UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON D.C., 20460

OFFICE OF
CHEMICAL SAFETY AND
POLLUTION PREVENTION

MEMORANDUM

DATE: January 31, 2013

SUBJECT: **Chlorpyrifos**; Preliminary Evaluation of the Potential Risks from Volatilization

PC Code: 059101	**DP Barcodes:** 399484 and 400781
Decision No.:	**Registration No.:** varied
Petition No.: N/A	**Regulatory Action:** Registration Review
Risk Assessment Type: Volatilization	**Case No.:** N/A
TXR No.: N/A	**CAS No.:** 2921-88-2
MRID No.: NA	**40 CFR:** N/A

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1. EXECUTIVE SUMMARY

1.1. Introduction

This assessment supplements the June 2011 Chlorpyrifos Preliminary Human Health Risk Assessment for Registration Review (HHRA)[1] and the recent spray drift assessment[2] by evaluating the potential risk to bystanders, from exposure to vapor phase chlorpyrifos and chlorpyrifos-oxon emitted from treated fields following the application of chlorpyrifos. For the purposes of this analysis bystanders are those who live and/or work in proximity to treated fields, including children. Pesticides emitted from treated fields can travel to non-target areas which, depending on concentrations, could present a risk of concern. Bystander exposure from chlorpyrifos and chlorpyrifos-oxon emitted from treated fields depends on two main factors: 1) the rate at which these chemicals are emitted (described as the off-gassing, emission or flux) off treated surfaces such as crops and 2) how those vapors disperse in the air over and around the treated field.

This assessment employs approaches EPA has used previously to assess inhalation exposures to fumigant pesticides[3,4]and is consistent with the recommendations of the December 2009 Federal Insecticide, Fungicide, and Rodenticide Act Scientific Advisory Panel (SAP)[5] meeting on the scientific issues associated with field volatilization of conventional (semi-volatile) pesticides.

1.1.1. Toxicity

This evaluation of bystander risk from chlorpyrifos volatilization focuses only on the inhalation route of exposure. This volatilization assessment is based on an acute inhalation toxicity study[6] using aerosolized chlorpyrifos which measured lung, plasma, red blood cell (RBC), and brain

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[1] Drew, D.; Britton, W.; Soderber, D.; Negrón-Encarnación, I.; Christensen, C.; Lowit, A.; Irwin, W.; Doherty, J.; Smegal, D. U.S. EPA Office of Chemical Safety and Pollution Prevention, Chlorpyrifos: Preliminary Human Health Risk Assessment for Registration Review, June 30, 2011 PC Code 059101 DP Barcode: 388070; EPA-HQ-OPP-2008-0850-0025

[2] Dawson, J.; Bohaty, R.; Mallampalli, N. U.S. EPA Office of Chemical Safety and Pollution Prevention, *Chlorpyrifos—Evaluation of the Potential Risks from Spray Drift and the Impact of Potential Risk Reduction Measures*, **June 20, 2012** PC Code 059101, DP Barcode 399483 and 399485; EPA-HQ-OPP-2008-0850-0105

[3] U.S. EPA 2004d. FIFRA Science Advisory Panel Meeting Minutes - Fumigant Bystander Exposure Model Review: Probabilistic Exposure and Risk Model for Fumigants (PERFUM) Using Iodomethane as a Case Study. Available at http://www.epa.gov/scipoly/sap/meetings/2004/august1/august2425minutes.pdf, also refer to the following for additional information http://www.epa.gov/oppsrrd1/reregistration/soil_fumigants/

[4] The assessments can be found in the dockets for each fumigant. Four of which are provided here chloropicrin - EPA-HQ-OPP-2007-0350; dazomet - EPA-HQ-OPP-2005-0128; metam sodium/potassium - EPA-HQ-OPP-2005-0125; and methyl bromide - EPA-HQ-OPP-2005-0123

[5] U.S. EPA 2009. FIFRA Science Advisory Panel Meeting Minutes - Scientific Issues Associated with Field Volatilization of Conventional Pesticides. Available at http://www.epa.gov/scipoly/sap/meetings/2009/december/120309meetingminutes.pdf

[6] **EPA MRID 48139303:** *Acute Inhalation Exposure of Adult Crl:CD(SD) rates to particulate chlorpyrifos aerosols: Kinetics of Concentration-Dependent Cholinesterase (CHE) Inhibition in Red Blood Cells, Plasma, Brain and Lung*; Authors: J. A. Hotchkiss, S. M. Krieger, K. A. Brzak, and D. L. Rick; Sponsor: Dow AgroSciences LLC, 9330 Zionsville Road Indianapolis, IN 46268-1054

cholinesterase (ChE) inhibition. Risk estimates were calculated for both lung and RBC ChE inhibition based on a 6-hour exposure duration and used quantitatively to estimate risk. The point of departures (PODs) for lung and RBC were calculated using the EPA's Reference concentration method for calculating human equivalent concentrations (HECs), which accounts for physiological differences between animals and humans.

1.1.2. Exposure

Dow AgroSciences (DAS) recently submitted a field volatility study[7] as part of the data call-in requirements for the registration review of chlorpyrifos. This study measured both vapor phase chlorpyrifos and chlorpyrifos-oxon, a transformation product, in air samples following an application of a low VOC (volatile organic compounds or volatile organic chemicals) formulation[8,9,10] of chlorpyrifos to alfalfa. Approximately 30% of the applied chlorpyrifos was emitted from the treated field in the first 24 hours (28% considering chlorpyrifos only; 30% considering chlorpyrifos and chlorpyrifos-oxon combined). The flux profile for chlorpyrifos is similar to those generally observed for fumigants in that there is a peak emission shortly after application during the warmer part of the day. The study measured chlorpyrifos for a period of 72 hours following application.

This assessment also incorporates a field volatility study published in the open literature; conducted with application of a non-low VOC formulation of chlorpyrifos to potatoes.[11] Since the raw data for this study could not be obtained, the flux rates could not be independently verified by EPA and, thus, evaluation of experimental details and associated data quality review of this study is not as rigorous as that associated with the alfalfa study. The open literature study only measured parent chlorpyrifos and did not measure concentrations of chlorpyrifos-oxon. The results from this study are presented in this assessment to provide another line of evidence of the potential volatility of chlorpyrifos, as demonstrated in the registrant submitted study, and to help describe the potential variability in chlorpyrifos flux rates due to different study conditions (***e.g.***,

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[7] **EPA MRID 48883201:** *Direct Flux Measurement of Chlorpyrifos and Chlorpyrifos-Oxon Emissions Following Applications of Lorsban Advanced Insecticide to Alfalfa*; Authors: Aaron Rotondaro and Patrick Havens; Sponsor: Dow AgroSciences LLC, 9330 Zionsville Road Indianapolis, IN 46268-1054, **2012**.

[8] California's Department of Pesticide Regulation (Cal DPR) defines a low VOC pesticide formulation when the total emission potential (see **footnote 9**) is 25% or less (see **footnote 10**). The emission rate corresponds to total VOC emissions and not specially one component of the formulation (*i.e.*, the active ingredient). EPA does not currently define low VOC pesticide formulations.

[9] Emission potential is based on Thermogravimetric Analysis; Oros, D., Spurlock, F. California Department of Pesticide Regulation, ESTIMATING PESTICIDE PRODUCT VOLATILE ORGANIC COMPOUND OZONE REACTIVITY. PART 1: SPECIATING TGA -BASED VOLATILE ORGANIC COMPUND EMISSIONS USING CONFIDENTIAL STATEMENTS OF FORMULA, January 27, 2011 http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/analysis_memos/2286_segawa.pdf

[10] Proposed regulation can be found at: http://www.cdpr.ca.gov/docs/legbills/rulepkgs/12-001/text.pdf

[11] **EPA MRID 48998801:** *Volatilization of the Pesticides Chlorpyrifos and Fenpropimorph from a Potato Crop*; Authors: Minze Leistra, Johan H. Smelt, J. Hilbrand Weststrate, Frederik VanDenBerg, and Rene Aalderink; Sponsor: This work was carried out within the framework of the EU APECOP project Effective Approaches for Assessing the Predicted Environmental Concentrations of Pesticides (QLK4-CT-1999-01338) and of Research Program 416, Pesticides and the Environment, of the Dutch Ministry of Agriculture, Nature and Food Quality; Citation: Leistra, M; Smelt, J. H.; Weststrate, J. H.; Van Den Berg, F; Aalderink, R. Environ. Sci. Technol. **2006**, *40*, 96-102.

crop canopy, formulation, and weather). While the absolute flux for chlorpyrifos observed in this study is higher than the alfalfa study the flux profiles[12] are similar in both studies.

The two field volatility studies suggest that volatilization of chlorpyrifos and/or chlorpyrifos-oxon from treated crops is a pathway of dissipation in the environment that may result in bystander exposure to vapor phase chlorpyrifos and chlorpyrifos-oxon. These studies were conducted at rates much lower than the current maximum single broadcast application; however, based on usage data, the rates used in these studies are consistent with typical average single application rates. In order to evaluate potential risks under varied conditions, offsite concentrations of chlorpyrifos and total toxic chlorpyrifos residues (chlorpyrifos and chlorpyrifos-oxon) were estimated using PERFUM and the flux rates derived from the two field volatility studies. This approach is consistent with what has been done for fumigant pesticides[4] and with the recommendations of the 2004[3] and 2009[5] SAP reviews.

1.2. Results Summary

Volatilization as a pathway of exposure was examined to quantify the potential risk estimates associated with bystander exposure to vapor phase chlorpyrifos and chlorpyrifos-oxon near a treated field. This was done by comparing peak 6 hour chlorpyrifos and total toxic chlorpyrifos vapor [chlorpyrifos and chlorpyrifos-oxon (expressed in chlorpyrifos toxicity equivalents)] concentrations estimated at various distances away from a treated field with endpoints based on lung and RBC ChE inhibition. The results indicate that offsite concentrations may exceed the target concentration established for lung ChE inhibition for many currently registered uses at distances away from the field edge. Concentrations are not expected to exceed the RBC ChE inhibition target concentration under all the conditions that were evaluated in this assessment.

Depending on which percentile of exposure and the field size considered, buffers zones[13] estimated to ensure concentrations of chlorpyrifos (only) are at or below the lung ChE target concentration range from 0 to greater than 4000 ft away from the perimeter of a treated field. Higher application rates and/or large field sizes lead to higher exposure and, therefore, large buffers. The spray drift buffers for protection of bystanders in sensitive sites[14] currently required on chlorpyrifos labels range from 0 to 100 feet depending on the application method. Consideration of vapor phase chlorpyrifos-oxon in addition to chlorpyrifos (only) increases the estimated buffer distances needed to ensure air concentrations are below the target concentration than those presented for chlorpyrifos only.

In addition to estimating buffer distances based on the peak air concentrations, a buffer duration analysis was completed by examining air concentrations over several days. This analysis is based

[12] A flux profile is the emissions from a treated field over a defined period of time (*i.e.*, an hourly time series of flux estimates during a period of measurement following application).

[13] In the context of presenting modeling results the term "buffer zone" does not refer to any regulatory decision pertaining to risk mitigation for chlorpyrifos. It refers to the distances determined based on a target concentration defined by the HEC adjusted by the uncertainty factor.

[14] Buffers are around sensitive sites (a circle drawn around the sensitive site with a radius equal to the buffer distance) and do not correspond to buffers around a given field (a circle drawn around a treated field with a radius equal to the buffer distance).

on whole field buffers as compared to maximum buffers. Depending on which percentile of exposure and the field size evaluated, the estimated buffers may need to remain for several hours. For example, buffers would need to be in place for at least 12 hours for l pound of active ingredient per acre (lb a.i./A) applications and for at least 36 hours for 6 lb a.i./A applications when considering the 95% percentile exposure concentration.

2. PROBLEM FORMULATION

Problem formulation provides a strategic framework in the risk assessment. In this case, it describes the history of EPA's air modeling approach and strategy used in this assessment to estimate potential risk due to volatilization of chlorpyrifos and its oxon following application in an agricultural setting. In addition, to identifying the chlorpyrifos application variables for the assessment, the problem formulation also outlines relevant physical-chemical properties, transformation products, usage data, hazard endpoints and exposure data needed for the assessment.

2.1. Approach

Pesticide volatilization can potentially impact those who are in proximity to treated fields following application events, as depicted in **Figure 1**. The example in **Figure 1** is an exposure pattern that is reasonably expected to occur with an emission event, given that farmers, residents (*e.g.*, homeowners, renters, visitors, etc.) and the general public may frequent areas adjacent to treated fields. To assess the potential risk from this exposure pathway, a residential/bystander assessment based on exposure to vapor phase residues at various distances away from a treated field was conducted. In order to evaluate the volatilization potential and associated risks, an approach based on dispersion modeling coupled with techniques used to evaluate inhalation exposure was utilized. In this case, dispersion modeling was completed for a variety of application scenarios including different field sizes, application rates, and metrological conditions.

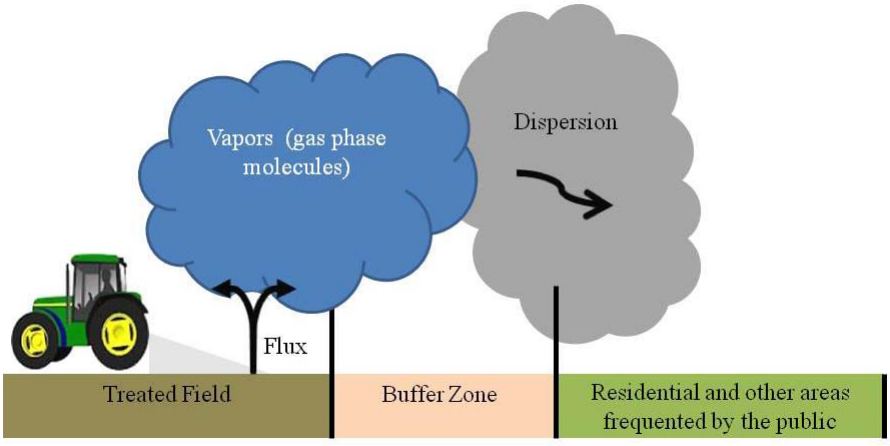

Figure 1. Conceptual Model of the Exposure Pathway Associated with Volatilization

2.1.1. Air Dispersion Modeling

2.1.1.1. Prior Consideration of Available Air Dispersion Models

Air dispersion modeling uses mathematical formulas to characterize how atmospheric processes will disperse a pollutant emitted by a source. For the fumigants, the EPA used dispersion models to estimate the downwind concentration emitted from an area source such as a treated field consistent with the EPA's air model development and implementation methods.[15] The EPA considered three air dispersion models for use in the soil fumigant risk assessments[16]. These models consisted of two "Gaussian Plume" models (ISCST3 model and AERMOD) and one "Gaussian Puff" model (CALPUFF). All three of these models are currently listed or have previously been listed in Appendix W of 40 CFR Part 51 (Guideline on Air Quality Models) which contains the EPA's guidance on the general regulatory applicability of various air quality dispersion models.[17] EPA selected the ISCST3 model, which in 2004 was the agency's recommended regulatory air model, for use in the fumigant assessments.[16]

After a modeling approach based on the use of ISCST3 was selected, a series of preliminary risk assessments were completed using ISCST3.[18] The findings indicated significant risk mitigation measures might be needed (*e.g.*, large buffer distances) but there was the potential for refinements to refine risk estimates. The key refinement was incorporating actual weather data as a basis for predicting risks instead of using constant atmospheric conditions. In essence, this refinement allowed for distributional consideration of changing weather conditions rather than the ISCST3 deterministic approach to weather which was based on wind speed, direction and atmospheric stability being constant.

The regulated community developed three models that incorporated actual weather data: Probabilistic Exposure and Risk model for Fumigants (PERFUM) [19], the Fumigant Emissions Modeling System (FEMS)[20], and the Soil Fumigant Exposure Assessment System (SOFEA)[21], were submitted to the EPA by the regulated community. All of these models are essentially pre- and post-processors for ISCST3 (and CALPUFF in the case of FEMS) that incorporate the ability to complete distributional and/or probabilistic analyses. Each of these models was reviewed by the 2004 SAP.[3] The SAP concluded that each of the three models could provide scientifically defensible estimates of the bystander exposures and risks associated with soil fumigation practices and also suggested modifications and additional data that could further refine risk estimates (for specifics see the final SAP report[3]). Many of the SAP's recommended modifications have been made to these models since that time. After the SAP reviews, the EPA

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[15] See http://www.epa.gov/scram001/ for more details.
[16] See http://www.epa.gov/oppsrrd1/reregistration/soil_fumigants/soil-fum-reg-backgrnd.html for more details
[17] http://www.epa.gov/ttn/scram/guidance/guide/appw_05.pdf
[18] There was a regulatory precedent for using ISCST3 as it had previously been used by EPA for air permitting, as well as to define buffer zones for methyl bromide in California.
[19] Reiss, R. and Griffin, J. 2006. User's Guide for the Probabilistic Exposure and Risk Model for FUMigants (PERFUM), Version 2. Arysta LifeScience North America Corporation. Cary, North Carolina.
[20] Fumigant Exposure Modeling System (FEMS), Background Document: Fumigant Emissions Modeling System, Sullivan, Hlinka, and Holdsworth, July, 2004
[21] SOil Fumigant Exposure Assessment System (SOFEA), SOFEA (User's and Programmer's Guide), van Wesenbeeck and Cryer, Copyright 2004

selected PERFUM as the probabilistic air model for use in the fumigant assessments. Other modeling analyses, using systems such as FEMS, SOFEA, AERMOD or CALPUFF, would also be considered should these models be developed and submitted to the EPA for consideration, since these models are also considered appropriate for regulatory purposes.

The 2009 SAP[5] discussed in limited fashion, as it was not part of their official charge, that the current dispersion models (mentioned above) have not been validated for non-fumigant pesticides. The EPA acknowledges that use of dispersion models was briefly discussed at the 2009 SAP[5] but no significant discussions were held on this particular issue. The SAP concluded that the concept of coupling a fate and transport model, to predict the flux of a chemical, with a dispersion model, to estimate air concentrations at different distances from the field is a sound approach.

In order for a model to be included as an EPA recommended air model (part of Appendix W), the model must go through an extensive peer review and testing process. This peer review process ensures that models are acceptable to be used for a variety of sources like point sources (*e.g.*, a stack on a building) and area sources (*e.g.*, a treated field), as well as for a variety of pollutants (*i.e.*, volatile organic compounds, semi-volatile organic compounds, and particulate matter). While this testing process did not explicitly consider pesticides, except for one case where a fumigant was released from a field (*i.e.*, the Prairie Grass Study[22]), it included semi-volatile organic compounds. Most pesticides fall under this classification given physical-chemical characteristics such as vapor pressure. Based on the EPA's model peer review process and the use of air dispersion modeling for the fumigants risk assessments over the last ten years, the use of dispersion modeling for semi-volatile pesticides is considered a valid and scientifically defensible methodology.

2.1.1.2. PERFUM Modeling Approach

Before a PERFUM analysis can be performed, hazard and exposure inputs need to be defined. The hazard inputs used in this assessment are discussed in detail in **Section 2.3**. Exposure inputs in the form of a flux profile [the flux or rate of pesticide emissions from the treated fields per unit area per unit time ($\mu g/m^2/sec$)] was determined from two different field volatility studies discussed further in **Section 2.4**. Numerous factors can influence flux rates, such as the application rate, the treated surface (*e.g.*, foliage or soil), field structure (*e.g.*, canopy type and shape), application practices, and atmospheric conditions such as temperature and humidity. A discussion of these factors is provided in **Section 4**. In the end, PERFUM compares a target concentration derived from the HEC and the uncertainty factor[23] to off field air concentrations estimated based on flux rates surrounding a treated field in order to estimate buffer zones[13], if needed.

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[22] United States Air Force. 1958. Project Prairie Grass, A Field Program in Diffusion, Volume I. Geophysics Research Directorate, Air Force Cambridge research Center, Air Research and Development Command Geophysical Research Papers No. 59, Document Number AD152572, July 1958

[23] The uncertainty factor is this case is a value developed to account for uncertainty associated with animal to human extrapolation of toxicity data, as well the potential sensitivity difference between humans within a given population (*e.g.*, sensitivity subpopulations). See **Section 2.3** for information on how the target concentration used in this assessment was derived.

Buffer zones[13] and risk estimates are presented in **Section 3** below for several different potential application scenarios (e.g., different meteorological conditions, field sizes, and application rates) for an array of percentiles of exposure for whole field and maximum buffers. A summary of the results is provided in **Section 4.** Note: PERFUM does not produce buffer zones greater than 4724 ft (1440 m), thus, buffer zones for cases where the 4724 ft (1440 m) limit is reached may be very large. These cases are indicated with a ">4724 ft".

