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Comparison of polyurethane foam and XAD-2 sampling matrices to measure airborne organophosphorus pesticides and their oxygen analogs in an agricultural community

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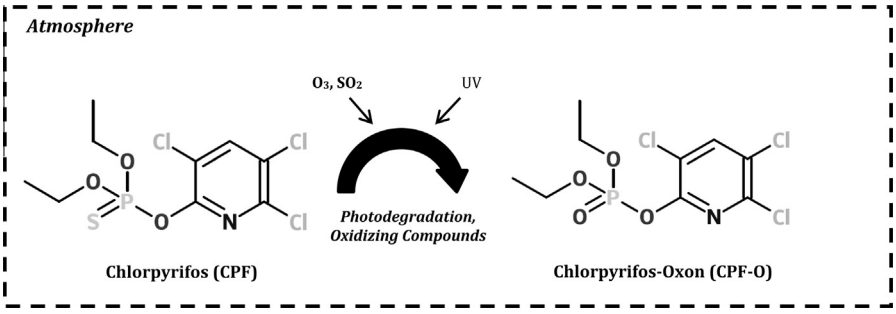
HIGHLIGHTS

- XAD-2 matrices artificially transform OPs to oxygen analogs during air sampling.
- PUF matrices are the superior method for air sampling OP/oxygen analog mixtures.
- Higher levels of more potent oxygen analogs are detected in air post-application.
- Higher concentrations oxygen analogs are detected farther distance from the source.
- Larger % OP oxygen analogs are identified in vapors than deposited particulate.

GRAPHICAL ABSTRACT



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ABSTRACT

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, polyurethane foam (PUF) tubes, and passive PUF deposition disks. The study compared the proportion of artificially transformed CPF-O in the laboratory and in the field during a tree fruit application in Washington State. Lab results demonstrated that the NIOSH-recommended OVS tubes artificially transformed up to 32% of CPF to CPF-O during the sampling process, whereas PUF tubes had little to no artificial transformation ($\leqslant$0.1%). In the field, the proportion of CPF-O in the sample was significantly higher on OVS tubes than on PUF tubes ($p < 0.001$), confirming 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 even when no artificial transformation was expected. We conclude that the PUF matrix is the superior sampling medium for OP oxygen analogs when compared to XAD-two resin. Community-located PUF tube samples 24 h post-application had considerably higher levels CPF-O (16–21 ng m^{-3}) than near field samples during application (2–14 ng m^{-3}), suggesting that the oxygen analog is volatile and formed during atmospheric transport. It is recommended that worker and community risk assessments begin to take into consideration the presence of the more toxic oxygen analogs when measuring for OP pesticide mixtures.

Abbreviations: CPF, chlorpyrifos; CPF-O, chlorpyrifos-oxon; LPM, liters per minute; LOD, limit of detection; OP, organophosphorus; OVS, OSHA versatile sampler; PUF, polyurethane foam.

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1. Introduction

Numerous toxicological studies have examined the relative potency of organophosphorus (OP) pesticides and their oxygen analogs in animal models (Chambers and Carr, 1993; Costa et al., 2005; Cole et al., 2005, 2011). These studies have found the toxicity of the oxon to be 5–100 times as toxic as the parent OP pesticide. This may pose a risk for genetically susceptible individuals who have lower levels of the paraoxonase enzyme[PON-1(-/-) genotypes]). Paraoxonase plays a critical role in biotransformation of OPs in humans, and 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).

OP pesticides that are used for agricultural applications may persist in the air as primary aerosols, be adsorbed onto other particulate matter, or be present in the vapor phase. All of these have potential for atmospheric transport and may undergo photolysis or reaction with oxidizing agents. Although oxygen analogs are formed *in vivo* as a metabolic product through breakdown mechanisms involving cytochrome p450 enzymes, recent evidence demonstrates that they can also be formed in the environment under certain conditions [See Fig. 1 (Timchalk et al., 2007; Armstrong et al., 2013; CARB, 1996)]. Past studies that have measured airborne exposures to both OP pesticides and their oxygen analogs have been primarily outdoor community studies (CARB, 1996; CDPR, 2003, 2006; Fenske et al., 2009), due to the importance of health risk assessments for young children as a susceptible population of concern.

