were confident that the samplers would not approach equilibrium after 30 d, if located indoors. However, there was some error in recovering low spike masses (<1 μg) from a large sampling matrix with precision. Some of the lowest spike recoveries were <65%, and there was large variation in percent recovery among triplicate samples observed after 5 d (see Fig. 3A and B).

Previous studies have demonstrated higher outdoor sampling rates due to meteorological factors influencing uptake (Tuduri et al., 2006; Hazrati and Harrad, 2007). During the outdoor studies, two CPF samples had percent recoveries <15% for chlopyrifos-methyl-D_6. This likely occurred due to higher than expected sampling rates under such windy conditions in the lower Yakima Valley. In retrospect, shortened sampling periods ($t_{days} < 30$, ~2 weeks) would have been preferred if we were certain that wind velocities would exceed 8 m s^{-1}. Future studies should incorporate modifications to the PUF-PAS in order to handle high wind velocities and presence of agricultural dusts. Such an improvement would be a protective stainless steel mesh or a glass fiber (<2 mm in diameter) placed between the 1.5 cm gap between the stainless steel chamber encasements, rather than leaving it open to rapid air movement. An additional benefit to this design would

Table 2
Sampling rates $R_{PUF\text{-}PAS}$ ($m^3\ d^{-1}$) for CPF and AZM. Laboratory and field sampling rates were compared to theoretical sampling rates with a one-sample *t*-test.

Passive methods development		Chlorpyrifos (CPF) $R_{PUF\text{-}PAS}$ $m^3\ d^{-1}$, (range)		Azinphos methyl (AZM) $R_{PUF\text{-}PAS}$ $m^3\ d^{-1}$, (range)
Expected				
Theoretical estimates		3.37		3.69
Observed	(N)		(N)	
Laboratory performance, DC	3	2.25 (1.42–2.89)	3	3.04 (1.12–4.78)
Laboratory comparison w/AAS	6	2.34 (1.60–2.99)	NA	NA
Field comparison w/AAS[a]	6	3.23 (2.47–4.39)	6	4.92[b] (4.36–5.50)
Field performance, DC	22	3.12 (2.10–7.49)	24	4.72[b] (2.29–8.42)

N = number of samples; DC = depuration compounds.
[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 ($\alpha = 0.05$).

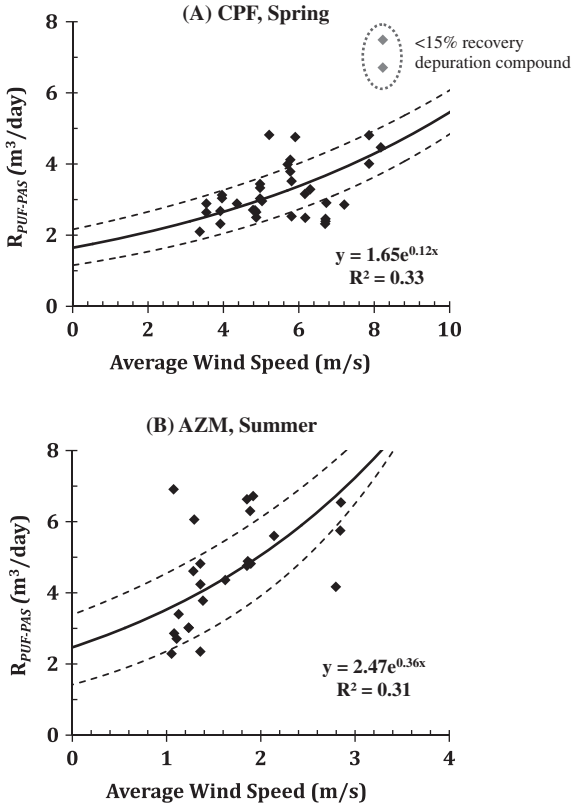

Fig. 4. (A and B) Sampling rates $R_{PUF-PAS}$ ($m^3\ d^{-1}$) and average wind velocities. Scatter plots with exponential fit demonstrating the effects of average wind velocity ($t_{days} = 30$) and measured sampling rates for CPF and AZM with depuration compounds. Wind velocities during the spring were greater than during the summer. (A and B) Sample rates by average wind velocity. Two data points >8 m s^{-1} had recoveries of depuration chlopyrifos-methyl-D_6 < 15%.

have been the protection against larger particles settling on the PUF disk as a result of wind (Fig. 5), and fewer steps in the treatment of these particles during sample extraction.

Although there was a linear relationship between increased $R_{PUF-PAS}$ and relative humidity for AZM, it was not significant. We did not observe a statistically significant relationship between air sampling rates and temperature, even though we expected changes in samplings rate with temperature due to its effect on gas-particle partitioning (Jayward et al., 2004). During the outdoor sample period, there was little geographical variation in average monthly temperatures across sampler locations (spring temperatures ranged 6–14 °C and summer temperatures ranged 20–23 °C). Due to the limited time periods of pesticide application in Washington State, we were unable to perform all dynamic exposure studies on different temperatures and humidity prior to field deployment. Before the sampler is utilized in widely varying temperature conditions, it is recommended that more dynamic exposure chamber tests examine these factors (e.g. effects of temperatures >25 °C) in a highly controlled environment.