2.2. Stressors of Concern

Chlorpyrifos (*O,O*-diethyl o-(3,5,6-trichloro-2-pyridyl phosphorothioate; CAS 2921-88-2) is a broad spectrum organophosphate (OP) insecticide. It is widely used in agriculture and has been measured in various air monitoring programs. Chemical identification and select physical chemical properties of chlorpyrifos are provided in **Table 1**.

Table 1. Chemical Identification and Select Physical-Chemical Properties of Chlorpyrifos and Chlorpyrifos-oxon

Parameter	Chlorpyrifos	Chlorpyrifos-oxon
Chemical Name	*O,O*-diethyl O-(3,5,6-trichloro-2-pyridyl phosphorothioate	*O,O*-diethyl O-3,5,6-trichloropyridin-2-yl phosphate
Chemical Abstracts Service (CAS) Registry Number	2921-88-2	5598-15-2
Empirical Formula	$C_{20}H_{17}F_5N_2O_2$	$C_9H_{11}Cl_3NO_4P$
USEPA Pesticide Code (PC #)	059101	--
Smiles Notation	S=P(OC1=NC(=C(C=C1Cl)Cl)Cl)(OCC)OCC	O=P(Oc1nc(c(cc1Cl)Cl)Cl)(OCC)OCC
Molecular Weight	350.57 g/mol	334.52 g/mol
Vapor Pressure (25 °C)	$1.87x10^{-5}$ torr	$6.65x10^{-6}$ torr[a]
Water Solubility (20 °C)	1.4 mg/L	26.0 mg/L[a]
Henry's Law Constant	6.2×10^{-6} atm - m^3/mol	5.5×10^{-9} atm - m^3/mol[a]
Log K_{ow}	4.7	2.89 mg/L[a]
Saturated Vapor Concentration (25 °C)	489 µg/m^3 [b] 353 µg/m^3 [c]	120 µg/m^3 [d]

a. EPI Suite estimated value.
b. See **footnote 24**
c. Calculated: n/V=P/RT; P=$1.87x10^{-5}$ torr x (1 atm/760 torr) =$2.46x10^{-8}$ atm @ 25 °C; R= 0.0821 L atm/ mol K; T= 25 °C= 298 K; 2.46 $x10^{-8}$ atm/ (0.0821 L atm/ mol K*298 K) = 1.0×10^{-9} mol/L x (350.57 g/mol) x 10^6 µg/g = 0.353 µg/L* 1L/$10^{-3}m^3$) = 353 µg/m^3
d. Calculated: n/V=P/RT; P=$6.65x10^{-6}$ torr x (1 atm/760 torr) =$2.46x10^{-8}$ atm @ 25 °C; R= 0.0821 L atm/ mol K; T= 25 °C= 298 K; 2.46 $x10^{-8}$ atm/ (0.0821 L atm/ mol K*298 K) = 3.6 $x10^{-10}$ mol/L x (334.52 g/mol) x 10^6 µg/g = 0.120 µg/L* 1L/$10^{-3}m^3$) = 120 µg/m^3

[24] Reported by Dow AgroSciences on December 11, 2012 in a presentation (Bartels, M., Cleveland, C., Hotchkiss, J., Juberg, D. Perspectives on Risk Assessment Elements for Chlorpyrifos) to EPA.

Based on available environmental fate data submitted to EPA, chlorpyrifos is expected to undergo several chemical transformations in the environment as shown in **Figure 2**.

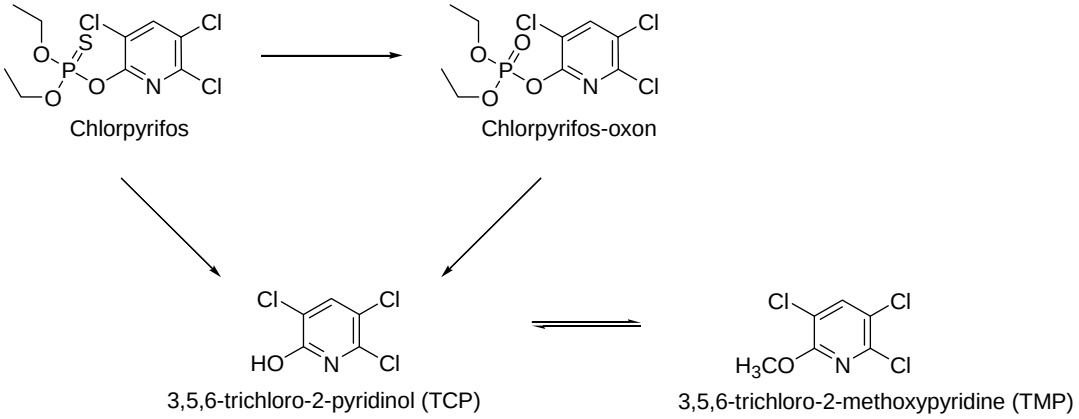

Figure 2. Environmental Transformation of Chlorpyrifos

Chlorpyrifos-oxon, a transformation product, is considered as a residue of concern which has greater potency for cholinesterase inhibition than chlorpyrifos. There are also air monitoring data that include both chlorpyrifos and chlorpyrifos-oxon detections supporting the potential exposure to both chemicals as a result of emission from a treated field and subsequent transport offsite.[25] It is unclear if the concentrations observed in the majority of air monitoring studies reported in the open literature are due to spray or vapor phase drift of chlorpyrifos and chlorpyrifos-oxon; however, the alfalfa field volatility study discussed in detail below indicate that it is likely that both vapor phase chlorpyrifos and chlorpyrifos-oxon vapors are present simultaneously downwind of a treated field. Therefore, in addition, to exposure to chlorpyrifos itself the potential exposure to both chlorpyrifos and chlorpyrifos-oxon at the same time is also explored in this assessment.

In a recently submitted air photolysis study[26] chlorpyrifos was reported to undergo indirect and direct photolysis [$t_{1/2}$ = 2 h (indirect) and 6 h (direct)]. These results have not been verified by EPA as the raw data submitted to the EPA are not adequate; however, the results obtained for indirect photolysis are consistent with the Estimation Program Interface (EPI) Suite[27] estimations.[28] EPI Suite is commonly used by EPA to estimate physical-chemical parameters when data are unavailable. This study confirms the formation of chlorpyrifos-oxon via photolysis. Chlorpyrifos-oxon was reported to undergo indirect and direct photolysis [$t_{1/2}$ = 11 h (indirect) and 6 h (direct)]. The EPI Suite estimated indirect photolysis was about half[29] that

[25] Glotfelty, D. E.; Majewski, M. S.; Selber, J. N. Distribution of Several Organophosphorus Insecticides and Their Oxygen Analogues in a Foggy Atmosphere. *Environ. Sci. Technol.*, **1990**, *24 (3)*, 353-357.

[26] **EPA MRID 48789701:** *Gas-Phase Photolysis and Photo-oxidation of Chlorpyrifos and Chlorpyrifos oxon*; Authors: Amalia Munoz; Sponsor: Dow AgroSciences European Development Centre, 3 Milton Park, Abington, Oxon, OX14 4RN

[27] http://www.epa.gov/opptintr/exposure/pubs/episuite.htm; The version used in this assessment is 4.00.

[28] $t_{1/2}$ = 3 h (indirect)

[29] $t_{1/2}$ = 7 h (indirect)

calculated by the study authors. The physical-chemical properties of chlorpyrifos-oxon are provided in **Table 1**.

2.2.1. Use Characterization

There are several different types of chlorpyrifos formulations currently registered including: liquid, dry flowable, microencapsulated, and granular products. Registered use sites include food crops such as fruit and nut trees, many types of fruits and vegetables, and grain crops; and non-food crops such as forage, golf course turf, industrial sites, greenhouse and nursery production, sod farms, and wood products. This section includes a summary of chlorpyrifos use, including: an evaluation of yearly chlorpyrifos percent crop treated (PCT), application rate information, and total acreage treated annually for all agricultural crops treated with chlorpyrifos.

A complete list of chlorpyrifos use sites and application rates are provided in **ATTACHMENT 1**. Broadcast application rates currently permitted on chlorpyrifos labels range from 0.5 to 6 lb a.i./A.

2.2.1.1. Agricultural Use

Based on private market research data[30], approximately 8 million pounds of chlorpyrifos are used annually in agriculture. Total chlorpyrifos usage by crop varies widely with the average PCT in the survey of years 2006-2010, unless otherwise noted –as low as 1% for several crops and as high as 62 % (for apples). The five crops with the highest PCT are apples (62%), broccoli (53%), walnuts (46%), onions (45%), and cauliflower (41%) as shown in **Table 2**. These five crops account for approximately thirteen percent of the total pounds of chlorpyrifos applied each year. Crops that have low total chlorpyrifos usage (EPA defined this as less than 20,000 pounds used, on average) but show relatively large area treated (EPA defined this as greater than 25% PCT) include: strawberries, asparagus, and cauliflower.

Table 2. Typical Use Data for Chlorpyrifos (all formulations combined; national level data)

Crop	Average Percent Crop Treated (PCT)	Average Pounds Applied per Year	Average Single Application Rate	Upperbound Rate (Lbs. a.i./A-single app.)
Soybeans	6	1,800,000	0.41	0.5 (90%), 0.75 (95%)
Corn	1	1,000,000	0.9	1.25 (84%), 1.5 (97%)
Oranges	24	630,000	2.5	5.75 (81%), 6.0 (100%)
Alfalfa	3	450,000	0.56	0.75 (79%), 1.0 (100%)
Almonds	24	440,000	1.86	2.0 (97%)
Wheat, Winter	2	400,000	0.42	0.5 (93%)
Apples	62	390,000	1.5	1.75 (52%), 2.0 (99.9%)
Walnuts	46	350,000	1.85	2.0 (99%)

[30] GfK Kynetec Database

Pecans	28	260,000	0.9	1.25 (91%)
Peanuts	7	160,000	1.72	2.0 (97%)
Sugar Beets	11	130,000	0.8	1.5 (88%)
Wheat, Spring	2	120,000	0.32	0.25 (65%), 0.5 (99%)
Cotton	2	100,000	0.3	0.75 (77%), 1.0 (100%)
Sweet Corn	11	100,000	0.96	1.25 (83%), 1.5 (94%)
Broccoli	53	100,000	1.36	2.0 (78%), 2.25 (100%)
Lemons	39	96,000	3.5	5.0 (88%)
Tobacco	13	90,000	1.96	3.0 (90%)
Cherries	37	84,000	1.5	2.0 (99.6%)
Sunflowers	6	66,000	0.46	0.5 (88%), 0.75 (94%)
Onions	45	65,000	0.9 3	1.0 (70%), 1.25 (99.8%) 3
Wine Grapes[c]	5	60,000	1.96	2.42
Peaches[b]	26	56,000	1.34 2	1.75 (69%), 2.0 (98%)2
Grapefruit	22	48,000	2.1	2.75 (90%)
Table Grapes[c]	13	27,000	1.88	2.43
Plums/Prunes	11	24,000	1.73	2.0 (100%)
Pears	17	20,000	1.85	2.0 (100%)
Cauliflower	41	17,000	1.09	1.25 (89%), 1.5 (97%)
Asparagus	39	16,000	0.99	1.0 (95%)
Strawberries	28	15,000	0.97	1.0 (99%)
Dry Beans/Peas[a]	1	13,000	0.48	0.5 (95%)
Cabbage	14	12,000	1.16	1.25 (86%), 1.5 (92%)
Sorghum (Milo) [a]	0.4	11,000	0.42	0.5 (80%), 0.75 (95%)
Hazelnuts[a]	10	4,800	1.27	1.5 (77%), 2.0 (100%)
Beans[a]	1	1,800	0.77	0.75 (84%), 1.0 (100%)
Peppers[a]	2	1,800	0.81	0.75 (77%), 1.0 (94%)
Pumpkins[a]	1	1,700	0.93	1.25 (100%)
Peas[a]	1	1,400	0.98	1.0 (98%)
Squash[a]	1	820	1.11	1.25 (88%), 1.5 (91%)
Cucumbers[a]	1	550	0.76	1.0 (100%)

Source: Proprietary Data 2006-2010. Table is sorted to show crops with highest to lowest total chlorpyrifos applied per year

a. Data are not robust (total sample size of <50 across 5 years and this crop not surveyed in USDA NASS)
b. Peaches: Higher values were reported in NASS. For a conservative value, EPA recommends: Rate: 1.6 lb a.i./A, Number of Applications: 1.4; 90th percentile rate: 2.6 lb a.i./A (USDA NASS 2009)
c. Updated Typical Use Data for Chlorpyrifos Used on Grapes in California (Average 2006 and 2009); Source: USDA NASS (2006, 2009) Agricultural Chemical Usage Fruit Summary

Chlorpyrifos use is highest on corn and soybean in terms of average pounds total chlorpyrifos applied per year, accounting for approximately thirty-nine percent of the total pounds of chlorpyrifos applied each year. Corn use is over 1,000,000 pounds per year while soybean use is nearly 2,000,000 pounds per year for the period surveyed. Chlorpyrifos use on orchard and trellis crops is about thirty-three percent of the total chlorpyrifos use per year.

2.2.1.1.1. Application Rate Information

Table 2 also provides use information such as the application rate (average single application rates and upper-bound single application rates) for national-level total chlorpyrifos use (all formulations and all application methods) on use sites where information was available from 2006-2010.[31] Seventeen crops (out of a total of 38 crops surveyed) show average application rates that are greater than 1 lb a.i./A. These crops are apples, almonds, broccoli, cabbage, cauliflower, cherries, grapefruit, hazelnuts, lemons, oranges, peaches, peanuts, pears, plums/prunes, squash, tobacco, and walnuts. The majority of growers surveyed reported use of single application rates of 2 lb a.i./A or less. For many of the crops included in **Table 2** the upper-bound single application rate is equal to the maximum single application rate currently permitted on the label.

Additional analysis of the data by formulation type is presented in **APPENDIX B**.

2.2.1.1.2. Acres Treated Information

Data on the size of fields treated per application of chlorpyrifos helps define current use practices. However, with the exception of the detailed pesticide use recording database maintained by the California Department of Pesticide Regulation (CDPR), EPA is not aware of data sources that would provide this kind of information for chlorpyrifos (or any other pesticide). Results of EPA's analysis of relevant CDPR data are presented in **APPENDIX B** (**Table B2**). These data describe chlorpyrifos usage in California, and may not reliably apply to other parts of the United States as different pest pressures and crop production practices are likely altering the relative use of chlorpyrifos. Additional discussion of the scope of these data is included in **APPENDIX B**.

Using the CDPR data, EPA determined that the area treated per application per day varies widely across use sites. In general, it appears that ground-based treatments covered larger acres treated per application per day than aerial treatments at the 90th percentile range. While the factors contributing to this result were not investigated, EPA speculates such factors as cost of application, efficacy, and accessibility of application equipment may influence the use of ground over aerial application methods. Although maximum area treated in some crops (*e.g.*, walnuts, almonds, asparagus, grapes, alfalfa) can be several hundred acres, these are often single data points (*i.e.*, only one grower/applicator was reporting this amount treated). The 50th and 90th percentile columns depicted in **Table B2** are probably more descriptive for typical use than the

[31] Stebbins, K. U.S. EPA Office of Chemical Safety and Pollution Prevention, Chlorpyrifos: Additional Typical Use Data for Chlorpyrifos, January 11, 2012 PC Code 059101

maximum reported number of acres treated per day. The percentile columns show the amount of acres treated per application per day at or below which 50 or 90 percent of applicator reports occur in the CDPR database (within each crop/product/application method grouping).

2.2.1.2. Non-Agricultural Use

Chlorpyrifos is used in settings that are not considered an agricultural use per se including agricultural farm premises, nurseries and plantations (*e.g.*, ornamental, non-bearing fruit tree, and Christmas tree), golf course turf, recreational areas, rights-of-way, and utility areas. However, usage data in these areas are not surveyed by the proprietary market databases that EPA uses to gather pesticide use information. In addition, use information for these sites is not collected by the CDPR in a form that allows reliable interpretation for risk assessment purposes. Therefore, EPA has no verifiable description of application rates or area treated in these uses. This remains an uncertainty.

2.3. Hazard Characterization

2.3.1. Mode of Action and Adverse Outcomes

Chlorpyrifos, like other OPs, binds to and phosphorylates the enzyme, acetylcholinesterase (AChE), in both the central (brain) and peripheral nervous systems leading to accumulation of acetylcholine and, ultimately, to clinical signs of toxicity. For OPs, AChE inhibition is most often the most sensitive dose response data for use in assessing human health risk. For chlorpyrifos, the EPA concluded in the 2011 preliminary HHRA, that ChE inhibition was the most sensitive dose response data for use in deriving a POD for all durations, routes of exposure, and lifestages.

EPA typically uses data on AChE inhibition data, the initiating event in the mode of action, for endpoint selection in human health risk assessment since protecting against inhibition of AChE thereby protects against potential acute neurotoxicity. EPA's ChE policy[32] describes the manner in which ChE data are used in human health risk assessment. Typically, experimental laboratory studies measure brain (central) and blood (plasma and red blood cell) ChE. Blood measures do not represent the target tissue, *per se*, but are instead used as surrogate measures for peripheral nervous tissue in studies with laboratory animals when peripheral data are missing or for potential peripheral and/or central toxicity in humans. In addition, RBC measures represent AChE, whereas plasma measures are approximately 50% butyryl-ChE (BuChE). Thus, RBC AChE data may provide a better representation of the inhibition in target tissues than plasma ChE data.

There are many experimental toxicology studies which measure RBC and plasma ChEs. In general, measurements of AChE or ChE inhibition in peripheral tissues (*e.g.*, liver, diaphragm, heart, lung, etc.) are rare. Data for chlorpyrifos are unique in that measures of some peripheral tissue are available in some experimental toxicity studies. For example, heart ChE was measured

[32] USEPA (2000) Office of Pesticide Programs, US Environmental Protection Agency, Washington DC 20460. August 18, 2000 Office of Pesticide Programs Science Policy of The Use of Data on Cholinesterase Inhibition for Risk Assessments of Organophosphorous and Carbamate Pesticides.

in the chlorpyrifos developmental neurotoxicity study[33,34], an associated companion study, in addition to an acute oral study by Dittenber.[35] Liver ChE was measured by Lassiter[36], Hunter[37], and Moser and Padilla[38]. Padilla[39] (measured diaphragm ChE) and Marable[40] (measured diaphragm, left atrium, and quadriceps ChE*)* evaluated chronic exposure in adult animals where blood, brain and peripheral tissue ChE inhibition were at steady-state. Lung ChE was measured in the special acute inhalation study being used to assess the risk from volatilization. Other data on lung ChE come from oral studies. Specifically, in an oral study by Carr[41] heart, lung, and skeletal muscle ChE were evaluated in post-natal pups dosed using a unique design that included every other day dosing and different durations and doses across different aged pups. Given the unique design of the Carr study, it is difficult to assess sensitivity of different tissues. Richard and Chambers[42] evaluated lung ChE in rat fetuses following oral exposure to the dams and showed that lung ChE was similar at the lowest dose on PND1 to brain and RBC AChE but lung ChE was more inhibited in PND1 pups than brain and RBC AChE at the higher doses (ChE inhibition was not measured in dams).

With respect to clinical signs of neurotoxicity, in experimental toxicity studies with chlorpyrifos acute, oral toxicity can be associated with signs typical of cholinergic overstimulation, such as hypothermia, salivation, lacrimation, diarrhea, incoordination, tremors, and fasciculations. In addition, altered motor function was one of the more sensitive endpoints evaluated in these studies.[43,38,44,45]

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[33] **EPA MRID 44648101**: *Effects of Chlorpyrifos Administered Via Gavage to CD Rats During Gestation and Lactation on Plasma, Erythrocyte, Heart and Brain Cholinesterase and Analytical Determination of Chlorpyrifos and Metabolites.* Authors: Mattsson J. L., Maurissen J. P., Spencer, P. J., Brzak K. A., Zablotny C.L.; Sponsor: The Dow Chemical Co. for Dow AgroSciences, August 31, 1998.

[34] Mattsson, J. L., Maurissen, J. P., Nolan, R. J., and Brzak, K. A. Lack of differential sensitivity to cholinesterase inhibition in fetuses and neonates compared to dams treated perinatally with chlorpyrifos. *Toxicol Sci,* **2000**, *53*, 438-46.

[35] **EPA MRID 44273901**: *Chlorpyrifos: Evaluation of Single Oral Doses on Cholinesterase and Neurotoxic Esterase Inhibition in F344 Rats.* Author: Dittenber, D. A., Sponsor: Dow Chemical Co. Study No. 960036. March 13, 1997.