Currently, three established methods for low volume active air monitoring for these compounds rely on collection with polyurethane foam (PUF) or XAD-2 resin matrices. XAD-4 resins are also used primarily in high volume sampling and not explored in this study. Both PUF and XAD-2 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); NIOSH Method 5600 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. Low volume OVS tubes containing XAD-2 may be as small as 8 mm diameter $\times$ 75 mm length (140/270 mg sorbent) in comparison to the more common 22 $\times$ 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 oxygen analogs.

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 5–30% of CPF was artifactually converted to chlorpyrifos-oxon (CPF-O), especially at lower concentrations ($\leqslant$30 ng m^{-3}) that are typical of previously reported community levels (Fenske et al., 2009; Armstrong et al., 2013). 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 oxygen analog formation from other OP pesticides (e.g., parathion) when actively sampling with XAD resins (Woodrow et al., 1978; Seiber et al., 1989).

However, none of the three OP pesticide air sampling methods discussed earlier (ASTM, EPA and NIOSH) include chemical analysis for the oxygen analogs. This means that results from studies using OVS tubes are likely underestimates of 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-2 in commercially prepared tubes) 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. XAD-2 resins were not explored passively due to difficulties arising from the physical disturbance of small macroreticular beads. We placed the passive collectors in areas directly near applications side by side with the active samples. Passive methods have not been formally reviewed by the EPA or ASTM, but past research has identified that deposition may be informative for surface area loading 2–4 h following a pesticide application (Tsai, 2007). In addition, such passive methods are very low cost and do not require an electricity source.

2. Materials and methods

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

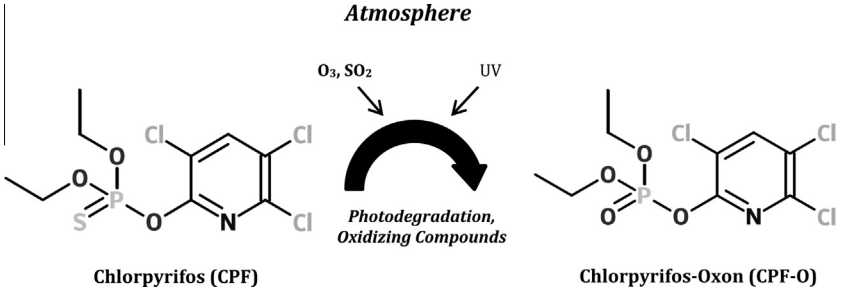

Fig. 1. Recent evidence demonstrates that CPF may undergo photolysis or reaction with oxidizing agents during atmospheric transport in the environment.

(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 2 L min^{-1} (LPM) for 24 h. 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).

2.2. Field

Twelve pairs of OVS/PUF tubes were co-located near an apple orchard during an air blast application of Lorsban® [a typical formulation contains 40–45% CPF active ingredient (Dow AgroSciences, 2002)] in Washington State's Yakima Valley in March 2010. Samples were hung side by side on a 1.5 meter (m) air sampling mast (Fig. 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 and far from the field perimeter. To capture air concentration data representative of higher levels, eight pairs of sampling tubes were co-located 6–8.5 m from the orchard perimeter in the four primary wind directions. Pumps were operated at 6 LPM for 6 h 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 h 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. 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 the site was 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.

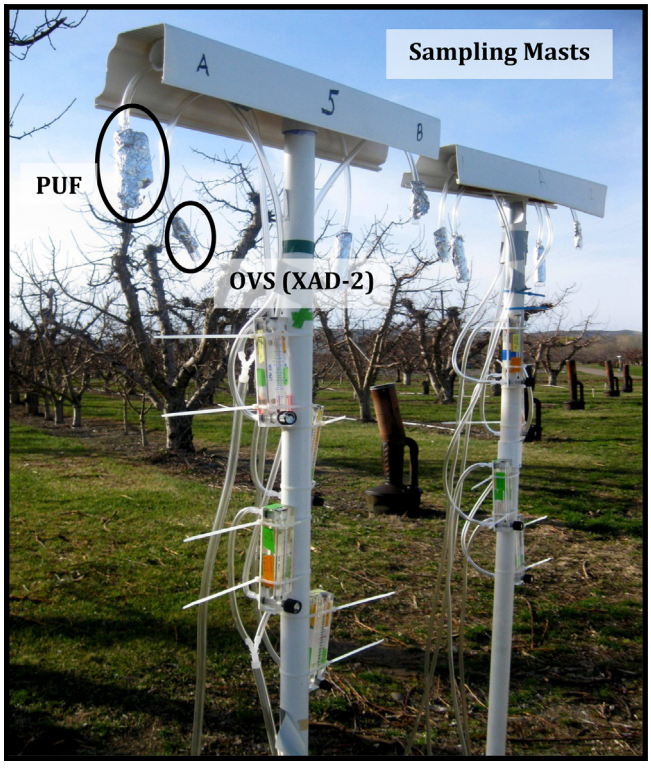

Fig. 2. Side by side collection PUF and OVS sampling matrices. Samples were co-located, hung from sampling masts, and wrapped with aluminum foil to reduce potential reactions with UV light. Flow rates were recorded using rotameters.