Finally, the study was limited by the chemical data on OP pesticides and their oxygen analogs. The theoretical estimates and depuration compound calculations for $R_{PUF-PAS}$ consider the gas-phase of OP pesticides. Although this may capture distant transport via volatilization, it may not account for particle-bound OP pesticides (i.e., on foliar residues, agricultural dusts). In addition, there is a lack of data on chemical properties of oxygen analogs; therefore we assumed their sampling rates to be equivalent to the parent compound.

4. Conclusions

In future studies, PUF-PAS can serve as a practical alternative to AAS because it results in little artificial transformation to the oxygen analog during sampling, provides cumulative weekly or monthly exposure estimates, and is more convenient to be deployed in remote locations with no electricity. Similar to previous studies, the outdoor experiments identified the presence of oxygen analogs in the environment. Substantial proportions (1–35%) of CPF-O and AZM-O were present on PUF-PAS devices after outdoor deployment. In a controlled exposure chamber, we demonstrated little artificial transformation to the analog during sampling, as

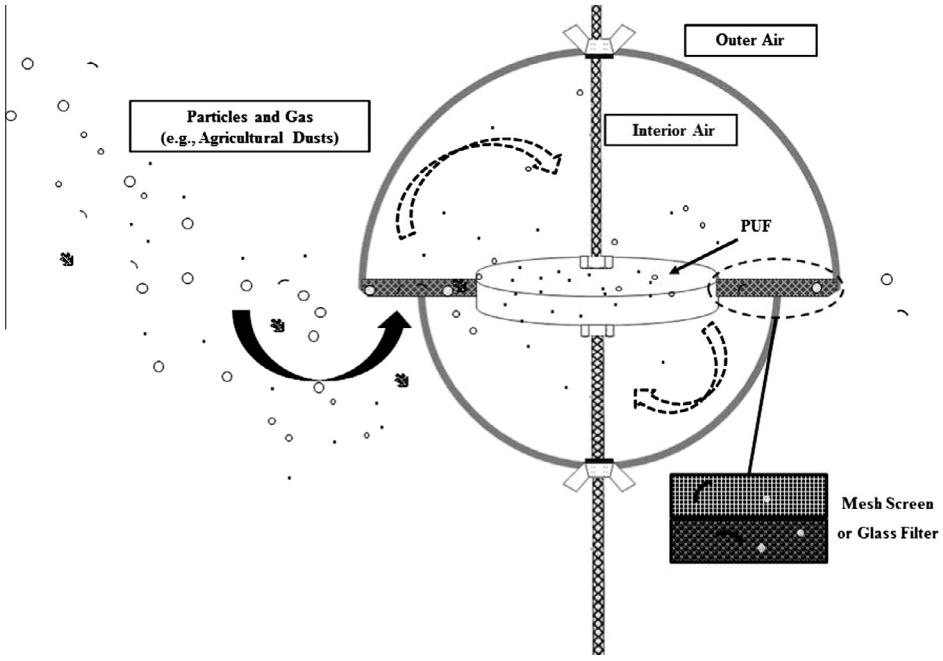

Fig. 5. Modified PUF-PAS for high wind velocities and filtering of agricultural dusts.

only 2 of 30 CPF-spiked samples reported <1 ng CPF-O and no AZM-O was identified.

Reported $R_{PUF\text{-}PAS}$ in the dynamic exposure chamber for both CPF and AZM were not markedly different from theoretical calculations. There was good agreement between $R_{PUF\text{-}PAS}$ calculated with depuration compounds and side-by-side calibration with AAS. As we expected, all measured sampling rates in the exposure chamber were significantly lower than rates outdoors. We observed a significant relationship between increased $R_{PUF\text{-}PAS}$ and elevated wind velocities, specifically >8 m s^{-1}.

The air measurements were greatly enhanced with the use of a recently published LC–MS/MS chemical analysis, which allowed for the use of large extraction volumes from the PUF disks and low limits of detection ranging 1–5 ng $sample^{-1}$ (and lower levels of quantification ranging 0.02–0.1 ng m^{-3}) (Armstrong et al., 2014). Even though some error was associated with the extractions of such small amounts from the larger sample matrix, we believe the sensitive analysis from a passive device was a major achievement. These passive sampling methods will improve our understanding of fate and transport of these OP pesticides in residential communities. The methods are useful when the exact timing and locations of applications are unknown. Passive sampling is ideal for community based participatory research due to low subject burden and simple deployment in remote areas where AAS is impractical.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2014.03.064.

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