[36] Lassiter T. L., Padilla S., Mortensen, S.R., Chanda, S.M., Moser, V.C., Barone, S . Gestational Exposure to Chlorpyrifos: Apparent Protection of the Fetus? *Toxicol. Applied Pharmacol.* **1998a,** *152*, 56-65

[37] Hunter, D. L., Lassiter, T. L., and Padilla, S. Gestational Exposure to Chlorpyrifos: Comparative Distribution of Trichloropyridinol in the Fetus and Dam. *Toxicol Applied Pharmacol.* **1999**, *158*, 16-23.

[38] Moser, V. C., Padilla, S. Age- and Gender-related Differences in the Time Course of Behavioral and Biochemical Effects Produced by Oral Chlorpyrifos in Rats. *Toxicol Applied Pharmacol.* **1998**, *149,* 107-19.

[39] Padilla, S., Marshall, R. S., Hunter, D. L., Oxendine, S., Moser, V. C., Southerland, S. B., Mailman, R. B. Neurochemical Effects of Chronic Dietary and Repeated High-level Acute Exposure to Chlorpyrifos in Rats. *Toxicol Sci.* **2005**, *88*, 161-71.

[40] Marable, B.R., Maurissen, J. P., Mattsson, J. L., Billington, R. Differential Sensitivity of Blood, Peripheral, and Central Cholinesterases in Beagle Dogs Following Dietary Exposure to Chlorpyrifos. *Regul. Toxicol. Pharmacol.* **2007**, *47*, 240-8.

[41] Carr, R. L., Chambers, H. W., Guarisco, J. A., Richardson, J. R., Tang, J., Chambers, J. E. Effects of Repeated Oral Postnatal Exposure to Chlorpyrifos on Open-field Behavior in Juvenile Rats. *Toxicol. Sci*. **2001**, *59*, 260-7.

[42] Richardson, J., Chambers, J. Effects of Repeated Oral Postnatal Exposure to Chlorpyrifos on Cholinergic Neurochemistry in Developing Rats. *Toxicol. Sci.* **2003**, *84*, 352-59.

[43] Mattsson, J. L., Wilmer, J. W., Shankar, M. R., Berdasco, N. M., Crissman,J. W., Maurissen, J.P., and Bond, D. M. Single-dose and 13-week Repeated-dose Neurotoxicity Screening Studies of Chlorpyrifos Insecticide. *Food Chem. Toxicol.* **1996**, *34*, 393-405.

With respect to the respiratory tract, although there are three chlorpyrifos inhalation studies, none measured apical outcomes relevant to pulmonary function. As such there are no data in experimental animals evaluating the potential effects of lung ChE inhibition on pulmonary function following inhalation chlorpyrifos exposure. Tracheobronchial glands receive parasympathetic innervation; AChE inhibitors can stimulate secretion of tracheobronchial fluid, in addition, to bronchorestriction and stimulation of chemoreceptors in the carotid and aortic bodies.[46]

Volatile nerve agents are highly potent OP chemicals that inhibit AChE, as do the OP pesticides. In humans, OP nerve agents cause paralysis of respiratory muscles (*e.g.*, diaphragm, abdominal, thoracic), airway secretions, edema and bronchoconstriction[47]. Experimental toxicology studies with laboratory animals exposed to OP war agents are consistent with these effects on the peripheral nervous system. For example, inhalation exposure to OP war agents in baboons induces cardiac arrhythmias, apnea, hypoxia, and respiratory disturbances.[48] There are some experimental studies in laboratory animals where lung, bronchoalveolar lavage fluid and/or diaphragm ChE has been measured following exposure to war agents (*e.g.*, VX, sarin, soman).[47,49,50,51]

EPA acknowledges that information on war agents needs to be interpreted with caution in the context of the toxicological profile for chlorpyrifos. Although, there are rat three inhalation studies[6,52,53] available with chlorpyrifos; none of these chlorpyrifos studies specially evaluated effects relevant to pulmonary function. Thus, the relationship between measures of ChE inhibition in the lung and pulmonary effects is not known. The war agent studies aid in

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[44] Nostrandt, A. C., Padilla, S., Moser, V. C. The Relationship of Oral Chlorpyrifos Effects on Behavior, Cholinesterase Inhibition, and Muscarinic Receptor Density in Rat. *Pharmacal. Biochem. Behav.* **1997**, *58*, 15-23.

[45] Moser, V. C., Chanda, S.M., Mortensen, S.R., Padilla, S. Age- and Gender-Related Differences in Sensitivity to Chlorpyrifos in the Rat Reflect Developmental Profiles of Esterase Activities. *Toxicol. Sci.* **1998**,*46*, 211-222.

[46] Taylor, P. Cholinergic Agonists in *Goodman and Gillman's The Pharmacological Basis of Therapeutics*. **1985** Seventh Edition.

[47] Graham, J.R., Wright, B.S., Rezk, P. E., Gordon, R. K., Sciuto, A. M., Nambiar, M. P. Butyrylcholinesterase in Guinea Pig Lung Lavage: A Novel Biomarker to Assess Lung Injury Following Inhalation Exposure to Nerve Agent VX. *Inhal Toxicol.*, **2006**, *18*, 493-500.

[48] Anzueto, A., deLemos, R.A., Seidenfeld, J., Moore, G., Hamil, H., Johnson, D., Jenkinson, S.G.,1990. Acute inhalation toxicity of soman and sarin in baboons. Fundam. Appl. Toxicol. 14, 676–687.

[49] Che, M.M., Song, J., Oguntayo, S., Doctor, B.P., Rezk, P., Perkins, M.W., Sciuto, A.M., Nambiar, M.P. Treatment with Endotracheal Therapeutics After Sarin Microinstillation Inhalation Exposure Increases Blood Cholinesterase Levels in Guinea Pigs. *Toxicol. Mech. Methods.* **2012**, *22*, 250-9.

[50] Perkins, M.W., Pierre, Z., Rezk, P., Song, J., Oguntayo, S., Sciuto, A. M., Doctor, B. P., Nambiar, M. P. Acute Changes in Pulmonary Function Following Microinstillation Inhalation Exposure to Soman in Nonatropenized Guinea Pigs. *Int. J. Toxicol.* **2011**, *30*, 348-57.

[51] Perkins, M.W., Pierre, Z., Rezk, P., Sabnekar, P., Kabra, K., Chanda, S., Oguntayo, S., Sciuto, A.M., Doctor, B. P., Nambiar, M. P. Acute Respiratory Toxicity Following Inhalation Exposure to Soman in Guinea Pigs. *Toxicol. Appl. Pharmacol.* **2010**, *245*, 171-8.

[52] **EPA MRID 40013901 and 40166501**: *Chlorpyrifos: 13-Week Nose-only Vapor Inhalation Exposure Study in Fischer 344 Rats Laboratory Project Id: HET K-044793-077*. Authors: Corley, R.; Landry, T.; Calhoun, L. et al.; Sponsor: Dow Chemical USA 1986

[53] **EPA MRID 40908401**: *A Thirteen Week Nose-Only Inhalation Toxicity Study of Chlorpyrifos Technical (Pyrinex) in the Rat: Project No. 88-8058.* Authors: Newton, P.; Prepared by Bio/dynamics, Inc.; 1988

considering the human relevance and toxicological adversity associated with changes in lung ChE and potential cholinergic effects on the respiratory system. The qualitative findings of the war agent studies provide a starting point for evaluating human incident reports for the kinds of potential respiratory effects which may result from exposure to high levels of chlorpyrifos.

2.3.2. Human Incidents: Summary of Respiratory Effects

EPA considers human incident data in order to assist in better defining and characterizing the risk of pesticides/pesticide products. It is important to recognize, however, that reports of adverse health effects allegedly due to a specific pesticide exposure are largely self-reported and therefore, generally speaking, neither exposure to a pesticide nor reported symptoms (nor the connection between the two) is validated. Therefore, only rarely can causation be determined or definitively identified based on incident data. However, incident information can provide important feedback to the EPA regarding the nature, circumstances, frequency, and severity of pesticide exposure events. Human incident data, considered jointly with the human health risk assessment, can assist the Agency in determining the risk pesticides/pesticide products may or may not pose and can help characterize that risk in a qualitative manner.

Following the chlorpyrifos incident report summarized in the 2011 HHRA, chlorpyrifos incidents from the OPP Incident Data System (IDS), the National Pesticide Information Center (NPIC), National Institute for Occupational Safety and Health's (NIOSH) Sentinel Event Notification System for Occupational Risk (SENSOR-Pesticides), and the California Pesticide Illness Surveillance Program (CA PISP) were further reviewed for an association with respiratory effects (such as wheezing, chest tightening, and difficulty breathing). Respiratory effects are consistent with what is seen in animal studies exposed to chlorpyrifos by inhalation. The incidents reviewed involved only the single active ingredient chlorpyrifos because incidents involving only one pesticide are considered to provide more certain information on the suspected substance that may be causing adverse effects. EPA's review of chlorpyrifos incidents showed an association between chlorpyrifos incidents and respiratory effects across all the databases reviewed. These incidents occurred due to both agriculture related use of chlorpyrifos and non-agriculture related use of chlorpyrifos. To focus the scope of the review in a manner relevant to this volatilization assessment and to be consistent with the current use pattern, EPA focused the review on incidents associated with drift, including volatilization, occurring post 2002.

In general, it should be noted that it is difficult to distinguish between incidents associated with drift and those associated with volatilization because information may be limited on the timing of exposure relative to the application event in each of the incident databases. In SENSOR, for example, drift is defined as "…the movement of pesticides away from the treatment site. The pesticide spray, mist, fumes, or odor are carried from the target site by air." As such, there is no clear distinction between cases exposed from volatilization versus spray drift when analyzing the SENSOR-Pesticides data. This is generally true of the other incident databases as well.

Incidents associated with chlorpyrifos from each of OPP's four databases are described below in additional detail:

OPP's Main Incident Data System: For OPP's Main Incident Data System (IDS), from January 1, 2002 to February 1, 2011, there were 141 incidents in which chlorpyrifos was the only active ingredient in the suspected substance.[54] Of these 141 incidents, 52 (37%) incidents reported respiratory effects including—but not limited to—dyspnea, throat irritation, irritated breathing, difficulty breathing, coughing/choking, and nasal congestion. These incidents were mostly categorized as HCs (Human Moderates); however, there was one fatality[55] and 4 incidents classified as major severity. Due to the limited and varying exposure scenario details available, it is not possible to distinguish between incidents occurring due to drift and those occurring due to volatilization.

National Pesticide Information Center: From 2002 to 2010, National Pesticide Information Center (NPIC) reported 88 cases in which chlorpyrifos was the only active ingredient in the suspected substance.[56] Of these 88 cases involving chlorpyrifos, 20 (23%) had respiratory symptoms such as difficulty breathing, coughing, runny nose, and tightness in chest. Ten incidents occurred due to drift exposure; however, only 4 of these drift incidents reported respiratory effects.

California Pesticide Illness Surveillance Program: For *California Pesticide Illness Surveillance Program (*CA PISP) from 2002 to 2009, there were 100 cases in which chlorpyrifos was the only active ingredient in the suspected substance.[57] Of these 100 cases, 56 (56%) reported respiratory effects, such as shortness of breath, difficulty breathing, coughing, chest tightness, throat irritation, respiratory discomfort. Sixty one of the chlorpyrifos incidents are associated with drift or volatilization. Of these 61 incidents associated with drift or volatilization, 39 (45%) reported respiratory effects. While the available data are insufficient to directly link respiratory effects to chlorpyrifos volatilization exposure, this may be because bystanders are less likely to associate respiratory symptoms with volatilization than they are, for example, with an obvious spray drift incident. A specific drift example involves an incident that occurred in 2007 in Tulare County, California. Twenty six vineyard workers reported effects from the drift/volatilization from a chlorpyrifos application to almonds in an adjacent field. Twelve of these workers reported respiratory effects. These respiratory effects include difficulty breathing, shortness of breath, cough, sore throat, chest tightness.

NIOSH Sentinel Event Notification System for Occupational Risk-Pesticides:
For NIOSH SENSOR-Pesticides from 2002 to 2009, there were 204 cases in which chlorpyrifos was the only active ingredient in the suspected substance.[58] Specifically:

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[54] There were 106 additional incident reported to IDS for chlorpyrifos that involved multiple chemicals.

[55] The death incident is described in the database as follows, "*A 58 year old male was reportedly exposed to a ULV product five to six times. Each time he was taken to the emergency room with difficulty breathing and an upset stomach. He was diagnosed with and treated for COPD. The last time he was exposed to the ULV product, he fell while taking a shower after the exposure. He was subsequently hospitalized and died about 10 days later. He also suffered from peeling skin."*

[56] There were 90 additional incidents reported to NPIC for chlorpyrifos that involved multiple chemicals.

[57] There were 133 additional incidents reported to CA PISP for chlorpyrifos that involved multiple chemicals.

[58] SENSOR-Pesticides 2002-2009 has a total of 409 cases involving Chlorpyrifos. Of these, 204 cases involve a single Active Ingredient (pc code=059101). For the purposes of this analysis, only the 204 cases involving a single AI will be included.

- Of the 204 cases, 91 cases (45%) reported one or more respiratory symptoms.

- Of the 91 cases with respiratory symptoms, 77 were low in severity, 11 were moderate in severity and 3 were high in severity.

- Of the 91 cases with respiratory symptoms, the most commonly reported respiratory effect was upper respiratory pain (n=44), followed by cough (n=27) and dyspnea/shortness of breath (n=26).

- 42 of the 204 cases (21%) were attributable to drift, including volatilization[59] and of these 42 drift cases, 20 (49%) reported one or more respiratory symptoms.

- There are 20 cases in SENSOR-Pesticides that are both attributable to drift and have a respiratory symptom. Six of these 20 cases involved bystander exposures to drift; 13 were work-related (exposure while conducting field work or applying pesticide), and one involved a residential application.

- Of the 42 chlorpyrifos drift cases, 12 cases (29%) involved a cited violation. These 12 cases all stem from one event in New Mexico (event ID # NM00001) where a certified applicator was cited for a drift event that resulted in these 12 case reports. Further, of the 42 chlorpyrifos drift cases, 20 cases have label use information, of which 19 cases did not follow the label and one case did follow the label. Twelve of the 19 cases that did not follow the label were in fact the same cases from New Mexico (event ID # NM00001).

SENSOR-Pesticides collects information on the activity that was performed at the time of the exposure. Of the 91 cases that involved a respiratory effect: 24 cases were applying the pesticide, 37 cases were conducting routine work activity (includes field residue), and 15 cases were conducting routine indoor living activities[60] (other activities were unknown or included a small number of cases and are not included here).

In summary, 45% of the chlorpyrifos cases reported in SENSOR-Pesticides from 2002-2009 had respiratory symptoms. It is important to note that in SENSOR-Pesticides, respiratory effects are the most commonly reported symptom with 45% of all cases in the database reporting a respiratory symptom.

Conclusion

EPA's review of chlorpyrifos incidents from IDS, NPIC, PISP, and SENSOR-Pesticides databases show numerous instances in which respiratory effects were seen following both occupational and residential chlorpyrifos exposures. While the available data are insufficient to directly link respiratory effects to chlorpyrifos volatilization exposure, the data suggest that

[59] The SENSOR-Pesticides program defines drift as "…the movement of pesticides away from the treatment site. The pesticide spray, mist, fumes, or odor are carried from the target site by air." There is no clear distinction between cases exposed from volatilization versus spray drift when analyzing the SENSOR-Pesticides data.

[60] Residential uses of chlorpyrifos are no longer allowed.

inhalation exposure to some forms of chlorpyrifos (vapor or aerosol) may result in respiratory health effects. The reported respiratory symptoms appear to be consistent with cholinergic stimulation of the respiratory tract. Specifically, symptoms commonly reported include difficulty breathing, nasal congestion coughing, and chest tightening which are qualitatively consistent with the anticipated cholinergic effects reported by Taylor[46] and by studies of OP war agents.

2.3.3. Dose Response and Endpoint Selection

2.3.3.1. Acute Inhalation Exposure

As discussed in detail in the 2011 preliminary HHRA, the agency did a thorough review of the scientific literature and determined that ChE inhibition provides the most robust dose response data for deriving PODs. Moreover, EPA determined that route-specific studies were most relevant to avoid uncertainties associated with route to route extrapolation. The evaluation of residential bystander risk from chlorpyrifos volatilization is focused only on the inhalation route of exposure, and for short durations.

For chlorpyrifos, there is a special acute inhalation toxicity study[6] available that can be used in the assessment of volatilization risk. In the special acute inhalation study, female rats were exposed by nose only to atmospheric concentrations of up to 53.9 mg/m^3 of particulate chlorpyrifos for 6 hours and allowed an additional 72 hours to recover. The mass median aerodynamic diameter (MMAD)/geometric standard deviations for these exposure levels were determined to be 1.93/1.58, 1.86/1.61, 1.79/1.59 and 1.9/1.51 microns, respectively. Plasma, RBC, brain, and lung ChE were measured.

The EPA uses the Reference concentration (RfC) methodology in extrapolating animal PODs to human equivalent concentrations (for details of the RfC calculations, see the 2011 HHRA). In the 2011 risk assessment, the POD was an HEC calculated based on 24 hour exposure duration which was appropriate for evaluating ambient air exposure. In this volatilization assessment, a 6 hour exposure duration was selected for the purpose of assessing residential bystander risk from volatilization to avoid the need for an exposure duration adjustment and to better match the off-field volatility data (samples were collected every six hours in the alfalfa field volatility study; see **Section 3.4**).

Consistent and significant lung and plasma ChE inhibition were noted at the lowest concentration tested of 3.7 mg/m^3, which is a lowest-observed-adverse-effect-level (LOAEL). RBC and brain ChE inhibition were noted at ≥ 12.9 mg/m^3 and 53.9 mg/m^3, respectively, indicating less sensitivity than lung and plasma ChE inhibition following acute inhalation exposures. A no-observed-adverse-effect-level (NOAEL) was not established. A benchmark dose (BMD) analysis was attempted with the lung ChE data but did not provide high confidence results (for details, see 2011 HHRA). A 6-hour HEC was calculated to be 2.5 mg/m^3 based on the LOAEL of 3.7 mg/m^3.

For the RBC ChE data, a benchmark response (BMR) level of 10% was used to calculate a benchmark response level of 10% ($BMDL_{10}$). The BMD_{10} is the estimated dose where ChE is inhibited by 10% compared to background. The $BMDL_{10}$ is the lower confidence bound on the

BMD_{10}. Extensive analyses conducted as a part of the OP cumulative risk assessment[61] have demonstrated that 10% is a level that can be reliably measured in the majority of rat toxicity studies, and is generally at or near the limit of sensitivity for discerning a statistically significant decrease in ChE activity. BMD analysis of the RBC ChE data resulted in a $BMDL_{10}$ = 4.3 mg/m^3. Using the RfC methodology, a 6-hour HEC was calculated to be 15 mg/m^3.

The inhalation endpoints and PODs used for this analysis are summarized in **Table 3**.

Table 3. Toxicological Concentrations, Human Equivalent Concentrations, Endpoints and Points of Departure for the Chlorpyrifos Residential Bystander Assessment from Volatilization

Exposure Scenario	Point of Departure (mg/kg/day)	Study and Toxicological Effects
Acute Inhalation (Lung)	Inhalation LOAEL = 3.7 mg/m^3 HEC = 2.5 mg/m^3 UFA = 3x UFH = 10x UFDB = 10x (LOAEL to NOAEL extrapolation Residential LOC for MOE = 300	Lung ChE Inhibition Special 6 hour acute inhalation study (MRID 48139303). (Aerosol) - 47% lung ChE inhibition (LOAEL = 3.7 mg/m^3, NOAEL not established)
Acute Inhalation (RBC)	$BMDL_{10}$ = 4.3 mg/m^3 HEC = 15 mg/m^3 UFA = 3x UFH = 10x Residential LOC for MOE = 30	RBC ChE Inhibition Special 6 hour acute inhalation study (MRID 48139303). (Aerosol) - 10 % lung ChE inhibition ($BMDL_{10}$ = 4.3 mg/m^3)
lowest observe affect level (LOAEL); no observe affect level (NOAEL); human equivalent concentration (HEC); uncertainty factor for animal to human extrapolation (UF_A); uncertainty factor for with human variability to account for sensitivity subpopulations (UF_H); uncertainty factor database (UF_{DB}); level of concern (LOC); margin or exposure (MOE); cholinesterase (ChE); red blood cell (RBC); benchmark response level of 10% ($BMDL_{10}$)		

2.3.3.2. Acute Toxicity Adjustment Factor for Chlorpyrifos-oxon

There is potential for bystander inhalation exposure to volatilized chlorpyrifos-oxon, a transformation product of chlorpyrifos. EPA developed a toxicity adjustment factor (TAF) to estimate the potency of chlorpyrifos-oxon relative to chlorpyrifos. An acute study evaluating ChE inhibition from inhalation exposure to the oxon is not available. As such, EPA must use the oral studies as a reasonable approximation.