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 1 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 h later. Field researchers wore personal protective equipment including coveralls, nitrile gloves, boots, and goggles 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™). 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 in Seattle.

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 (0.1 ng); 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 T Test for paired samples. Similar to previous studies (Fenske et al., 2009; Armstrong et al., 2013), we estimated the %CPF-O while adjusting for the difference in molecular weight.

3. Results

3.1. Laboratory

As indicated in Table 1, recoveries were lower for OVS tubes (mean 78.5%) than for PUF tubes (mean 100.6%) or PUF deposition plates (mean 90.2%) and all recoveries were in the acceptable range of 60–120% (EPA, 1999). 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 only very small amounts artifact formation of CPF-O (0.1%) at spike levels $\geqslant$2000 ng, and PUF deposition plates also yielded no detectable CPF-O formation.

3.2. Field

3.2.1. Perimeter samples

During the pesticide application, outdoor temperatures ranged from 2 to 14 °C and wind conditions were relatively calm, with northwesterly winds at an average speed of 1.3 m s^{-1} (wind rose data available in supplementary figures). As indicated in Fig. 3, measured CPF air concentrations near the orchard ranged from 32 to 647 ng m^{-3} on OVS, and 97 to 2039 ng m^{-3} on PUF. Overall, the mean CPF concentrations on PUF tubes were significantly greater than the mean concentrations on OVS tubes ($p \leqslant 0.001$).

Mean air concentrations were strongly influenced by wind patterns. The east and south directions perimeter (downwind) reported air concentrations more than four times higher than in the north and west (upwind). 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 ($p \leqslant 0.001$): mean values were only 1–2% on the PUF matrix; mean values ranged from 4% to 13% on the OVS matrix. In both cases, %CPF-O had an inverse relationship to total CPF air concentration.

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 Fig. 4 ($p = 0.0001$). 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 h 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 to 0.21 mg m^{-2}) near the field.

3.2.2. Community samples

The 24-h post application community samplers measured CPF air concentrations that ranged from 375 to 660 ng m^{-3} on the OVS, and 965 to 1162 ng m^{-3} on the PUF, with mean concentrations of 500 and 1100 ng m^{-3}, respectively. Mean concentrations on PUF tubes were significantly greater than concentrations measured by OVS tubes ($p \leqslant 0.001$). Although the samples were located further away than the perimeter samples and continued 24 h post application, the measured concentrations were within the range of the orchard perimeter concentrations. During the sampling period following application, outdoor temperatures ranged from 8 to 18 °C and wind speed (1.2 m s^{-1}) 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 ($p \leqslant 0.001$, See Fig. 2). In addition, all community samples had higher %CPF-O than the orchard perimeter samples during application for both matrices ($p < 0.01$).

Table 1
Total mass CPF (ng), percent CPF-O, and percent recovery in laboratory measured after 24 h 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, ×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% and 120% (EPA, 1999). Recoveries >100% were likely due to small amounts of spiking error, laboratory blanks demonstrated no contamination with CPF or CPF-O.

4. Discussion

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. If researchers are interested in measuring airborne concentrations of both CPF and CPF-O, PUF is the superior sampling matrix when compared to XAD-2.

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.

