



Presence of organophosphorus pesticide oxygen analogs in air samples

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H I G H L I G H T S

- ▶ 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.

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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 exposures.

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1. Introduction

Although banned for residential use in 2000, the common organophosphorus pesticide chlorpyrifos (CPF) remains an

effective tool for agricultural protection from more than 200 pests. CPF continues to be widely used because few chemical substitutes are as effective. In Washington State, CPF is often applied in aerosolized form to tree fruits and vegetables using a large sprayer attached behind a tractor. A number of past studies have found that some semi-volatile organophosphorus pesticides (OP) can drift in air far from source of application, as indicated in past community studies (see Table 1). Recent monitoring in the agricultural regions

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Table 1
Occupational and community chlorpyrifos and chlorpyrifos-oxon air monitoring studies since 1996.

Air concentration range > MDL ^a (ng m ⁻³)		Sampling location	Sampling medium (resin)	Analytical method	MDL ^a (ng m ⁻³)	Reference
Chlorpyrifos	Chlorpyrifos-oxon					
Occupational studies						
48–2000	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
16–1340	16–230	Tulare County, CA	XAD-4	GC–MS	5.25	CARB, 1998b, 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 and Hornbuckle, 2005
5000 (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	5×10^{-4} – 8×10^{-4} ^b	LeNoir et al., 1999

^a Method detection limit.

^b High volume sampling.

of California and Washington has reported both the parent compound (CPF) and the presence of chlorpyrifos-oxon (CPF-O), the oxygen analog of CPF, in community air samples.

The airborne presence of the oxons of OP pesticides is a human health concern because *in vivo* toxicity studies have found that the toxicity of the oxon can be 5–100 times more toxic than the parent OP pesticide (Chambers and Carr, 1993; Cole et al., 2005, 2011; Huff et al., 1994; Timchalk et al., 2007). CPF-O is believed to pose a special risk for genetically susceptible individuals who have lower levels of the paraoxonase [PON-1(–/–)] enzyme playing a key role in metabolism of OPs in the body. In addition, 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). The presence of oxon in community air samples is a concern because children may be particularly susceptible to its toxicity (Harnly et al., 2005; Costa et al., 2005) due to differences in metabolic functioning during development.

CPF-O may be present in the atmospheric environment, as the transformation of OP pesticides to their oxons has been documented for foliar residues (Popendorf and Leffingwell, 1978; Spear et al., 1978) and in air samples (Seiber et al., 1989). The environmental formation of oxons has been attributed to conditions such as higher temperatures, ozone, dry weather, or photodegradation via ultraviolet light (Spear et al., 1978; Aston and Seiber, 1997; Bavcon Kralj et al., 2007). Very little is known about transformation or changes in levels of CPF-O as the total pesticide mixture drifts from site of application to more residential areas.

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), with higher proportions oxon being reported at residential locations >250 m from agricultural fields. This was a concern for public health because the study area is home to many farmworker families, and greater than a third of the population consists of children and adolescents <18 years of age (US CENSUS, 2010). The oxon represented as much as 94% percent of the total CPF in some cases; this raised the issue of potential transformation during air sampling. It is important to rule out sampling transformation in order for researchers to correctly assess health risk from exposure to airborne CPF-O.

The 2008 Washington study used OSHA Versatile Sampling (OVS) tubes, a popular sampling matrix that contains XAD-2 resin. The OVS tube is part of the standard method recommended by the

National Institute for Occupational Safety and Health (NIOSH, 1994), and the XAD-2 resin is identified in current guidance documents as an appropriate sampling matrix by the U.S. Environmental Protection Agency and the American Society for Testing and Materials (USEPA, 1999; ASTM, 2011). The resin has been used in a large number of community and occupational air sampling studies (Table 1).

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. 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. Sampling methods

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 6 L per minute (LPM) for approximately 24 h. 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, 1998a; CDPR, 2003; Fenske et al., 2009). Larger spike masses were applied at higher flow rates (~6 LPM) 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

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