In order to determine a TAF for chlorpyrifos-oxon, BMD modeling of available oxon data for acute oral dosing studies was conducted as part of the preliminary risk assessment.[1] The complete BMD analysis is described in the 2011 preliminary HHRA; only summary information is provided here.

[61] U.S. Environmental Protection Agency. Revised Organophosphorous Pesticide Cumulative Risk Assessment; June 10, 2002. Available at: http://www.epa.gov/pesticides/cumulative/rra-op/.

There is a high quality comparative ChE study for the oxon and parent, chlorpyrifos using the oral route of exposure.[62] The comparative ChE study evaluates effects of brain and blood ChE in juvenile and adult rats following acute exposures and following 11 repeated exposures. Only the results of the acute study are relevant for the acute TAF and thus only the results of the acute study are discussed here. The most sensitive endpoint from the acute comparative ChE study is RBC ChE inhibition for both chlorpyrifos and chlorpyrifos-oxon.

When deriving PODs, the agency uses the BMDL, not the BMD, since the BMDL accounts for variability of the data. When making comparisons among chemicals, the BMD provides the more appropriate point of comparison across studies. In the case of this assessment, the BMD_{10} provides the basis for determining the relative toxicity of the chlorpyrifos oxon compared to chlorpyrifos. A toxicity factor for chlorpyrifos-oxon was calculated by dividing the chlorpyrifos BMD_{10} for the endpoint associated with the most sensitive compartment from the most sensitive sex for the duration of interest by the corresponding BMD_{10} for the oxon. Acute (all populations) toxicity factors of 8.8 (males) and 11.9 (females) were calculated from BMD analysis of inhibition of male and female pup RBC ChE (acute phase of the comparative ChE study). The toxicity factors may be used in assessments where exposures to chlorpyrifos and chlorpyrifos-oxon are to be combined (*i.e.*, when exposure to both chemicals is expected to occur simultaneously).

2.4. Exposure Characterization

2.4.1. Field Volatility Data

EPA reviewed and incorporated the results from two field volatility studies (applied to alfalfa and potato) conducted with chlorpyrifos. While chlorpyrifos is not currently registered for use on potatoes in the United States, potatoes are thought to be reasonable representative, for the purposes of extrapolation of field volatility data, of other field crops treated with chlorpyrifos and the results of potato field volatility study provide useful information on the potential volatility of chlorpyrifos under field conditions. As previously mentioned, the majority of chlorpyrifos is applied to field crops (67% of the total chlorpyrifos applied per year) including alfalfa (6% of the total chlorpyrifos applied per year).

These studies were conducted at rates much lower than the current maximum single broadcast application rate; however, based on usage data the rates used in these studies are consistent with typical average single application rates for these crops. These two studies are summarized in the sections below and were used to estimate flux rates (*i.e.*, rate of volatilization) off treated crops. Additional study details are provided in the data evaluation record (DER) for each of the respective studies.[7,11]

[62] Marty and Andrus 2010, MRID No.: 48139301 TXR No. 0055409

2.4.1.1. Alfalfa (MRID 48883201)[7]

2.4.1.1.1. Study Summary

The concentration of chlorpyrifos, chlorpyrifos-oxon, and 3,5-6 tricloropyridinol (TCP)[63] in air were measured following application of Lorsban Advanced Insecticide[64] (EPA Reg. No. 62719-591; a liquid, low VOC formulation containing 3.66 lb/gal chlorpyrifos as the active ingredient), to a 7.59 acre alfalfa field (a crop height of 10 inches) via ground broadcast application at an application rate of 0.877 lb a.i./A. The study was conducted in Los Baños, California. The application was made on September 9, 2011, between 9:10 – 10:40 am.

Air sampling was conducted for three days during and after the application. Air samples were collected from eight off-field monitoring stations placed uniformly around each field (30 m from the edge of the treated area) during the first sampling period, which included the application event. The sampling height of the off-field monitors was 1.5 m. After the application, an on-site profile monitoring station was set up in the center of the field to measure concentrations at heights of 0.15, 0.33, 0.55, 0.90, and 1.5 m. The on-field air samples were taken at approximately 6 hour intervals from time 0 (after the application) through 24 hours and at 12 hour intervals from time 24 to 72 hours. The 12 hour samples coincided approximately with sunrise and sunset and were centered at 07:00 and 19:00 hours when possible. On-site meteorological conditions were monitored continuously at the site.

Flux rates for chlorpyrifos and total toxic chlorpyrifos residues (TTCR; chlorpyrifos and chlorpyrifos-oxon) in $\mu g/m^2$-s were calculated using the Indirect Flux Method (IFM) for the first period when the application was in progress (Sampling Period 1) and both the Integrated Horizontal Flux (IHF) method and the Aerodynamic (AD) method for the other sampling periods. A brief description of these methods is provided in **APPENDIX C**. Approximately 28% (chlorpyrifos) and 30% (TTCR) of the applied active ingredient was observed to volatilize within the first 24 hours. For dispersion modeling and subsequent buffer calculations, TTCR is defined in terms of toxic parent equivalents—the sum of the chlorpyrifos concentration and the oxon concentration that has been corrected to parent equivalents using a toxicity adjustment factor (TAF; discussed in detail in **Section 2.3**) of 12.[65]

This study is classified as acceptable and is used quantitatively in this assessment.

2.4.1.1.2. Flux Rates

EPA calculated flux rates for chlorpyrifos (parent only) and TTCR (chlorpyrifos and chlorpyrifos-oxon) in $\mu g/m^2$-s for the first period (*e.g.*, during application) (Sampling Period 1) employing the IFM. Flux rates for the subsequent sampling periods (thru day 3) were calculated using both the IHF method and the AD flux method. Flux rates were calculated accounting for field fortifications (FF) as well as storage stability and are reported in the DER. **Table 4** contains the flux rates for chlorpyrifos (parent only) calculated using both methods (AD and IHF)

[63] TCP is not considered as a residue of concern.
[64] Marketed as a low VOC chlorpyrifos formulation.
[65] Email from Wade Britton (OPP/HED) to Rochelle Bohaty (OPP/EFED) September 10, 2012.

incorporating data for both FF and storage stability for all sampling periods and based on the application rate of 0.877 lb a.i./A used in the study.

Table 4. Estimated Flux Rates for Chlorpyrifos Using AD and IHF Methods for the Alfalfa Study

Period	Sample Start Times	Sample End Times	Duration (hh:mm)	Hours Post Application at Sample Collection	AD Method	IHF Method*
					Estimated Flux FF ($\mu g/m^2$-s)	Estimated Flux FF ($\mu g/m^2$-s)
2	9/9/2011 10:45	9/9/2011 13:00	2.25	2.25	0.824	0.591
3	9/9/2011 13:00	9/9/2011 19:00	6.00	8.25	0.260	0.759
4	9/9/2011 19:00	9/10/2011 1:00	6.00	14.25	0.038	0.171
5	9/10/2011 1:00	9/10/2011 7:00	6.00	20.25	0.026	0.054
6	9/10/2011 7:00	9/10/2011 19:00	12.00	32.25	0.081	0.167
7	9/10/2011 19:00	9/11/2011 7:00	12.00	42.25	0.012	0.021
8	9/11/2011 7:00	9/11/2011 19:00	12.00	54.25	0.020	0.033
9	9/11/2011 19:00	9/12/2011 7:00	12.00	66.25	0.007	0.006
10	9/12/2011 7:00	9/12/2011 19:00	12.00	78.25	0.018	0.012
11	9/12/2011 19:00	9/13/2011 7:00	12.00	90.25	0.002	0.005

Field Fortification (FF)
*Flux profile used in assessment for quantitative assessment (*i.e.*, used in PERFUM modeling).
Data provided in this table are based on the application rate used in the study (0.877 lb a.i./A).

The results for chlorpyrifos (parent only) for the AD method compared well against the values calculated by the study authors; however, the results for the IHF method were higher than those calculated by the study author. A review of the study author's calculations indicated that the IHF analysis was truncated at 150 cm, which resulted in lower flux rate estimates. The IHF method provided slightly more conservative flux profiles; therefore, the flux rates from this method were used in the PERFUM analyses.

EPA examined the flux rate values for oxon only; however, attempts at conducting a regression analysis generated poor fitting results. The study authors also completed this analysis and their results are consistent with EPA's analysis. It is unclear if the chlorpyrifos-oxon concentrations are a result of chlorpyrifos-oxon flux off the field or from transformation of chlorpyrifos in the air or on the tube.[66] In any case, it suggests the potential for exposure to chlorpyrifos oxon. In order to account for the formation and potential increased toxicity from exposure to chlorpyrifos-oxon, EPA used a total toxic residue approach which combines chlorpyrifos and chlorpyrifos-oxon residues. Initial attempts at conducting a regression analysis for the TTCR generated poor fitting results. In general, the oxon concentrations did not follow a decreasing trend with height as did the chlorpyrifos concentrations, resulting in poor fitting results. In an effort to use the available data, a conversion factor was developed for each sampling period, which took the total mass of oxon for all four air samplers and divided this total by the total mass of chlorpyrifos for

[66] The study authors conducted an additional analysis and developed a correction factor to adjust the chlorpyrifos-oxon concentrations to account for chlorpyrifos-oxon formation on the sample tubes during the study.

all four air samplers. The mass of chlorpyrifos at each height was then multiplied by this conversion factor to estimate the mass of oxon at the same height.
Table 5 contains the TTCR flux profile developed for all sampling periods for the alfalfa study.

Table 5. Estimated Flux Rates for Total Toxic Chlorpyrifos Residues (Chlorpyrifos and Chlorpyrifos-oxon) Using AD and IHF Methods for the Alfalfa Study

Sampling Period	Sample Start Times	Sample End Times	Duration (hh:mm)	Hours Post Application at Sample Collection	AD Method	IHF Method*
					Estimated Flux FF ($\mu g/m^2$-s)	Estimated Flux FF ($\mu g/m^2$-s)
2	9/9/2011 10:45	9/9/2011 13:00	2.25	2.25	0.83	0.59
3	9/9/2011 13:00	9/9/2011 19:00	6.00	8.25	0.27	0.78
4	9/9/2011 19:00	9/10/2011 1:00	6.00	14.25	0.038	0.17
5	9/10/2011 1:00	9/10/2011 7:00	6.00	20.25	0.026	0.051
6	9/10/2011 7:00	9/10/2011 19:00	12.00	32.25	0.088	0.18
7	9/10/2011 19:00	9/11/2011 7:00	12.00	42.25	0.012	0.024
8	9/11/2011 7:00	9/11/2011 19:00	12.00	54.25	0.021	0.033
9	9/11/2011 19:00	9/12/2011 7:00	12.00	66.25	0.007	0.006
10	9/12/2011 7:00	9/12/2011 19:00	12.00	78.25	0.020	0.013
11	9/12/2011 19:00	9/13/2011 7:00	12.00	90.25	0.002	0.004

Field Fortification (FF)
*Flux profile used in assessment
Data provided in this table are based on the application rate used in the study (0.877 lb a.i./A).
Flux profile is based on mass only and does not take into account the difference in toxicity between chlorpyrifos and chlorpyrifos-oxon.

2.4.1.2. Potato (MRID 48998801)[11]

2.4.1.2.1. Study Summary

The rate of volatilization of chlorpyrifos only was measured following a 0.61 lb a.i./A ground broadcast application of Dursban EC, an emulsifiable concentration, non-low VOC formulation containing 4.0 lb a.i./gal chlorpyrifos as the active ingredient [the currently marketed equivalent is Dursban 4E (EPA Reg. No.62719-220)], to a potato field (crop height of 22 inches). This study did not measure chlorpyrifos-oxon concentrations. The study was conducted in the Netherlands on June 25, 2002, with the application beginning at 11:30 am.

Air concentration samples were collected beginning at 12:35 pm and ending the following day at 1:37 pm. Samples were collected at 1.0, 1.6, and 1.9 m above the top of ridges on the soil surface at the center of a potato field. Wind speed and temperature data were collected at various heights using equipment positioned at the center of the field during the sample collection period.

Flux rates for chlorpyrifos in $\mu g/m^2$-s were calculated using the AD method. Approximately 71% of the applied chlorpyrifos was estimated to volatilize within 24 hours following application assuming continuous flux. Sampling did not occur at night; therefore, in order to develop a 24

hour flux profile. EPA developed a flux rate for the missing sampling periods by averaging the flux rate prior to and after the time period when sample collection did not occur.

This study is classified as supplemental and is used for characterization purposes in this assessment.

2.4.1.2.2. Flux Rates

EPA developed a flux profile (shown in **Table 6**) for chlorpyrifos in mg/m^2-hr using the flux rates calculated by the study authors using the AD method for the first 24 hours following application of chlorpyrifos at 0.61 lb a.i./A to potatoes. During the overnight hours (approximately 21:00 to 10:00) sample collection did not occur. In order to develop a 24 hour flux profile, the average flux rate for the sampling period immediately before and immediately after the overnight hours (Periods 4 and 5 in **Table 6**) were averaged and assumed to represent the flux that occurred during the overnight period. The raw data for this study have not been made available to EPA so the flux rates could not be independently verified by EPA. However, the results from this study are presented here to provide another line of evidence to characterize the observations in the registrant submitted study to help describe the potential variability in flux rates due to difference in study conditions (*e.g.*, crop canopy, formulation, and weather).

Table 6. Estimated Flux Rates for Chlorpyrifos AD Method For the Potato Study

Sampling Period	Sample Start Times	Sample End Times	Duration (hh:mm)	AD Method
				Estimated Flux (µg/m^2-s)
1	6/25/2002 12:35	6/25/2002 13:56	1:21	1.87
2	6/25/2002 14:01	6/25/2002 15:34	1:33	2.17
3	6/25/2002 15:42	6/25/2002 17:26	1:44	0.82
4	6/25/2002 19:20	6/25/2002 20:44	1:24	0.17
5	6/26/2002 09:54	6/26/2002 11:32	1:38	0.16
6	6/26/2002 11:42	6/26/2002 13:37	1:55	0.08
Data provided in this table are based on the application rate used in the study 0.61 lb a.i./A.				

2.4.2. Conclusions and Modeling Inputs

In general, the flux trends estimated by EPA and those by the study author for the alfalfa study are consistent. In addition, although the magnitudes of the peak flux rate are different, the results of the potato study are consistent with the alfalfa study (**Figure 3**).

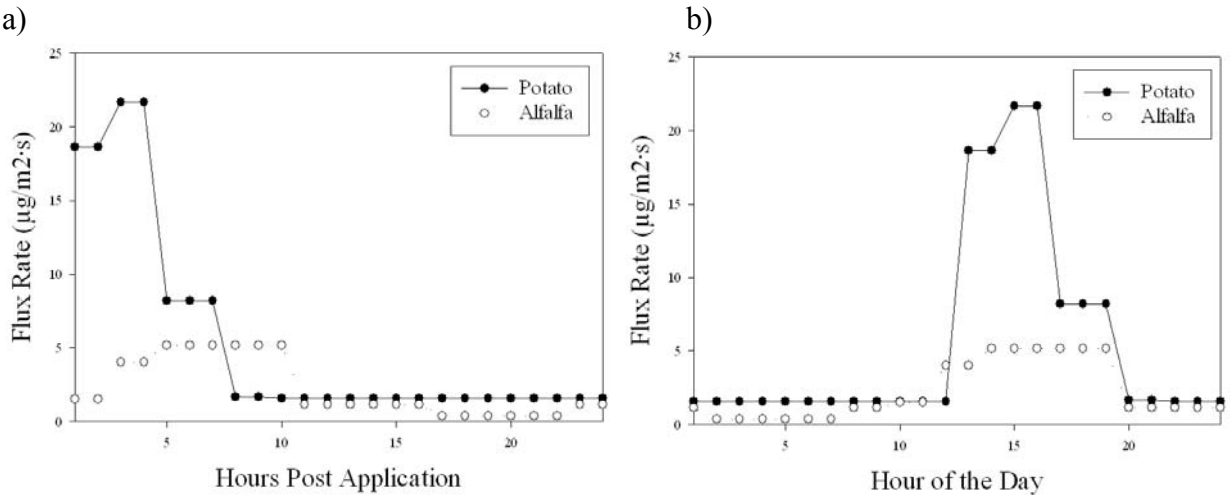

Figure 3. 24 Hour Flux Profile Generated Based on the Two Available Field Volatility Studies for Chlorpyrifos (Parent Only); a) the flux rate compared to hours post application and b) the flux rate compared to the time of day. *NOTE: Flux profiles are scaled up from the actual application rates of 0.877 lb a.i./A (alfalfa) and 0.61 lb a.i./A (potato) to 6 lb a.i./A (current the highest single maximum broadcast application rate registered).*

The difference in the peak flux values estimated between the two studies may be the result of several different factors including: the product formulation used, the crop treated (alfalfa compared to potato), environmental conditions (temperature, humidity, etc.), differences in plant foliage and canopy structure, or a combination of these and other factors. In addition, the difference in the peak values obtained may also be the result of the difference in sample collection periods which could have led to an averaging out of the peak flux based on the longer sampling period used in the alfalfa study as compared to the potato study. **Figure 3** shows the flux profile for both studies for the first 24 hours following chlorpyrifos application based on the calculated flux rates.

The flux profile for chlorpyrifos is similar to those observed for fumigants in that there is a peak emission shortly after application (**Figure 3a**) and during the warmer part of the day (**Figure 3b**). The peak is followed by a much lower emission rate that generally decreases over time. While the potato study does not extend beyond 24 hours post application, the alfalfa study shows a general decrease in emission rates over the next two days. However, a secondary "peak" flux was observed on day two of the alfalfa field volatility study. This observed increase in the flux rate following the overnight hours is likely due to an increase in temperature.

For PERFUM modeling the flux rates from the field volatility studies were adjusted to an application rate of 6 lb a.i./A (currently, the highest single maximum broadcast application rate registered). In the past, flux rates and subsequent modeling were completed by scaling down results for studies conducted at higher application rates; however, in this case, the available studies were conducted at application rates [0.877 lb a.i./A (alfalfa); 0.61 lb a.i./A (potato)] which is below the maximum labeled single broadcast application rate (6 lb a.i./A for citrus). The single application rate used in the alfalfa study is lower than the currently labeled maximum single application rate for alfalfa (1 lb a.i./A).

The flux profiles used in PERFUM model runs are presented in **Table 7** (alfalfa) and **Table 8** (potato). To account for the increased toxicity of the oxon (alfalfa study) compared to the parent chlorpyrifos, the observed oxon concentration was adjusted by a TAF of 12 to generate an exposure concentration in units of parent equivalent toxicity[67]. The adjusted concentration value ([oxon]*TAF) was added to chlorpyrifos (parent only) concentration to develop a TTCR flux profile for PERFUM analyses (shown in **Table 7**).

Table 7. Flux Profile Used in PERFUM Analysis Generated from the Alfalfa Study

Hour of the Day	Chlorpyrifos (only)[a] µg/m^2/sec			Total Toxic Chlorpyrifos Residues[a,b] µg (parent toxicity equivalent units)/m^2/sec		
	Day 1	Day 2	Day 3	Day 1	Day 2	Day 3
1	1.17	0.14	0.04	1.35	0.32	0.05
2	0.37	0.14	0.04	0.44	0.32	0.05
3	0.37	0.14	0.04	0.44	0.32	0.05
4	0.37	0.14	0.04	0.44	0.32	0.05
5	0.37	0.14	0.04	0.44	0.32	0.05
6	0.37	0.14	0.04	0.44	0.32	0.05
7	0.37	0.14	0.04	0.44	0.32	0.05
8	1.14	0.23	0.04	2.63	0.39	0.26
9	1.14	0.23	0.23	2.63	0.39	0.26
10	1.50	1.14	0.23	3.14	2.63	0.39
11	1.50	1.14	0.23	3.14	2.63	0.39
12	4.04	1.14	0.23	5.41	2.63	0.39
13	4.04	1.14	0.23	5.41	2.63	0.39
14	5.19	1.14	0.23	8.68	2.63	0.39
15	5.19	1.14	0.23	8.68	2.63	0.39
16	5.19	1.14	0.23	8.68	2.63	0.39
17	5.19	1.14	0.23	8.68	2.63	0.39
18	5.19	1.14	0.23	8.68	2.63	0.39
19	5.19	1.14	0.23	8.68	2.63	0.39
20	1.17	0.14	0.04	1.35	0.32	0.05
21	1.17	0.14	0.04	1.35	0.32	0.05
21	1.17	0.14	0.04	1.35	0.32	0.05
22	1.17	0.14	0.04	1.35	0.32	0.05
23	1.17	0.14	0.04	1.35	0.32	0.05
24	1.17	0.14	0.04	1.35	0.32	0.05

[67] Parent equivalent toxicity is not representative of the mass balance.