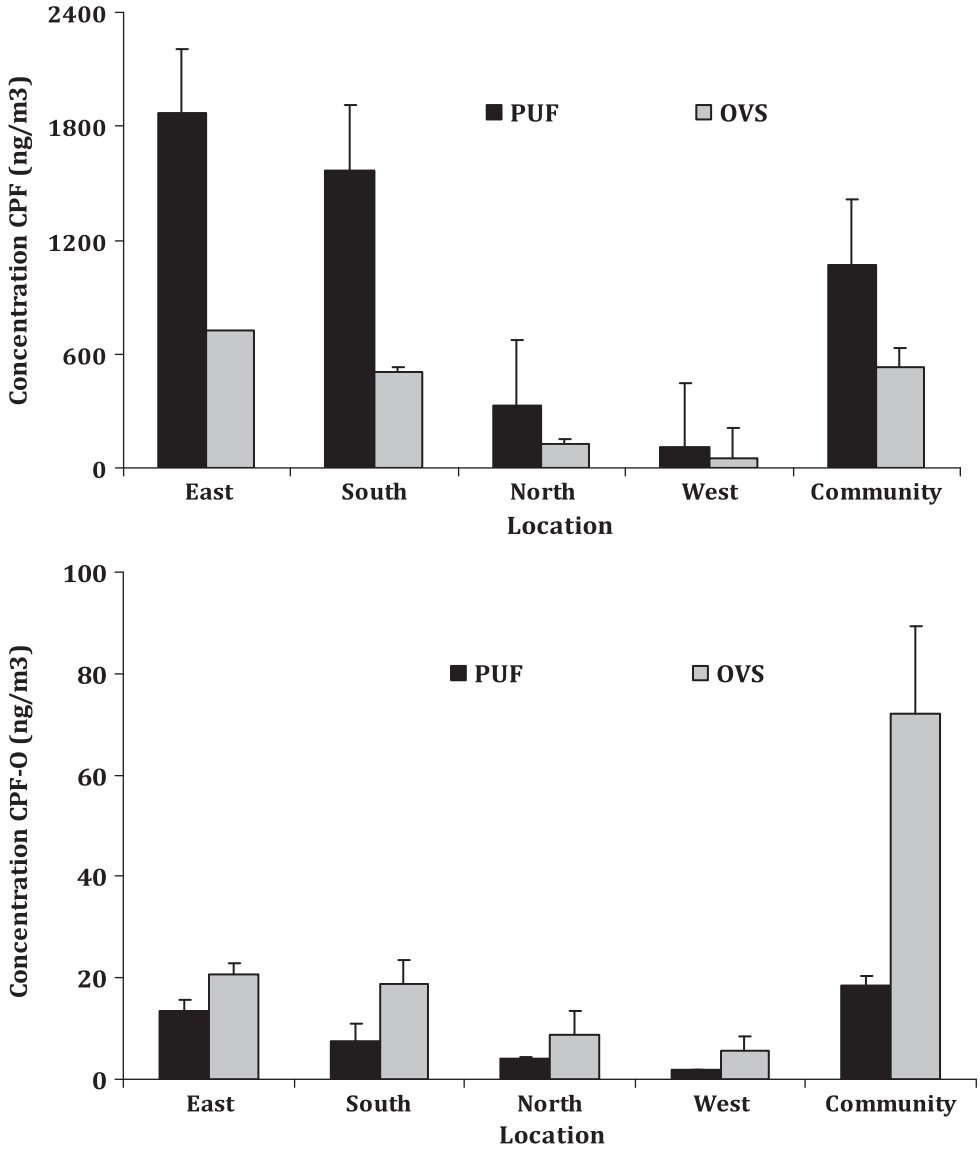

Fig. 3. Side-by-side PUF and OVS Comparison of near field CPF and CPF-O sampling (orchard perimeter) during an application (6 h sampling period) and far field sampling (community) post application (24 h sampling period). Bars and whiskers represent mean and standard deviation values, respectively.

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 currently recommended by the EPA (Method TO-10A) (1999) and may strongly influence regulatory decision making.

4.2. Environmental 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 16–21 ng m^{-3} in community samples post application) were still observed on PUF in the field. These experiments confirmed that the CPF-O is likely environmentally present in air and should be a concern in health risk assessments. Unlike measured concentrations of its parent compound, levels of CPF-O were found to be even higher 24 h post application (See Fig. 3).

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. Some researchers speculate the oxygen analogs have slightly higher vapor pressures than their parent compound, leading to potentially greater dispersion and longer half-life in air (Van den Berg et al., 1999). Further tests should examine the presence and levels of environmental CPF-O over time, and if these amounts differ in particulate vs. vapor.