Hour of the Day	Chlorpyrifos (only)[a] µg/m^2/sec			Total Toxic Chlorpyrifos Residues[a,b] µg (parent toxicity equivalent units)/m^2/sec		
	Day 1	Day 2	Day 3	Day 1	Day 2	Day 3

a. Flux profile has been scaled up from an application rate of 0.877 lb a.i./A to 6 lb a.i./A (current maximum single broadcast application rate) and are based on the flux profile that considers FF samples.
b. To account for the increased toxicity of the oxon compared to the parent chlorpyrifos, the observed oxon concentration was adjusted by a toxicity adjustment factor (TAF) of 12 to generate an exposure concentration in units of parent equivalent toxicity[67]. The adjusted concentration value ([oxon]*TAF) was added to chlorpyrifos (parent only) concentration to develop a TTCR flux profile. These values do not directly correlate to 12x the values presented in **Table 5**.

Table 8. Flux Profile Used in PERFUM Analysis Generated from the Potato Study

Hour	Chlorpyrifos (only)[a] µg/m^2/sec
	Day 1
1	1.58
2	1.58
3	1.58
4	1.58
5	1.58
6	1.58
7	1.58
8	1.58
9	1.58
10	1.58
11	1.58
12	1.58
13	18.67
14	18.67
15	21.67
16	21.67
17	8.22
18	8.22
19	8.22
20	1.68
21	1.68
21	1.58
22	1.58
23	1.58
24	1.58

Hour	Chlorpyrifos (only)[a] µg/m^2/sec
	Day 1
a. Flux profile has been scaled up from an application rate of 0.61 lb a.i./A to 6 lb a.i./A (current maximum single broadcast application rate).	

3. RISK ASSESMENT

Chlorpyrifos can be used under a variety of agricultural and environmental conditions. In order to understand the impact such varied conditions can have on exposure (and subsequent risk assessments), analyses were completed using PERFUM to examine the impact of varied application rates, field sizes, and meteorological data (see bullets below). These are the same parameters which have been used as the basis for other similar analyses completed for soil fumigants by EPA. For brevity only a subset of these analyses are presented in the sections below. Example PERFUM output files are provided in **ATTACHMENT 2**. The results of this analysis are presented in the sections below. *Note: the PERFUM analyses do not provide insight into the potential impact of topography, field layout crop canopy, and formulation, on air concentrations. These variables are further discussed in* ***Section 4****.*

- Application rates: 6, 5, 4, 3, 2.3, 2, 1, 0.5, and 0.1 lb a.i./A
- Field size: 1, 5, 10, 20, 40, 60, 80, 100, and 120 acres
- Meteorological data: Bakersfield, California; Bradenton, Florida; Flint, Michigan; Tallahassee, Florida; Ventura, California; and Yakima, Washington

3.1. Buffer Distributions

3.1.1. Alfalfa

3.1.1.1. Chlorpyrifos (Parent Only)

Table 9 presents the PERFUM results based on lung ChE inhibition and the flux profile derived from the alfalfa study. The results are provided for chlorpyrifos (parent only) at an application rate of 1 lb a.i./A. An application rate of 1 lb a.i./A as presented in **Table 9** is close to the actual application rate made in the alfalfa study (0.877 lb a.i./A) and many applications for various crops (*e.g.*, alfalfa, asparagus, bean, sweet corn, cotton, onions, peas, soybean, strawberries, and wheat) are made at approximately 1 lb a.i./A or less. The results from three of the six meteorological datasets (*i.e.*, Ventura, California, Bradenton, Florida, and Flint, Michigan) used in model simulations are presented as these three meteorological datasets are thought to reasonably represent the range of environmental conditions across the United States.

Table 9. Comparison of Results For Chlorpyrifos (parent only) PERFUM Buffer Distributions Based On Alfalfa Study[a, b]

Percentiles	Meteorological Station Location					
	Ventura, CA		Bradenton, FL		Flint, MI	
	Max Buffer[c] (ft)	Whole Field Buffer[d] (ft)	Max Buffer[c] (ft)	Whole Field Buffer[d] (ft)	Max Buffer[c] (ft)	Whole Field Buffer[d] (ft)
10 A, 1 lb a.i/A						
50	16	-	33	-	-	-
75	16	-	148	-	16	-
90	66	16	262	33	16	-
95	148	16	377	98	49	16
99	377	82	607	246	148	16
20 A, 1 lb a.i/A						
50	16	-	98	-	-	-
75	33	-	246	16	16	-
90	164	16	427	82	66	16
95	262	16	607	164	131	16
99	623	180	1001	394	279	82
60 A, 1 lb a.i/A						
50	16	-	262	-	16	-
75	148	16	558	16	82	-
90	410	33	935	213	230	16
95	623	131	1312	377	344	66
99	1345	443	2100	804	640	262
120 A, 1 lb a.i/A						
50	82	-	443	-	16	-
75	279	16	902	66	180	-
90	689	98	1542	361	410	49
95	1050	230	2165	591	607	148
99	2215	722	3510	1263	1198	459

a. Lung: 6 h HEC 2,500 µg/m^3, UF=300, target concentration 8.3 µg/m^3
b. Registrant study conducted on alfalfa using Lorsban Advanced
c. Max buffers are the largest buffer estimated from any given direction away from the field.
d. Whole field buffers are estimated based on an array of results for the entire perimeter of a field.

The results presented in **Table 9** show how buffer distances (whole field[68] and maximum[69] buffers) change in relation to field size, percentile of exposure, and meteorological conditions. Buffer distances are calculated based on the distance at which the target concentration [*i.e.*, toxicity point of departure (HEC for lung ChE inhibition) divided by the uncertainty factor] of 8.3 µg/m^3 is reached. Depending on the percentile of exposure and the field size considered, the maximum buffers needed to be at or below the target concentration range from 0 to greater than 3500 ft. Spray drift buffers to protect bystanders in sensitive sites[70] required on chlorpyrifos

[68] Whole field buffers are estimated based on an array of results for the entire perimeter of a field.
[69] Max buffers are the largest buffer estimated from any given direction away from the field.
[70] Buffers are around sensitive sites (a circle drawn around the sensitive site and do not correspond to buffers around a given field (a circle drawn around a treated field).

labels range from 0-100 feet depending on the application method. The buffers currently required on all chlorpyrifos labels are summarized in **APPENDIX D**.

Considering an application scenario similar to that reported in the alfalfa study—1 lb a.i./A (actual: 0.877 lb a.i./A) chlorpyrifos application made to a 10 A (actual: 7.59 A) alfalfa field in Ventura, California (actual: Los Baños, California) —a 16 foot whole field buffer and a 148 foot maximum buffer were estimated by PERFUM to ensure that 95% of the time bystanders offsite would not be exposed to concentrations higher than the target concentration. If, however, a similar application where to occur in an area with meteorological conditions similar to Bradenton, Florida[71] PERFUM estimates that a 98 foot whole field buffer and a 377 foot maximum buffer are needed to ensure that 95% of the time bystanders are not exposed to air concentrations higher than the target concentration. When considering a larger treatment area, for example, a 120 A alfalfa field similar to the study site.[72] PERFUM estimates that a 230 foot whole field buffer and a 1050 foot maximum buffer are needed to ensure that 95% of the time bystanders are not exposed to air concentrations higher than the target concentration.

Although not presented in detail in this assessment, similar analyses using a target concentration of 497 $\mu g/m^3$ derived based on the RBC ChE inhibition endpoint, indicate that currently labeled buffers (**APPENDIX D)** would result in bystander exposure to offsite concentrations that are less than the target concentration. The target concentration based on the RBC ChE inhibition endpoint is approximately equal to the saturated vapor concentration (489 $\mu g/m^3$) of chlorpyrifos.**Error! Bookmark not defined.** This suggests that in the environment, due to mixing and dispersion, chlorpyrifos vapor concentrations are not likely to occur near the RBC ChE inhibition target concentration except under extreme conditions (*e.g.*, inversion).

Table 10 presents the buffer distributions for a range of applications rates. Again, these results are based on the lung ChE inhibition endpoint and the alfalfa flux profile. Model run results reported in **Table 10** are for chlorpyrifos (only) using the Bradenton, Florida meteorological data. Generally this meteorological dataset results in the largest estimated buffers of all six meteorological stations. Examination of the buffer distributions resulting from the PERFUM runs for all the meteorological datasets show results similar to those presented in **Table 10**. This analysis indicates that higher application rates lead to larger estimated buffers as expected. For example, when considering a same chlorpyrifos application scenario to that presented above for alfalfa in Bradenton, Florida[71], but using a higher application rate (*i.e.*, turf at 4 lb a.i./A—the current maximum single application rate) the estimated buffer is approximately seven times higher. For chlorpyrifos (only), a 673 foot whole field buffer and a 2215 foot maximum buffer would be needed to ensure that 95% of the time the air concentration that bystanders are exposed is not higher than the lung ChE inhibition target concentration.

[71] 1 lb a.i./A (actual: 0.877 lb a.i./A) chlorpyrifos application made to a 10 A (actual: 7.59 A) alfalfa field in Bradenton, Florida (actual: Los Baños, California)

[72] 1 lb a.i./A (actual: 0.877 lb a.i./A) chlorpyrifos application made to a 120 A (actual: 7.59 A) alfalfa field in Ventura, California (actual: Los Baños, California)

Table 10. Comparison of Results For Chlorpyrifos (parent only) PERFUM Buffer Distributions Based On Different Application Rates[a,b]

Percentiles	Bradenton, FL									
	0.5 lb a.i./A		1 lb a.i./A		2 lb a.i./A		4 lb a.i./A		6 lb a.i./A	
	Max Buffer[c] (ft)	Whole Field Buffer[d] (ft)	Max Buffer[c] (ft)	Whole Field Buffer[d] (ft)	Max Buffer[c] (ft)	Whole Field Buffer[d] (ft)	Max Buffer[c] (ft)	Whole Field Buffer[d] (ft)	Max Buffer[c] (ft)	Whole Field Buffer[d] (ft)
10 A										
50	-	-	33	-	328	-	886	-	1394	-
75	16	-	148	-	541	33	1280	148	1969	230
90	16	-	262	33	820	213	1804	459	2674	640
95	16	16	377	98	1033	328	2215	673	3248	968
99	131	16	607	246	1476	623	2871	1230	4347	1772
20 A										
50	-	-	98	3	525	-	1362	-	2133	16
75	16	-	246	16	837	98	1969	246	3018	344
90	16	-	427	82	1296	328	2822	689	4298	935
95	98	16	607	164	1624	509	3510	1017	>4724	1427
99	262	66	1001	394	2264	935	>4724	1870	>4724	2641
60 A										
50	16	-	262	-	1066	-	2740	16	4511	66
75	33	-	558	16	1722	213	4183	492	>4724	689
90	180	16	935	213	2674	640	>4724	1296	>4724	1722
95	279	33	1312	377	3461	984	>4724	1936	>4724	2723
99	640	213	2100	804	>4724	1821	>4724	3707	>4724	3
120 A										
50	16	-	443	-	1706	16	4511	66	>4724	131
75	115	-	902	66	2789	344	>4724	755	>4724	1017
90	328	16	1542	361	4446	984	>4724	1919	>4724	2575
95	509	98	2165	591	>4724	1493	>4724	2936	>4724	4183
99	1099	361	3510	1263	>4724	2838	>4724	>4724	>4724	>4724

a. Registrant study conducted on alfalfa using Lorsban Advanced
b. Lung: 6 h HEC 2,500 µg/m^3, UF=300, target concentration 8.3 µg/m^3
c. Max buffers are the largest buffer estimated from any given direction away from the field.
d. Whole field buffers are estimated based on an array of results for the entire perimeter of a field
e. *Note: PERFUM does not produce buffer zones greater than 4724 ft (1440 m), thus, buffer zones for cases where the 4724 ft (1440 m) limit is reached may be very large. These cases are indicated with a ">4724 ft ".*

3.1.1.2. Total Toxic Chlorpyrifos Residues

To account for the potential exposure to both chlorpyrifos and chlorpyrifos-oxon simultaneously, PERFUM was also used to estimate buffer distances based on exposure to TTCR. This technique incorporates a toxicity adjustment factor that accounts for the potential difference in toxicity between the two chemicals (discussed in **Section 2.3**). **Table 11** presents the PERFUM results, again based on the toxicity endpoint derived from lung ChE inhibition and the flux profile derived from the alfalfa study, for both chlorpyrifos (parent only) and TTCR [in parent equivalents (*i.e.*, chlorpyrifos + chlorpyrifos-oxon*TAF)].

Table 11. Comparison of Results For Chlorpyrifos (parent only) and Total Toxic Chlorpyrifos Residues PERFUM Buffer Distributions[a]

Percentiles	Bradenton, FL					
	Chlorpyrifos (parent only)				TTCR (Chlorpyrifos + Oxon*TAF)	
	Alfalfa[b]		Potato[c]		Alfalfa[b]	
	Max Buffer[d] (ft)	Whole Field Buffer[e] (ft)	Max Buffer[d] (ft)	Whole Field Buffer[e] (ft)	Max Buffer[d] (ft)	Whole Field Buffer[e] (ft)
10 A , 1 lb a.i/A						
50	33	-	394	-	213	-
75	148	-	558	82	394	16
90	262	33	738	262	623	148
95	377	98	902	377	804	246
99	607	246	1280	623	1165	492
20 A, 1 lb a.i/A						
50	98	-	607	-	361	-
75	246	16	837	148	623	49
90	427	82	1132	394	984	246
95	607	164	1362	558	1263	377
99	1001	394	1919	919	1821	755
60 A, 1 lb a.i/A						
50	262	-	1132	16	738	-
75	558	16	1624	295	1296	148
90	935	213	2198	738	2034	492
95	1312	377	2690	1033	2641	771
99	2100	804	3904	1722	3953	1460
120 A, 1 lb a.i/A						
50	443	-	1690	33	1181	-
75	902	66	2510	459	2067	246
90	1542	361	3494	1083	3379	755
95	2165	591	4364	1526	4380	1165
99	3510	1263	>4724	2625	>4724	2264

a. Lung: 6 h HEC 2,500 µg/m^3, UF=300, target concentration 8.3 µg/m^3
b. Registrant study conducted on alfalfa using Lorsban Advanced
c. Open literature study conducted on potato using Dursban
d. Max buffers are the largest buffer estimated from any given direction away from the field.
e. Whole field buffers are estimated based on an array of results for the entire perimeter of a field

Based on exposure to the total toxic residues (expressed in parent equivalents), the modeling results indicate that larger buffers are necessary to ensure air concentrations that bystanders could be exposed to are lower than the target concentration estimated, compared to those estimated for chlorpyrifos (parent only). When considering chlorpyrifos (parent only) in the application scenario (10A, 1 lb a.i./A) presented above for Bradenton, Florida[71] a 98 foot whole field buffer and a 377 foot maximum buffer are needed for the 95th% percentile of exposure. However, when the concentrations of chlorpyrifos (parent only) and chlorpyrifos-oxon are combined and accounted for, the increased toxicity of chlorpyrifos-oxon are taken into account, the buffer estimates are larger—246 feet (whole field buffer) and 804 feet (maximum buffer) for the 95th percentile of exposure.

While the flux profiles are derived from concentrations measured on the field of application, PERFUM modeling does not account for the potential transformation of chlorpyrifos and chlorpyrifos-oxon as these chemicals move offsite (flux study sampling occurs on the application site). Potential transformation pathways in air for chlorpyrifos and chlorpyrifos-oxon include direct and indirect air photolysis. To evaluate the impact of air photolysis on chlorpyrifos air concentrations, EPA ran simulations for a 20 acre square field using AERMOD[73] with and without the half-life term of 7200 seconds, or 2 hours (based on indirect photolysis), in the control pathway. All other input parameters (*e.g.*, field size, meteorological conditions, receptor locations, etc) remained the same for both simulations. In both cases, the maximum 1-hour chlorpyrifos concentration occurred at the same receptor location (near the edge of the corner of the field) and meteorological conditions. The chlorpyrifos air concentration incorporating air photolysis was approximately 7% lower than the air concentration, which did not account for air photolysis. Therefore, the concentration of chlorpyrifos is not expected to markedly change and little impact on the estimated buffer distances for chlorpyrifos (parent only) generated using PERFUM and a 6-hour endpoint is expected, if air photolysis is considered.

This analysis reinforces the hypothesis that chlorpyrifos can be converted to chlorpyrifos-oxon in the air via direct and indirect photolysis, and demonstrates that even at low concentrations (≤7%) formation of chlorpyrifos-oxon can have an appreciable impact on the estimated buffers distances for TTCR due to the expected increased toxicity (12x) of chlorpyrifos-oxon compared to chlorpyrifos. The formation of chlorpyrifos-oxon in the air over a treated field is expected to be captured in the flux profile for TTCR derived from the alfalfa study.

[73] AERMOD is a steady-state plume model that incorporates air dispersion based on planetary boundary layer turbulence structure and scaling concepts, including treatment of both surface and elevated sources, and both simple and complex terrain. Developed by the American Meteorological Society/Environmental Protection Agency Regulatory Model Improvement Committee (AERMIC), AERMOD became EPA's preferred air dispersion model in 2005, replacing the Industrial Source Complex (ISC) model. AERMOD uses a simple runstream setup file, which contains information on the selected modeling options, as well as source location and parameter data, receptor locations, meteorological data file specifications, and output options. Unlike ISC, AERMOD requires two types of meteorological data files that are provided by the AERMET meteorological preprocessor program. One file consists of surface scalar parameters, and the other file consists of vertical profiles of meteorological data.

3.1.2. Potato

3.1.2.1.Chlorpyrifos (Parent Only)

In addition to the buffer distribution analysis considering chlorpyrifos (parent only) and TTCR based on the alfalfa study, **Table 11** also includes buffer distributions based on the flux profile for chlorpyrifos (parent only) derived from the potato study. This table shows that both whole and maximum field buffers calculated using PERFUM are larger based on the potato flux study as compared to the alfalfa study. For example, in the application scenario presented above for alfalfa in Bradenton, Florida,[71] PERFUM estimates that based on the potato flux profile for chlorpyrifos (parent only) a 98 foot whole field buffer and a 377 foot maximum buffer are needed to ensure that 95% of the time the concentration bystanders may be exposed to is less than the target concentration based on the alfalfa study. For the potato study the estimated buffers are 377 ft (whole field buffer) and 902 ft (maximum buffer) related to the same scenario.

The difference in the flux profile and the results of the dispersion modeling (buffer size) between the two studies may be the result of different experimental conditions between the two studies including: the crop treated (alfalfa compared to potato), meteorological conditions (temperature, humidity, etc.), the product formulation used (low VOC compared to a non-low VOC formulation), or a combination of these and other factors. In addition, some of the variation in the estimated buffer distances may be an artifact of the study design given the differences in sample collection periods [6 h (alfalfa) versus 1.5 h (potato)]. This could have led to an averaging out of the peak flux due to the longer sampling periods used in the alfalfa study as compared to the potato study. The aforementioned issues are further discussed **Section 3.5**.

3.2. Buffer Durations

This assessment is based on peak offsite exposure concentrations estimated using PERFUM modeling based on flux profiles derived from two available field volatility studies. An analysis on the potential duration that a buffer would need to be in place to ensure bystanders are not exposed to chlorpyrifos and chlorpyrifos-oxon concentrations higher than the target concentration is presented below. The shape of flux profiles was an important consideration included in the soil fumigant assessments conducted in the past (*e.g.*, how long significant emissions occur after application).

3.2.1. Alfalfa

3.2.1.1.Chlorpyrifos (Parent Only)

Based on the six hour exposure duration, six hour toxicity endpoint for lung, and the 95th percentile exposure, a 50 foot buffer would need to be in place for at least 12 hours for a 10A field treated at 1 lb a.i./A. A 300 foot buffer would need to be in place for 18 hours for the same size field treated at 6 lb a.i/A, in order to ensure that bystanders are not exposed to concentrations of chlorpyrifos (parent only) higher than the target concentration. A graphical

depiction of this analysis is provided in **Figure 4**. The same analysis was conducted for 20, 60, and 120 acre field sizes. Results for 1 lb a.i./A and 6 lb a.i./A are presented for all the field sizes assessed in terms of risk estimations in **Section 4**. The results indicate the peak concentration of chlorpyrifos (parent only) estimated offsite occurs on the day of application; however, on the day following application, there is an increase in the estimated flux concentrations likely due to an increase in temperature following the overnight hours. For some application scenarios, concentrations exceed the target concentration on the second day even when concentrations observed for the 6 hours sampling period prior to this secondary peak concentrations are lower than the target concentration. For some scenarios large buffers (*e.g.*, 300 ft) may need to be inplace for a shorter duration (*e.g.*, 12 hr) than a smaller buffer (*e.g.*, 200 ft; 18hr); however, since the buffer duration for the smaller buffer may be longer, the longer duration may be considered for the larger buffers.

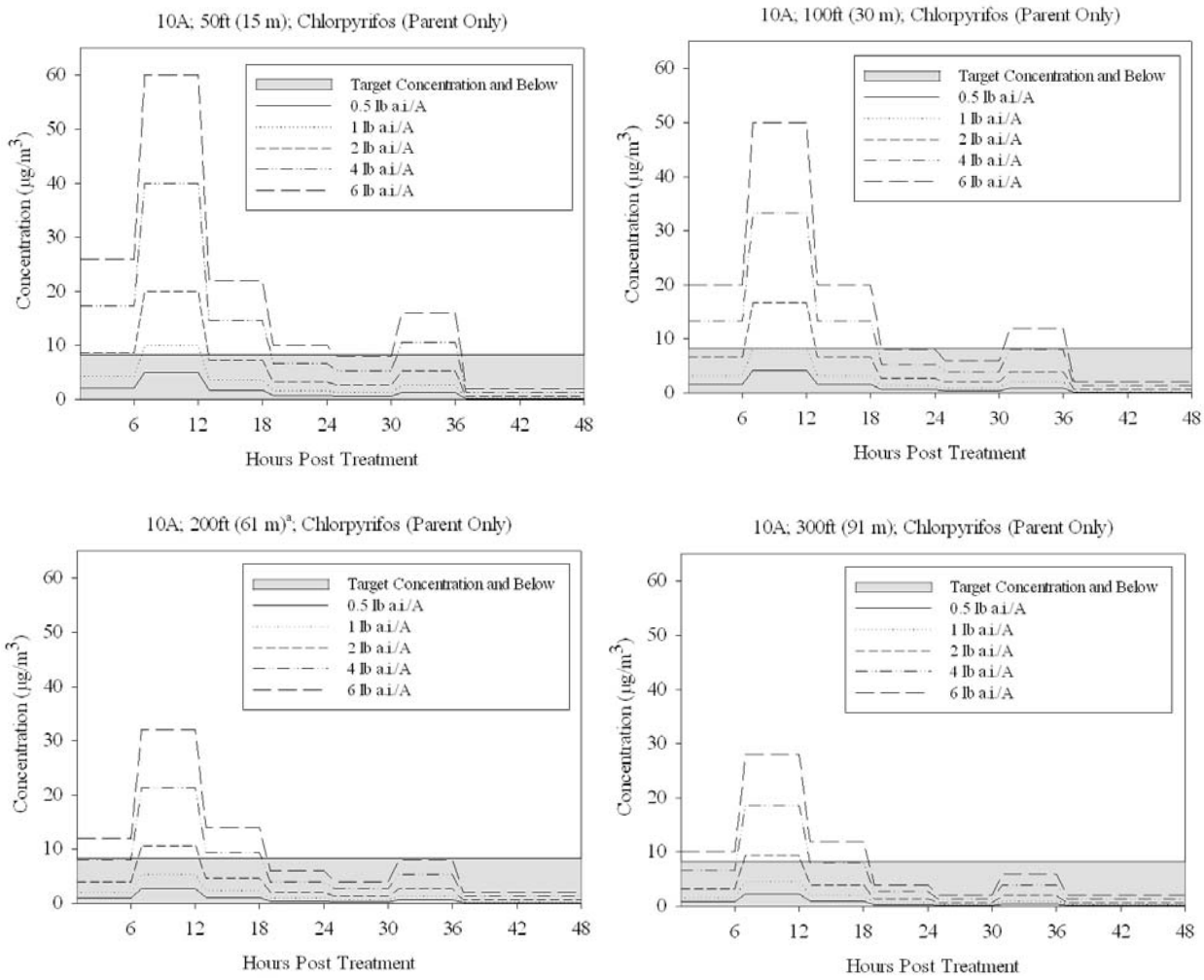

Figure 4. Buffer Duration Analysis for Various Buffer Distances for a 10 Acre Field Considering Chlorpyrifos (parent only) using Bradenton, Florida Meteorological Data; Registrant conducted field volatility study on alfalfa using Lorsban Advanced; Lung: 6 h HEC

2,500 µg/m^3, UF=300 (*i.e.*, MOE =300), target concentration 8.3 µg/m^3; a. actual distance: 230 ft (70 m)

3.3. Risk Estimations

The risk estimates associated with bystander inhalation of vapor phase chlorpyrifos and chlorpyrifos-oxon (specific to the alfalfa application scenario) were calculated based on estimated air concentrations (based on an average concentration around the entire field similar to the whole field buffer concept) at various buffer distances away from a chlorpyrifos treated field for a range of percentiles of exposure and application rates. This provides an additional, conceptual approach of evaluating the potential for bystander risks. The results for chlorpyrifos (parent only) are presented in **Table 12**. The toxicological endpoint used in this analysis is lung ChE inhibition (6 h HEC 2,500 µg/m3). The total applicable uncertainty factor is 300, so a margin of exposure (MOE) < 300, with cells highlighted in red, would be of concern.

The buffer duration analysis presented in **Section 3.2** is presented in terms of risk estimations for all field sizes assessed for 1 lb a.i./A and 6 lb a.i./A in **Table 13**. These results are for chlorpyrifos (parent only), are specific to the alfalfa application scenario and are based on whole field buffers. This buffer duration analysis indicates that buffers need to be in place for at least 12 hours for l lb a.i./A application and for at least 36 hours for 6 lb a.i./A application when considering the 95% percentile exposure concentration. This analysis is based on estimated air concentrations (based on an average concentration around the entire field similar to the whole field buffer concept) at various buffer distances away from a chlorpyrifos treated field.

Table 12. MOEs Comparison for Chlorpyrifos (parent only) Based on Various PERFUM Buffers [a,b]

Bradenton, FL										
Scenario			50 ft (15 m)[c]		100 ft (30 m)[c]		200 ft (61 m)[c]		300 ft (91 m)[c]	
Application Rate (lb a.i./A)	Percentile	Field Size (A)	[Conc. (µg/m^3)]	MOE	[Conc. (µg/m^3)]	MOE	[Conc. (µg/m^3)]	MOE	[Conc. (µg/m^3)]	MOE
0.5	50	10	0	15000	0	--	0	--	0	--
		20	0	7500	0	15000	0	--	0	--
		60	1	3000	1	5000	0	--	0	--
		120	1	2143	1	3000	0	7500	0	15000
	75	10	2	1250	2	1667	1	3750	1	5000
		20	3	938	2	1250	1	2143	1	3000
		60	4	652	3	789	2	1250	2	1500
		120	5	556	4	652	3	938	2	1071
	90	10	4	652	3	789	3	1250	2	1500
		20	5	517	4	612	3	938	2	1154
		60	6	390	6	455	4	612	4	714
		120	8	333	7	375	5	484	5	556
	95	10	5	500	4	600	3	938	2	1071
		20	6	405	5	484	4	682	3	789
		60	8	313	7	353	5	469	5	536
		120	9	268	9	294	7	375	6	417
	99	10	14	174	2	200	9	288	8	333
		20	12	211	11	234	8	300	7	341
		60	11	221	10	242	8	313	7	341
		120	13	188	12	205	10	254	9	278
1	50	10	0	-	0	-	0	--	0	--
		20	1	3750	0	7500	0	--	0	--
		60	2	1500	1	2500	0	--	0	--
		120	2	1071	2	1500	1	3750	0	7500
	75	10	4	625	3	833	1	1875	1	2500
		20	5	469	4	625	2	1071	2	1500
		60	8	326	6	395	4	625	3	750
		120	9	278	8	326	5	469	5	536
	90	10	8	326	6	395	4	625	3	750
		20	10	259	8	306	5	469	4	577
		60	13	195	11	227	8	306	7	357
		120	15	167	13	188	10	242	9	278
	95	10	10	250	8	300	5	469	5	536

Bradenton, FL										
Scenario			50 ft (15 m)[c]		100 ft (30 m)[c]		200 ft (61 m)[c]		300 ft (91 m)[c]	
Application Rate (lb a.i./A)	Percentile	Field Size (A)	[Conc. (µg/m^3)]	MOE	[Conc. (µg/m^3)]	MOE	[Conc. (µg/m^3)]	MOE	[Conc. (µg/m^3)]	MOE
		20	12	203	10	242	7	341	6	395
		60	16	156	14	176	11	234	9	268
		120	19	134	17	147	13	188	12	208
	99	10	29	87	25	100	17	144	15	167
		20	24	106	21	117	17	150	15	170
		60	23	110	21	121	16	156	15	170
		120	27	94	24	103	20	127	18	139
2	50	10	1	3750	0	--	0	--	0	--
		20	1	1875	1	3750	0	--	0	--
		60	3	750	2	1250	0	--	0	--
		120	5	536	3	750	1	1875	1	3750
	75	10	8	313	6	417	3	938	2	1250
		20	11	234	8	313	5	536	3	750
		60	15	163	13	197	8	313	7	375
		120	18	139	15	163	11	234	9	268
	90	10	15	163	13	197	8	313	7	375
		20	19	129	16	153	11	234	9	288
		60	26	97	22	114	16	153	14	179
		120	30	83	27	94	21	121	18	139
	95	10	20	125	17	150	11	234	9	268
		20	25	101	21	121	15	170	13	197
		60	32	78	28	88	21	117	19	134
		120	37	67	34	74	27	94	24	104
	99	10	9	87	25	100	17	144	15	167
		20	35	72	31	82	23	110	20	125
		60	45	55	41	60	32	78	29	85
		120	53	47	49	51	39	64	36	69
4	50	10	1	1875	0	--	0	--	0	--
		20	3	938	1	1875	0	--	0	--
		60	7	375	4	625	0	--	0	--
		120	9	268	7	375	3	938	1	1875
	75	10	16	156	12	208	5	469	4	625
		20	21	117	16	156	9	268	7	375
		60	31	82	25	99	16	156	13	188

Bradenton, FL										
Scenario			50 ft (15 m)[c]		100 ft (30 m)[c]		200 ft (61 m)[c]		300 ft (91 m)[c]	
Application Rate (lb a.i./A)	Percentile	Field Size (A)	[Conc. (µg/m^3)]	MOE	[Conc. (µg/m^3)]	MOE	[Conc. (µg/m^3)]	MOE	[Conc. (µg/m^3)]	MOE
6		120	36	69	31	82	21	117	19	134
	90	10	31	82	25	99	16	156	13	188
		20	39	65	33	77	21	117	17	144
		60	51	49	44	57	33	77	28	89
		120	60	42	53	47	41	60	36	69
	95	10	40	63	33	75	21	117	19	134
		20	49	51	41	60	29	85	25	99
		60	64	39	57	44	43	59	37	67
		120	75	33	68	37	53	47	48	52
	99	10	57	44	50	50	35	72	30	83
		20	69	36	61	41	45	55	40	63
		60	91	28	83	30	64	39	59	43
		120	107	23	97	26	79	32	72	35
	50	10	2	1250	0	--	0	--	0	--
		20	4	625	2	1250	0	--	0	--
		60	10	250	6	417	0	--	0	--
		120	14	179	10	250	4	625	2	1250
	75	10	24	104	18	139	8	313	6	417
		20	32	78	24	104	14	179	10	250
		60	46	54	38	66	24	104	20	125
		120	54	46	46	54	32	78	28	89
	90	10	46	54	38	66	24	104	20	125
		20	58	43	49	51	32	78	26	96
		60	77	32	66	38	49	51	42	60
		120	90	28	80	31	62	40	54	46
	95	10	60	42	50	50	32	78	28	89
		20	74	34	62	40	44	57	38	66
		60	96	26	85	29	64	39	56	45
		120	112	22	102	25	80	31	72	35
	99	10	86	29	78	33	52	48	45	56
		20	104	24	92	27	68	37	60	42
		60	136	18	124	20	96	26	88	28
		120	218	11	204	12	170	15	158	16

a. Registrant study conducted on alfalfa using Lorsban Advanced

Bradenton, FL										
Scenario			50 ft (15 m)[c]		100 ft (30 m)[c]		200 ft (61 m)[c]		300 ft (91 m)[c]	
Application Rate (lb a.i./A)	Percentile	Field Size (A)	[Conc. (µg/m^3)]	MOE	[Conc. (µg/m^3)]	MOE	[Conc. (µg/m^3)]	MOE	[Conc. (µg/m^3)]	MOE

b. Lung: 6 h HEC 2,500 µg/m^3, UF=300 (i.e., MOE =300), target concentration 8.3 µg/m^3

c. 50 ft (15 m)[c] reported for Ring; 100 ft (30 m) reported for Ring 6; 200 ft (61 m) reported for Ring 8 [actual distance: 230 ft (70 m]; 300 ft (91 m) reported for Ring 10

Table 13. Buffer Duration Comparison for Chlorpyrifos (parent only) Based on Various PERFUM Buffers[a,b,c]

Bradenton, FL										
Scenario			50 ft (15 m)[d]		100 ft (30 m)[d]		200 ft (61 m)[d]		300 ft (91 m)[d]	
Application Rate (lb a.i./A)	Field Size (A)	Hours Post-treatment	[Conc. (µg/m^3)]	MOE	[Conc. (µg/m^3)]	MOE	[Conc. (µg/m^3)]	MOE	[Conc. (µg/m^3)]	MOE
1	10	6	4	577	3	750	2	1250	2	1500
		12	10	250	8	300	5	469	5	536
		18	4	682	3	750	2	1071	2	1250
		24	2	1500	1	1875	1	2500	1	3750
		30	1	1875	1	2500	1	3750	0	7500
		36	3	938	2	1250	1	1875	1	2500
		42	0	7500	0	7500	0	7500	0	7500
		48	0	7500	0	7500	0	7500	0	7500
		54	0	7500	0	7500	0	--	0	--
		60	0	7500	0	7500	0	7500	0	--
		66	0	--	0	--	0	--	0	--
		72	0	--	0	--	0	--	0	--
	20	6	5	500	4	625	3	938	2	1071
		12	12	203	10	242	7	341	6	395
		18	5	536	4	577	3	833	3	938
		24	2	1250	2	1500	1	2500	1	2500
		30	2	1500	1	1875	1	3750	1	3750
		36	3	833	3	938	2	1250	2	1500
		42	1	3750	1	3750	0	7500	0	7500
		48	1	3750	0	7500	0	7500	0	7500
		54	0	7500	0	7500	0	--	0	--
		60	0	7500	0	7500	0	7500	0	7500
		66	0	--	0	--	0	--	0	--
		72	0	--	0	--	0	--	0	--

Bradenton, FL										
Scenario			50 ft (15 m)[d]		100 ft (30 m)[d]		200 ft (61 m)[d]		300 ft (91 m)[d]	
Application Rate (lb a.i./A)	Field Size (A)	Hours Post-treatment	[Conc. (µg/m^3)]	MOE	[Conc. (µg/m^3)]	MOE	[Conc. (µg/m^3)]	MOE	[Conc. (µg/m^3)]	MOE
	60	6	6	395	5	469	4	682	3	750
		12	16	156	14	176	11	234	9	268
		18	6	395	6	417	5	536	4	577
		24	3	938	2	1071	2	1500	2	1500
		30	2	1250	2	1500	1	2500	1	2500
		36	4	625	4	682	3	938	2	1071
		42	1	2500	1	2500	1	3750	1	3750
		48	1	3750	1	3750	0	7500	0	7500
		54	0	7500	0	7500	0	7500	0	7500
		60	1	3750	1	3750	0	7500	0	7500
		66	0	7500	0	7500	0	--	0	--
		72	0	--	0	--	0	--	0	--
	120	6	7	341	6	395	5	536	4	625
		12	19	134	17	147	13	188	12	208
		18	8	326	7	341	6	417	6	441
		24	3	833	3	938	2	1250	2	1250
		30	2	1071	2	1250	1	1875	1	1875
		36	5	500	4	577	3	750	3	833
		42	1	2500	1	2500	1	2500	1	3750
		48	1	2500	1	3750	1	3750	1	3750
		54	0	7500	0	7500	0	7500	0	7500
		60	1	3750	1	3750	1	3750	0	7500
		66	0	7500	0	7500	0	7500	0	7500
		72	0	--	0	--	0	--	0	--
6	10	6	26	96	20	125	12	208	10	250
		12	60	42	50	50	32	78	28	89
		18	22	114	20	125	14	179	12	208
		24	10	250	8	313	6	417	4	625
		30	8	313	6	417	4	625	2	1250
		36	16	156	12	208	8	313	6	417
		42	2	1250	2	1250	2	1250	2	1250
		48	2	1250	2	1250	2	1250	2	1250
		54	2	1250	2	1250	0	--	0	--

Bradenton, FL										
Scenario			50 ft (15 m)[d]		100 ft (30 m)[d]		200 ft (61 m)[d]		300 ft (91 m)[d]	
Application Rate (lb a.i./A)	Field Size (A)	Hours Post-treatment	[Conc. (µg/m^3)]	MOE	[Conc. (µg/m^3)]	MOE	[Conc. (µg/m^3)]	MOE	[Conc. (µg/m^3)]	MOE
		60	2	1250	2	1250	2	1250	0	--
		66	0	--	0	--	0	--	0	--
		72	0	--	0	--	0	--	0	--
	20	6	30	83	24	104	16	156	14	179
		12	74	34	62	40	44	57	38	66
		18	28	89	26	96	18	139	16	156
		24	12	208	10	250	6	417	6	417
		30	10	250	8	313	4	625	4	625
		36	18	139	16	156	12	208	10	250
		42	4	625	4	625	2	1250	2	1250
		48	4	625	2	1250	2	1250	2	1250
		54	2	1250	2	1250	0	--	0	--
		60	2	1250	2	1250	2	1250	2	1250
		66	0	--	0	--	0	--	0	--
		72	0	--	0	--	0	--	0	--
	60	6	38	66	32	78	22	114	20	125
		12	96	26	85	29	64	39	56	45
		18	38	66	36	69	28	89	26	96
		24	16	156	14	179	10	250	10	250
		30	12	208	10	250	6	417	6	417
		36	24	104	22	114	16	156	14	179
		42	6	417	6	417	4	625	4	625
		48	4	625	4	625	2	1250	2	1250
		54	2	1250	2	1250	2	1250	2	1250
		60	4	625	4	625	2	1250	2	1250
		66	2	1250	2	1250	0	--	0	--
		72	2	1250	2	1250	0	--	0	--
	120	6	44	57	38	66	28	89	24	104
		12	112	22	102	25	80	31	72	35
		18	46	54	44	57	36	69	34	74
		24	18	139	16	156	12	208	12	208
		30	14	179	12	208	8	313	8	313
		36	30	83	26	96	20	125	18	139

Bradenton, FL										
Scenario			50 ft (15 m)[d]		100 ft (30 m)[d]		200 ft (61 m)[d]		300 ft (91 m)[d]	
Application Rate (lb a.i./A)	Field Size (A)	Hours Post-treatment	[Conc. (µg/m^3)]	MOE	[Conc. (µg/m^3)]	MOE	[Conc. (µg/m^3)]	MOE	[Conc. (µg/m^3)]	MOE
		42	6	417	6	417	6	417	4	625
		48	6	417	4	625	4	625	4	625
		54	2	1250	2	1250	2	1250	2	1250
		60	4	625	4	625	4	625	2	1250
		66	2	1250	2	1250	2	1250	2	1250
		72	2	1250	2	1250	2	1250	2	1250

a. Registrant study conducted on alfalfa using Lorsban Advanced
b. Lung: 6 h HEC 2,500 µg/m^3, UF=300 (*i.e.*, MOE =300), target concentration 8.3 µg/m^3
c. For brevity, the results are presented for the 95% percentile of exposure.
d. 50 ft (15 m)[c] reported for Ring; 100 ft (30 m) reported for Ring 6; 200 ft (61 m) reported for Ring 8 [actual distance: 230 ft (70 m]; 300 ft (91 m) reported for Ring 10

4. ISSUES FOR CONSIDERATION

4.1. Air Monitoring Data

There are 15 available chlorpyrifos air monitoring studies which were summarized in the preliminary HHRA.[1] These include two application site studies done in Tulare and Lompoc Counties, California by the California Air Resources Board (CARB), and 13 ambient air studies in which the particular source of chlorpyrifos within the impacted areas was not identified. These ambient air studies were conducted in the North Central and Yakima Valleys of Washington by the University of Washington Department of Environmental and Occupational Health Sciences. The remaining11 studies were conducted by Pesticide Action Network North America (PANNA), two in Cowiche and Tieton, Washington, and nine in Lindsay, California.