The 24 h post application community samples reported concentrations similar to 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 h following application (Zhou et al., 2010). In Fig. 3, the community samples report significantly higher concentrations CPF-O (ng m^{-3}) and %CPF-O than in the orchard perimeter samples on both PUF and OVS tubes. We

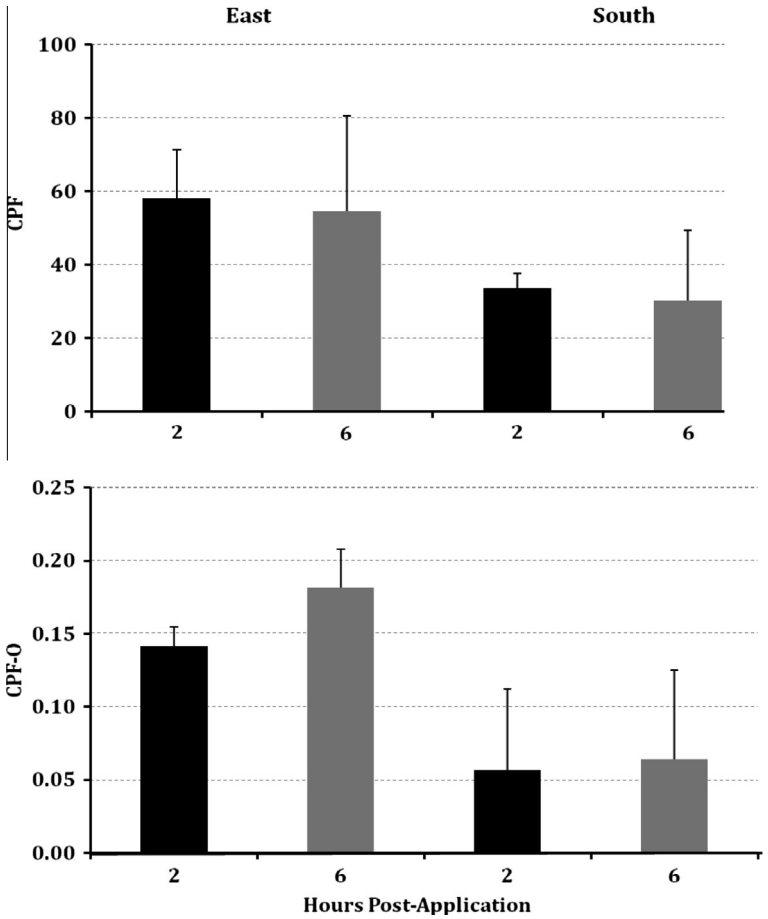

Fig. 4. Mass loading (mg m^{-2}) for chlorpyrifos (CPF) and chlorpyrifos-oxon (CPF-O). Particle deposition sampling after removal upon re-entry 2 h later and an extended 6 h later, near the orchard perimeter. Bars and whiskers represent mean and standard deviation values, respectively.

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. Our findings support previous research by Aston and Sieber (1997) that demonstrated increasing CPF-O residues with residence time in air. The previous study used a different method including examination of residues on pine tree needles, but also found that sampling locations further from the source of CPF had increased oxygen analog ratios in light of lower amounts of measured OP pesticide residues.

5. Conclusions

Both the presence of CPF-O and high concentrations of total CPF in these representative community samples are a concern when considering potential exposures to humans living in nearby residential areas. Future research should employ the PUF sampling matrix in residential air monitoring studies, with a focus on the influence of meteorological factors (e.g., wind and temperature) on the environmental transformation of OP pesticides to their oxygen analogs. It is likely that the formation of oxygen analogs will be of increasing importance as climate change produces increased ultraviolet radiation, higher temperatures, greater concentrations of oxidizing compounds in the atmosphere (e.g., ozone), and additional pesticide applications due to changing pest lifecycles (Boxall et al., 2008).

CPF-O is an important part of the mixture when considering total concentrations of OP pesticides, but is often not measured. The failure to account for CPF-O will lead to an underestimation of total CPF pesticide concentrations in many cases.

We have found the NIOSH recommended sampling matrix (OVS tubes with XAD-2 resin) to artificially transform substantial amounts CPF to CPF-O in both the lab and field; and that this leads to inaccuracies in reported levels CPF and CPF-O in field studies. 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. Based on these findings, we cannot conclude that PUF is superior to XAD resin in all cases; a limitation to this study was that the XAD-4 resins commonly used in high volume sampling were not tested. The method of preparing or cleaning the resin for sampling may also influence the accuracy of sampling for OP pesticides and oxygen analogs. Nevertheless, these findings demonstrate that researchers can use the PUF matrix as an alternative to properly quantify exposures to CPF-O in the environment.

Acknowledgments

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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.2013.01.109.

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