The risk associated with air concentrations measured in these studies was assessed as part of the 2011 preliminary HHRA which also provides more detail concerning the conduct of the studies.[1] Risks of some degree were identified in both the ambient and application site monitoring data. Risks associated with ambient monitoring do not directly relate to the type of analysis presented herein because the monitoring data may represent multiple chlorpyrifos applications but the data suggest chlorpyrifos is found in air samples which may be the result of volatilization off a treated field. The risks identified for application sites monitoring studies are directly related to this analysis and are consistent with the findings of this assessment. These data coupled with the alfalfa and potato flux studies further indicate that chlorpyrifos volatilize from treated crops after applications at levels which could lead to bystander exposure at levels of concern.

4.2. Uncertainties

4.2.1. Hazard Assessment

The special, acute inhalation study evaluated measures of the central (brain) and peripheral nervous system *(e.g.*, pulmonary tissues) and the blood measures. This study also includes time course data to establish the time to peak effect and time to recovery for ChE inhibition in each tissue. As noted in EPA's ChE policy, measures of peripheral nervous tissue are preferred over surrogate measures; specifically, use of lung ChE alleviates the uncertainties associated with use of surrogate tissue (*i.e.*, RBC AChE) which are not innervated. Measurements of lung ChE provide a direct measure relevant to the route of interest and thus protecting against lung ChE should thereby protect against cholinergic effects in the respiratory system. Because there are no measures of pulmonary function in the acute inhalation study, the relationship between measures of lung ChE inhibition and respiratory effects is not known. Thus, there is uncertainty associated with relating the degree of lung ChE inhibition with adverse apical outcomes (*e.g.*, pulmonary function). However, human incident reporting is consistent with the anticipated respiratory effects associated with cholinergic stimulation. The incident reported in the databases suggest difficulty breathing, nasal congestion, coughing, and chest tightening which are qualitatively consistent with the anticipated cholinergic effects reported by Taylor[46] and by studies of OP war agents.[48,49,50,51] While the available human incident data are insufficient to directly link respiratory effects to chlorpyrifos volatilization exposure, this information qualitatively supports

the lung ChE effects reported in the acute inhalation study in rats as being relevant for human health risk assessment.

In addition to the lung ChE POD, the EPA is also estimating volatilization risk using the RBC ChE endpoint. Despite the uncertainties associated with surrogate measures, the EPA is taking this approach because 1) the agency has significant experience with the blood endpoints in risk assessment and thus provides a historical comparison point(s); 2) the RBC AChE inhibition data can be used as a surrogate for other peripheral tissues (*e.g.*, digestive tract, heart) for which such inhalation data are not available; 3) PODs for other routes (*i.e.*, dermal, oral) are being derived from RBC AChE data; and 4) the acute TAF is derived from RBC AChE data.

There are areas of uncertainty associated with the hazard characterization/identification in the volatilization assessment such as the toxicity adjustment factor derived from oral data and the nature of the exposure (aerosol) in the acute inhalation study used to assess volatilization exposure (vapor). The tissue dosimetry appears to be different between oral and inhalation exposure. With oral exposure, the liver primarily metabolizes chlorpyrifos prior to circulation to the remainder of the body. In contrast, from inhalation exposure, chlorpyrifos enters the blood stream directly. Given the different patterns of tissue dosimetry between oral and inhalation, there is uncertainty in the extent to which the oral toxicity adjustment factor is predictive of inhalation exposure. Nonetheless, the comparative ChE oral study is the best available source of dose response data comparing the parent and its transformation product and thus provides a source of data to develop a toxicity adjustment factor. If additional inhalation data for chlorpyrifos-oxon become available in the future, the EPA will, if appropriate, reconsider the adjustment factor.

The special acute inhalation study involves aerosolized chlorpyrifos with relatively small particles (MMAD/geometric standard deviations:1.93/1.58, 1.86/1.61, 1.79/1.59 and 1.9/1.51 microns). There are two subchronic inhalation studies which involved exposure to vapor phase chlorpyrifos. Toxicity studies based on vapor exposure are believed to be more relevant for assessing risks of volatilization exposure. The vapor studies showed no biologically relevant findings up to 287 $\mu g/m^3$ (albeit, lung ChE, the most sensitive endpoint from the aerosol study was not measured). In contrast, the aerosol study shows close to 50% lung ChE inhibition at the lowest concentration of 3.7 mg/m^3 (370 $\mu g/m^3$). Given the high quality design and conduct of the aerosol study, that the particle size was < 2 microns, and that the aerosol study involves acute exposure which is more relevant to volatilization, EPA has chosen to use the special acute inhalation study for deriving a POD for this volatilization assessment.

In the preliminary HHRA, the EPA determined that for acute oral exposures, RBC AChE data from post-natal day 11 (PND11) represented the most sensitive life stage. With respect to this assessment, the special acute inhalation study involved testing of only adult female rats. As such, there is some uncertainty as to whether or not juvenile rats may be more sensitive than adults to inhalation exposure of chlorpyrifos. It is noteworthy that the degree of sensitivity noted in the oral CCA study for PND11 rats compared to adult rats is only 2-fold. There are two literature studies which evaluated lung ChE in fetuses exposed to chlorpyrifos during gestation[39] or rat pups directly dosed postnally but neither provides useful information about the relative sensitivity between post-natal pups and adults with respect to lung ChE inhibition.[41] Given the small (2-fold)

difference in sensitivity between PND11 and adult rats in the CCA study, the lack of inhalation data in rats pups does not contribute large uncertainty to this volatility assessment.
Despite the noted uncertainties related to aerosolized chlorpyrifos vs. vapor chlorpyrifos and the lack of inhalation data in post-natal pups, given the robust study design and conduct of the special acute inhalation study, EPA has confidence in the hazard assessment for chlorpyrifos presented in this assessment.

4.2.2. Application Rate Scaling

The flux studies available for consideration in this assessment were conducted using application rates [0.877 lb a.i/A (alfalfa) and 0.61 lb a.i./A (potato)] and are much lower than the maximum single broadcast application rate of 6 lb a.i./A for citrus currently permitted on chlorpyrifos products. In addition to citrus, several other uses also have maximum single application rates higher than those used in the available flux studies including: mint (2.0 lb a.i./A), turf (4.0 lb a.i./A) and alfalfa (1 lb a.i./A).

In past assessments (*e.g.*, conducted for the soil fumigants), maximum application rates were used in the flux studies and, for mitigation purposes, EPA assumed that there was a linear correlation between pesticide application rate and the flux rate (*i.e.*, as the application rate decreased, the flux rate should decrease directly). This assumption was justified, as one would not expect less material to leave the field on a per unit basis if the application rate were lowered. There is also regulatory precedent for this type of approach in human health risk assessment (*e.g.*, scaling of dislodgeable foliar residue data to calculate Restricted Entry Intervals). There is some additional uncertainty, however, with scaling up based on the application rate; it is unclear as to how the diffusion of the material into the air would be impacted by adding more material to the foliar surface or by increasing the layer of active ingredient on the foliar surface. Thus, the magnitude of the resulting buffers could be higher than expected based on the current approach (*i.e.*, a linear scale up based on the application rate).

4.2.3. Crop to Crop Variation (Flux and Dispersion)

The difference in flux rates and subsequent dispersion of vapor phase chlorpyrifos and chlorpyrifos-oxon residues from different crops is unknown. There are several crop related factors including canopy shape and height, leaf area index, leaf type, crop density, surface roughness length, and possibly others factors that may influence the flux rate of a given pesticide on a particular treated crop and the dispersion of the pesticide in and around the treated area. Therefore, the extrapolation of the flux rates measured in both the alfalfa and potato field volatility studies to other crops is an uncertainty.

There is some uncertainty in using PERFUM for dispersion modeling of semi-volatile pesticides applied to elevated crops such as orchards and trellis crops. At this time, EPA has not evaluated if this uncertainty is due to the flux estimates not being representative of emissions from these types of crops, or is a result of insufficient model parameterization. The use of PERFUM to model dispersion associated with an application to crops was an issue discussed by the 2009 SAP[5] as there are no validated methods available to explore this uncertainty and very limited monitoring data are available to do a comparison. As a follow-up to the 2009 SAP, and in

addition to searching the open scientific literature, EPA has engaged government, academic, and industrial scientists either directly or at various scientific conferences to gain a better understanding of the various crop related factors and how such factors may impact pesticide volatilization from vegetative surfaces. To date, EPA is not aware of research that addresses this area of uncertainty.

Nevertheless, for the particular scenarios used in this assessment a validation study was conducted that closely resembles the scenario considered in this assessment for chlorpyrifos treated field crops with strongly supports the approach used in this analysis. This study is referred to as the Prairie Grass study[22] that was used to support the ground level release algorithms in the ISCST model is the underlying PERFUM engine. This study was conducted on an uncultivated field covered with natural prairie grasses using a volatile pesticide with field conditions similar to the available flux studies conducted on alfalfa and potato.

To provide some characterization of the PERFUM model for an elevated source, EPA looked at monitoring data (offsite concentrations) collected following a chlorpyrifos citrus application and compared the measured concentrations to the model estimated results, based on the flux derived from the alfalfa flux study. The measured and estimated concentrations are in good agreement as far as magnitude [30 $\mu g/m^3$ (peak observed); 20-40 $\mu g/m^3$ (peak estimated)]. An explanation of this analysis is provided below.

In June of 1996, the CARB conducted an air monitoring study around a 60-acre orange orchard that had been treated with chlorpyrifos at a rate of 6 lb a.i./A. The maximum 6-hour measured air concentration for chlorpyrifos was approximately 28 $\mu g/m^3$ measured 57 feet from the edge of the field. In order to characterize the magnitude of air concentration around an orchard (*i.e.*, to see if the levels from the model were approximately the same as those observed in the CARB monitoring study), EPA used PERFUM and the flux rates from the alfalfa study. EPA ran PERFUM in the greenhouse mode to simulate an elevated source. The source had an area of 60 acres and a release height of 4 m. The flux profile was the same one developed from the alfalfa study for chlorpyrifos (parent only), scaled for a 6 lb a.i./A application rate. Ventura, California meteorological data for June 1995-1999 were used. The maximum 6-hour concentration 60 feet from the edge of the field was 24 ug/m^3. Although PERFUM has yet to be validated for semi-volatile emissions from an orchard and chlorpyrifos flux data are not available for an orchard, the modeling simulations are in reasonable agreement with the 28 $\mu g/m^3$ observed in the CARB study.

EPA is aware of one literature article[74] that describes a method for adjusting flux rates to develop an estimated flux profile for orchard crops taking into account the leaf surface area and orchard tree density. Using the method reported in the literature article, flux rates would be much higher and as a result, EPA expects that the buffer zones would need to be even larger than the estimated buffers reported in this assessment to ensure bystanders are not exposed to concentrations higher than the target concentration. It is important to note that the method

[74] Woodrow, J. E.; Seiber, J. N. Correlation Techniques for Estimating Pesticide Volatilization Flux and Downwind Concentrations, *Environ. Sci. Technol*. **1997**, *31*, 523-529.

described in this article has not been validated and it is uncertain if this is a suitable method for scaling flux profiles to account for volatilization of pesticides from orchard canopies.

In summary, there is uncertainty related to the emissions of pesticides applied to orchard and trellis crops. This includes the methods that can be used for quantify emissions from treated orchard and trellis crops. Also, there are ongoing discussions in the scientific community on the driving factors for emission from treated crops (*e.g.*, alfalfa) and how these factors may affect flux rates for other crops such as orchard and trellis crops. The disparate findings between the two analysis (CARB monitoring comparison and the leaf area index scale up method) attempted by EPA also underscore this uncertainty. Given these considerations, at this time EPA believes it is appropriate to acknowledge the uncertainties and note that these factors should be considered when developing a risk management strategy for orchard and trellis crops.

4.2.4. Formulation

Two formulations of chlorpyrifos were used to generate the available emissions data (Lorsban Advance and Dursban EC). There are marked differences in the emission rates for each. This could be based on a variety of factors as discussed above such as field conditions, crop, weather, formulation, etc. It is unclear how the volatility of chlorpyrifos may differ between formulations (*i.e.*, between one low VOC formulation and another or a low VOC formulation, and a non-low VOC formulation) as the low VOC designation is solely based on a reduction in the total amount of mass loss from a given formulation including components such as solvents, and is not specific to the active ingredient. Exploration of the potential formulation effect on volatility following application was done using CDPR's online VOC Emissions Calculator.[75] This tool was developed based on Thermogravimetric analysis (TGA) data submitted to the State of California. TGA allows for the comparison of one formulation to another by comparing the amount of total material that can be displaced as a result of heating. Examination of several different formulations suggests that non-low VOC formulations may result in volatilization that is twice as high as low-VOC formulations on a total mass basis (see **Figure 5**). These results are for total mass—that is the total amount of volatility organic chemicals—and is not necessarily reflective of one component of the formulation (*i.e.*, the active ingredient). In general, the low VOC formulations developed for chlorpyrifos replace volatile solvents with water to reduce the volatility of the overall formulation. In the case of the Lorsban Advanced formulation, it is unclear if the change in formulation reduces the volatility of chlorpyrifos or simply reduces the amount of total VOC emitted.

[75] http://apps.cdpr.ca.gov/voc-calculator/start.cfm; accessed September 19, 2012

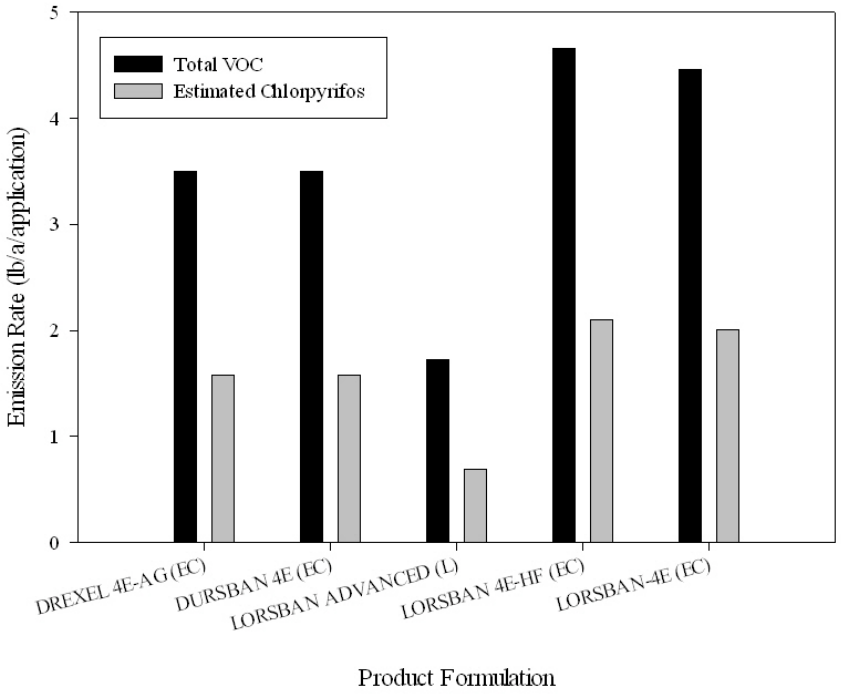

Figure 5. Volatility Comparison for Various Chlorpyrifos Formulated Products

Chlorpyrifos emissions presented in **Figure 5** were calculated based on the percentage included in the product formulation and may not reflect actual emissions concentrations. In addition, this analysis was based on an application rate of 1 gallon formulated product/acre applied to a 20 acre field. Since the studies used in the development of the VOC Emissions Calculator[75] are not chemical specific (*i.e.*, the studies did not specially measure the amount of chlorpyrifos emitted), the formulation effect on the volatilization rate of chlorpyrifos is unclear.

A report[76] recently submitted by Dow AgroSciences to EPA indicates that under laboratory conditions the volatility of chlorpyrifos does not vary between liquid formulations except when the active ingredient is encapsulated. This study was done by applying aqueous dilutions of various chlorpyrifos formulations to an inert sand surface. The samples were stored in an uncapped vial in a 54 °C (129 °F) oven. At selected time points, chlorpyrifos was extracted from the sand samples and quantified. **Figure 6** shows the results from this study in terms of remaining chlorpyrifos—that is the amount of chlorpyrifos that was extracted from the sand.

[76] **EPA MRID 49005301**: *Lab Volatility Study of selected Chlorpyrifos Products*; Author: Dennis Wujek Study Sponsor: Dow AgroSciences LLC, 9330 Zionsville Road Indianapolis, IN 46268-1054

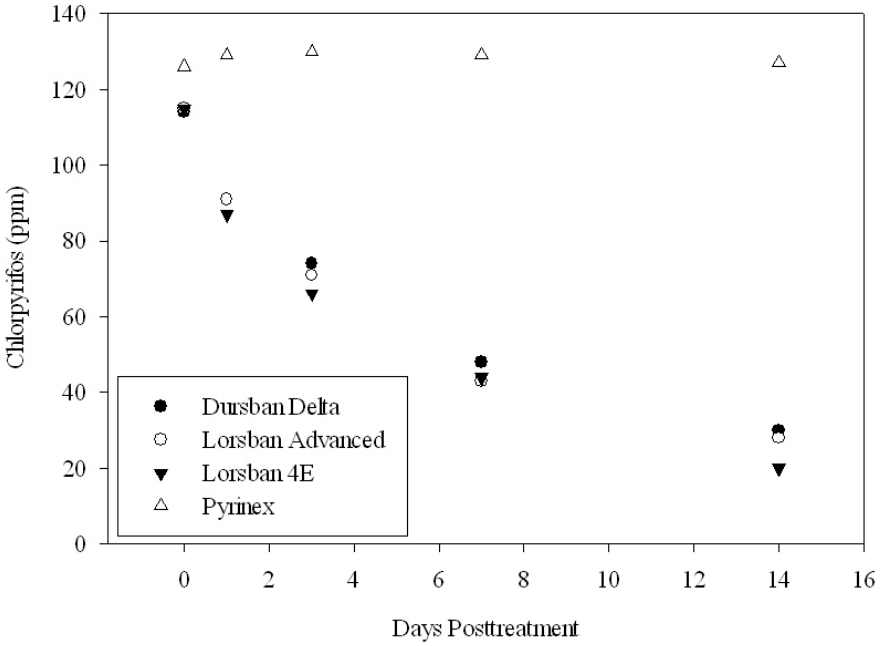

Figure 6. Laboratory Volatility Comparison for Various Chlorpyrifos Formulations

Encapsulation (pyrinex), as expected, was shown to reduce the volatility of chlorpyrifos. However, this study did not specifically measure the amount of chlorpyrifos that volatilized, just the amount remaining in the sand, assuming volatilization was the only pathway of dissipation. It is also unclear how the conditions in this study can be extrapolated to environmental conditions [*e.g.*, cooler temperatures, higher or lower humidity, surface properties (crop surfaces)] and used quantitatively for risk estimation.

Formulations that include the encapsulation of chlorpyrifos either in a microcapsule or within a granular (as long as the microcapsule is not allowed to rest in an application solution where the active ingredient can diffuse into solution or granular is not dissolved prior to application) are likely to result in lower concentrations of chlorpyrifos and chlorpyrifos-oxon off field as chlorpyrifos would be expected to be released slowly over time. At this time, EPA does not have any data to conduct an assessment on volatilization of chlorpyrifos and chlorpyrifos-oxon following the application of microencapsulated or granular formulations. In order to address this uncertainty, additional studies would be necessary to evaluate flux rates following applications of microencapsulated and granular chlorpyrifos formulations.

4.2.5. Application Method

Different applications methods may result in different surface coverage of chlorpyrifos on crops, and may impact volatilization of chlorpyrifos and chlorpyrifos-oxon from treated crops. Additional data would be needed that explores the surface coverage of chlorpyrifos using different application methods and the subsequent volatilization.

Applications made directly to soil surfaces will likely result in reduced chlorpyrifos volatilization, as chlorpyrifos is expected to sorb to soil surfaces. Furthermore, incorporation of

liquid formulations of chlorpyrifos should also reduce volatility; however, the magnitude of the reduction is unknown. To address this uncertainty, a flux study conducted on a bare-soil plot could be completed with and without soil incorporation.

4.2.6. Weather

In addition to temperature, environmental factors such as wind speed, air turbulence, humidity, and rainfall may influence the amount of chlorpyrifos and chlorpyrifos-oxon observed in air samples. While the temperature throughout the alfalfa flux study may have been high, higher humidity may increase the amount of chlorpyrifos and chlorpyrifos-oxon observed in air samples. It is uncertain how the results obtained from the alfalfa flux study conducted in the San Joaquin Valley of California, compare to the results that may be obtained for other sites in the United States. The same uncertainty can be said for extrapolation of the potato study conducted in the Netherlands to represent areas within the United States. While the weather was slightly different (lower average temperature and higher winds reported in the potato study as compared to the alfalfa study) in both of these studies, the studies were conducted during the typical growing reason and, therefore, reasonably represent the potential volatilization of chlorpyrifos and chlorpyrifos-oxon under those specific conditions.

To address this uncertainty, when limited studies were available for fumigant risk assessments, PERFUM modeling was conducted using all six of the available meteorological stations and the largest buffers calculated for all the scenarios were reported for risk assessment purposes. In addition, for some soil fumigants, this uncertainty was addressed by submission of additional field volatility data. For chlorpyrifos, additional studies permit an empirical evaluation of flux rate variability under different environmental conditions in different regions of the country.

4.2.7. Degradation in Air

In an air photolysis study[77], chlorpyrifos was observed to convert to chlorpyrifos-oxon. PERFUM modeling results presented in this assessment do not account for the potential for degradation to occur during dispersion as the modeling results are based on flux profiles derived from air concentrations measured on the field of applications. Based on a tier I analysis using AERMOD, the rate of direct and indirect photolysis for chlorpyrifos is not likely to impact the buffers estimated for chlorpyrifos (parent only). Conversion of chlorpyrifos to chlorpyrifos-oxon may result in the need for larger buffers due to the increased toxicity of chlorpyrifos-oxon; however, EPA's current methods for dispersion modeling of pesticides do not permit the consideration of the rate of formation and decline of transformation products. Nevertheless, the total toxic residue approach utilized in this assessment is thought to reasonably capture the potential exposure to both chlorpyrifos and chlorpyrifos-oxon simultaneously.

[77] **EPA MRID 48789701:** *Gas-phase Photolysis and Photo-oxidation of Chlorpyrifos and Chlorpyrifos-oxon*; Authors: Amalia Munoz; Sponsor: Dow AgroSciences, European Development Centre, 3 Milton Park, Abingdon, Oxon, OX144RN

5. CONCLUSIONS

In summary, two different field volatility studies suggest that volatilization of chlorpyrifos and/or chlorpyrifos-oxon from treated crops is a pathway of dissipation in the environment that may result in bystander exposure to vapor phase chlorpyrifos and chlorpyrifos-oxon. Based on these two studies as well as monitoring data bystander exposures were examined to quantify the potential risks associated with vapor phase chlorpyrifos and chlorpyrifos-oxon near a treated field.

The approaches used to evaluate the volatilization of chlorpyrifos and chlorpyrifos-oxon and associated risks are consistent with assessments conducted in the past for fumigant pesticides and have been vetted through a public peer review process.[3,5] While there are a number of uncertainties associated with this assessment, as discussed in the previous section, available data indicate that bystander exposure to vapor phase chlorpyrifos and chlorpyrifos-oxon is possible, and can occur at concentrations higher than the concentration of concern established in this assessment for lung. Generally application rates greater than 1 lb a.i./A and large field sizes results in concentrations that are higher than the target concentration at distances ranging from 0 to greater than 4724 feet depending on the percentile of exposure. The uncertainties which have been identified should also be considered in the interpretation of this assessment and any subsequent regulatory actions based on its findings.

Further refinements may require additional research that could be focused on eliminating or reducing the uncertainties associated with this analysis and its findings. The design of any such research should be discussed with the Agency. Given the current available information and the state of the science concerning volatilization of pesticides, this preliminary risk assessment indicates risks of concern are exceeded for bystanders. While the risk to bystanders in terms of the distance from treated fields over time, the information currently evaluated indicates that the risks are likely offsite regardless of how the stated uncertainties are interpreted.

APPENDIX A

LIST OF ABBREVIATIONS AND ACRONYMS

AChE	acetylcholinesterase
AD	Aerodynamic
AERMIC	American Meteorological Society/Environmental Protection Agency Regulatory Model Improvement Committee
BMD	benchmark dose
$BMDL_{10}$	benchmark response level of 10%
BMR	benchmark response
BuChE	butyryl-ChE
CA PISP	California Pesticide Illness Surveillance Program
CARB	California Air Resources Board
CAS	Chemical Abstract Service
CDPR	California Department of Pesticide Regulation
ChE	cholinesterase
DAS	Dow AgroSciences
DER	data evaluation record
EC	emulsifiable concentration
EPA	Environmental Protection Agency
FEMS	Fumigant Emissions Modeling System
FF	field fortifications
HECs/HEC	Human Equivalent Concentrations/ Human Equivalent Concentration
HHRA	Chlorpyrifos Preliminary Human Health Risk Assessment for Registration Review
IDS	OPP Incident Data System
IFM	Indirect Flux Method
IHF	Integrated Horizontal Flux
ISC	Industrial Source Complex
ISCST3	Industrial Source Complex-short term
lb a.i./A	Pound active ingredient per acre
LOAEL	lowest-observed-adverse-effect-level
LOC	level of concern
MMAD	Mass Median Aerodynamic Diameter
MOE	margin or exposure
NIOSH	National Institute for Occupational Safety and Health
NOAEL	no-observed-adverse-effect-level
NPIC	National Pesticide Information Center
OP	organophosphate
OPP	Office of Pesticide Programs
PANNA	Pesticide Action Network North America
PCT	chlorpyrifos percent crop treated
PERFUM	Probabilistic Exposure and Risk model for Fumigants
PODs/POD	point of departures/ point of departure
RBC	red blood cell
SAP	Federal Insecticide, Fungicide, and Rodenticide Act Scientific Advisory Panel
SENSOR-Pesticides	NIOSH's Sentinel Event Notification System for Occupational Risk
SOFEA	Soil Fumigant Exposure Assessment System
TAF	toxicity adjustment factor
TCP	3,5-6 tricloropyridinol
TTCR	total toxic chlorpyrifos residues
UF	uncertainty factor

UF_A	uncertainty factor for animal to human extrapolation
UF_{DB}	uncertainty factor database
UF_H	uncertainty factor for with human variability to account for sensitivity subpopulations
VOC	volatile organic compounds or volatile organic chemicals

APPENDIX B

CHLORPYRIFOS USE BY FORMULATION

The discussion below, along with the data presented, is excerpted from a supporting memorandum developed by OPP's Biological and Economic Analysis Division (BEAD). This paper[78] will also be included in the chlorpyrifos docket.

Chlorpyrifos Application Rate Information

Table B.1. presents chlorpyrifos application rates with information for low VOC formulations broken out separately from other formulations. The low VOC products identified in the usage data presented are Lorsban Advanced™ and Chlorpyrifos 4E AG™. For about one-half of the non-low VOC formulations the number of observations was large enough that the rate information should be quite reliable. However, for most of the low VOC formulations the number of observations was much lower. The average and 90th percentile single application rates for the non-low VOC and low VOC formulations are generally quite close. Although not noted in the tables, for some crops and formulations the 90th percentile was equal to the 100th percentile (maximum).

Table B.1. Chlorpyrifos Single Application Rate Data for Low VOC and Non-low VOC Formulations[a]

Crop	Formulation	Application Rate (lb a.i./A)				
		Average Single Application Rate (Non-low VOC Products[b])	90th Percentile Single Application (Non-low VOC Products)	Average Single Application (Low VOC Products[c])	90th percentile Single Application (Low VOC Products)	Ratio[d] of Low VOC to Non-low VOC Products Applications
Oranges	Liquid	2.6	6	2.3	5.7	0.28
Lemons	Liquid	3.4	5	3.4	5.7	0.28
Grapes, Table	Liquid	2.9	4	1.6	2.2	0.14
Grapefruit	Liquid	2.1	3	1.6	2.4	0.37
Broccoli	Liquid	1.5	2.3	1.9	2.2	0.28
Broccoli	Granular	1.5	2.1	.	.	.
Cabbage	Granular	1.2	2.1	.	.	.
Almonds	Liquid	1.9	2	1.8	2	0.22
Apples	Liquid	1.6	2	1.4	2	0.12
Cherries	Liquid	1.8	2	1.7	2	0.11
Grapes, Raisin	Liquid	2	2	1.6	2.2	0.18
Grapes, Wine	Liquid	2	2	1.8	1.9	0.38

[78] Mallampalli, N. A. Grube, and J. Becker. "Information on Application Rates and Acres Treated per Application per Day for Selected Chlorpyrifos Formulations". USEPA/OCSPP/OPP/BEAD memorandum.

Peaches	Liquid	1.3	2	2.1	3	0.04
Peanuts	Granular	1.8	2	.		.
Pears	Liquid	1.8	2	2	2	0.09
Plums/Prunes	Liquid	1.9	2	1.4	2	0.1
Sugar Beets	Granular	1.3	2	.		.
Tobacco	Liquid	1.9	2	2	2	0.01
Walnuts	Liquid	1.9	2	1.8	2	0.15
Apples	Dry Flowable	1	1.6	.	.	.
Apples	Wettable	1	1.5	.	.	.
Hazelnuts	Liquid	1.1	1.5	1.9	1.9	0.07
Cauliflower	Granular	1.2	1.4	.	.	.
Corn	Granular	1.1	1.4	.	.	.
Sweet Corn	Granular	1.2	1.4	.	.	.
Cherries	Dry Flowable	0.9	1.2	.	.	.
Onions	Granular	0.9	1.1	.	.	.
Pumpkins	Granular	0.7	1.1	.	.	.
Alfalfa	Liquid	0.5	1	0.6	0.9	0.03
Asparagus	Liquid	0.9	1	0.9	1	0.26
Beans, Green	Liquid	0.9	1	0.9	1	1.21
Broccoli	Dry Flowable	0.9	1	.		.
Broccoli	Wettable	1	1	.		.
Cabbage	Liquid	1	1	1.6	2.2	0.27
Cauliflower	Dry Flowable	1	1	.	.	.
Cauliflower	Liquid	1	1	1.1	1.9	0.17
Corn	Liquid	0.6	1	0.4	0.5	0.09
Cotton	Liquid	0.7	1	0.9	1	0.13
Onions	Liquid	0.9	1	0.9	1	0.13
Oranges	Granular	0.8	1	.	.	.
Pecans	Liquid	0.9	1	0.9	1	0.08
Pumpkins	Liquid	0.9	1	.		.
Squash	Liquid	0.8	1	1	1	0.05
Strawberries	Liquid	1	1	0.9	1	0.1
Sugar Beets	Liquid	0.5	1	0.5	0.6	0.09
Sweet Corn	Liquid	0.9	1	0.9	1	0.22
Soybeans	Dry Flowable	0.4	0.7	.	.	.
Sorghum	Liquid	0.4	0.6	.	.	.
Dry Beans/Peas	Liquid	0.5	0.5	0.8	1	0.17
Soybeans	Liquid	0.4	0.5	0.3	0.5	0.07
Sunflowers	Liquid	0.4	0.5	0.5	0.6	0.05
Wheat, Spring	Liquid	0.3	0.5	0.3	0.5	0.23
Wheat, Winter	Liquid	0.4	0.5	0.3	0.5	0.03

a. The table is arranged to show data for the 90th percentile application rate for non-low VOC products in descending order.
b. Examples include: Lorsban 75WG (EPA Reg. No. 62719-301), Lorsban 4E (EPA Reg. No. 62719-220)
c. Examples include: Lorsban Advanced™ (EPA Reg. No. 62719-591), Chlorpyrifos 4E AG™ (EPA Reg. No. 19713-520); The "Ratio" column provides a comparison of the number of applications of "low VOC" products compared to the number of applications of "traditional" products.

Crops and formulations with very low numbers of observations (less than a total of 10 observations over the five year period) are not included.

"." Entry indicates no data for use of any low VOC product. Note that low VOC products are all liquid formulations.

The ratio of the number of low VOC product applications to the number of traditional chlorpyrifos product applications in each crop were calculated when data were available. The number of applications of each type of product was summed across the five year period before the ratios were computed. A ratio of one means equal numbers of grower observations for both formulation types; a ratio of less than one indicates higher use of non-low VOC formulations, while a ratio greater than one indicates higher use of low VOC products.

Scope and Data Limitations

For many crops and formulations, there were a limited number or reported users over the survey period, which leads to uncertainty with how representative the usage data are for the respective crop/formulation combinations. For chlorpyrifos used on only a small percentage of a crop, the sampling procedure may lead to no use being reported, simply because none of the users happened to be among those surveyed.

Crop/formulation combinations with very low numbers of observations (less than a total of 10 observations over the five year period) were excluded. Crops where data on some (but not all) formulations were excluded due to low sample size include: alfalfa, almonds, apples, apricots, asparagus, green beans, cabbage cantaloupes, cauliflower, celery, cherries, corn, cotton, grapefruit, lemons, lettuce, onions, oranges, peaches, peanuts, green peas, pecans, peppers, pistachios, potatoes, sorghum, soybeans, squash, strawberries, sunflowers, sweet corn, tobacco, tomatoes, and walnuts.

There are also some labeled crops for which pesticide use data are not available in the pesticide usage database, and these crops are, therefore, not included in this analysis. These crops include Brussels sprouts, collards, cranberries, figs, kale, kohlrabi, kumquats, limes, nectarines, radishes, rutabagas, sweet potatoes, tangelos, tangerines, and turnips.

Based on private pesticide marketing survey data, over the five year period from 2007 to 2011 twenty nine different chlorpyrifos formulated products were used on agricultural sites. For individual crop/year combinations, anywhere from one to eight different products were reported as having been used. Liquid formulations accounted for about 90% of total national use. One Lorsban 4E™, accounted for more than one-half (approximately 4,000,000 pounds) of all chlorpyrifos use on agricultural crops. Lorsban products also accounted for most granular use of chlorpyrifos. Application rates for chlorpyrifos varied significantly among crops. Rates for the citrus crops and grapes were higher than for any other crops. Field crops tended to have the lowest average application and 90th percentile application rates.

According to the available usage data, two "low VOC" products show substantial use in the agricultural crops surveyed. These products are Lorsban Advanced™ (approximately 400,000 pounds of chlorpyrifos applied across all crops) and Chlorpyrifos 4E AG™ (approximately 200,000 pounds of chlorpyrifos applied across all crops). Together, these products accounted for about 10% of the liquid formulation pounds of chlorpyrifos applied and about 9% of the total pounds of chlorpyrifos applied nationally, as described in the proprietary database.

For most crops, the low VOC formulations account for a relatively small percentage of the liquid chlorpyrifos applications. This would be expected since the low VOC formulations account for about ten percent of all liquid chlorpyrifos formulations when measured in pounds of chlorpyrifos applied. The exception is green beans, where more than half the applications were with the low VOC formulations. About 30% of the applications to wine grapes, broccoli, lemons and grapefruit were made with the low VOC formulations.

Chlorpyrifos Area Treated per Application per Day Information

Data and Scope

Since 1990 California has required the full reporting of annual agricultural pesticide use. Under this program, all agricultural pesticide use is reported monthly to county agricultural commissioners, who in turn, report the data to the CDPR. These data are accessible from CDPR's website and provide the most detailed information available on the use of agricultural pesticides in California. No other state has comparable information on pesticide use.

Data files for 2006 through 2010 were downloaded from CDPR's website (CDPR, 2012). These data were then extracted and imported into a SAS dataset. Supplemental data on crop sites, county, chemical, product, and formulation were added to this dataset. An analytical chlorpyrifos dataset was created from this comprehensive dataset by keeping only data records that met all of the following criteria: active ingredient is chlorpyrifos, record is not a CDPR identified error, area treated is in units of acres, record is an individual application (i.e., not a monthly summary), application was made to an agricultural site. Using these criteria, a total of 60,910 observations are summarized in **Table B.2** below.

There are some limitations that should be considered when interpreting these data. Caution should be used when extrapolating these results to areas outside of California, as different pest pressures, crop production practices, etc. in these areas will likely alter the relative use of chlorpyrifos. BEAD also notes here that the data are shown as reported by individual county staff. Some counties sometimes enter crop type specifically, while others may use generic crop codes (*e.g.*, the one for "grapes" instead of "grapes, wine"). Furthermore, CDPR does not have crop codes for some types of crops (*e.g.*, there is no specific code for "table grapes"). These limitations are reflected in the table below.

Table B.2. Acres Treated with Chlorpyrifos per Application per Day[a, b]

Crop[c]	Application	Product	Sample	Acres treated per application per day

	Method[d]	Applied[e]	Size	Minimum	50th Percentile	90th Percentile	Maximum
Corn (human consumption)	Air	Liquid	7	13	30	160	160
Avocado	Ground	Liquid	10	1	6	158	300
Almonds	Air	Liquid	267	4	51	156	640
Grapes (wine)	Ground	Liquid	1117	0	32	146	595
Sorghum (Forage/Fodder)	Air	Liquid	13	36	70	140	160
Sorghum (Milo)	Air	Liquid	11	10	59	130	160
Sugarbeets	Air	Liquid	19	18	70	128	146
Almond	Ground	Liquid	1394	1	36	120	626
Grapes (wine)	Air	Liquid	3	14	27	116	116
Cotton	Air	Liquid	300	4	47	114	316
Asparagus	Air	Liquid	171	1	18	110	235
Wheat (unspecified type)	Air	Liquid	97	5	45	102	216
Lemons	Air	Liquid	15	5	28	100	100
Wheat (forage/fodder)	Air	Liquid	426	4	62	100	185
Alfalfa	Air	Liquid	11735	1	50	96	518
Alfalfa	Other	Liquid	33	2	40	95	101
Tomatoes (processing)	Air	Liquid	3	58	76	93	93
Walnuts	Air	Liquid	745	1	34	93	430
Sugarbeets	Ground	Liquid	2	59	76	92	92
Corn (forage/fodder)	Air	Liquid	1539	1	39	91	399
Corn (forage/fodder)	Ground	Liquid	582	1	38	85	308
Sorghum (Forage/Fodder)	Ground	Liquid	6	10	55	85	85
Strawberries	Ground	Liquid	558	1	28	84	220
Prunes (dried plums)	Ground	Liquid	40	2	34	82	120
Alfalfa	Ground	Liquid	1846	0	37	80	217
Corn (forage/fodder)	Other	Liquid	28	20	47	80	100
Figs	Air	Liquid	1	80	80	80	80
Sunflowers	Air	Liquid	35	2	25	78	170
Corn (grain)	Air	Liquid	2	38	57	77	77
Sunflowers	Other	Liquid	4	14	58	75	75
Wheat (forage/fodder)	Ground	Liquid	11	38	70	75	113
Cotton	Ground	Liquid	82	3	38	74	160
Grapes (unspecified type)	Ground	Liquid	237	1	25	73	322
Asparagus	Ground	Liquid	141	1	30	69	586
Walnuts	Ground	Liquid	3271	1	20	65	517
Citrus (unspecified type)	Ground	Liquid	32	2	7	60	240
Mint	Ground	Liquid	25	2	25	60	160
Beans (dried)	Air	Liquid	2	25	40	55	55
Lemons	Ground	Liquid	1402	0	14	54	145

Crop[c]	Application Method[d]	Product Applied[e]	Sample Size	Acres treated per application per day			
				Minimum	50th Percentile	90th Percentile	Maximum
Almond	Other	Liquid	9	6	20	53	53
Tomatoes	Air	Liquid	2	38	46	53	53
Orchard floor (unspecified crop)	Ground	Liquid	1	46	46	46	46
Figs	Ground	Liquid	1	40	40	40	40
Oranges	Ground	Liquid	3152	0	15	40	240
Oranges	Other	Liquid	28	1	19	40	42
Pecans	Ground	Liquid	33	2	19	40	42
Grapes (wine)	Other	Liquid	14	4	14	39	41
Plums	Ground	Liquid	325	1	10	38	140
Sweet potatoes	Ground	Liquid	10	8	19	38	38
Beans (dried)	Ground	Liquid	27	5	19	37	43
Brussels sprouts	Ground	Liquid	363	1	12	35	52
Lemons	Other	Liquid	2	15	25	35	35
Turf/Sod	Other	Liquid	6	7	27	35	35
Oranges	Air	Liquid	3	9	10	33	33
Onions (dry)	Ground	Liquid	30	1	15	32	45
Peaches	Air	Liquid	3	8	10	30	30
Pomelo	Ground	Liquid	14	2	5	30	30
Walnuts	Other	Liquid	5	10	18	30	30
Turf/Sod	Ground	Liquid	23	5	17	27	60
Grapes (unspecified type)	Other	Liquid	2	10	18	25	25
Sudangrass	Air	Liquid	1	25	25	25	25
Tangelo	Ground	Liquid	87	1	10	25	80
Strawberries	Air	Liquid	1	24	24	24	24
Corn (human consumption)	Ground	Liquid	35	4	10	23	39
Tangerines	Ground	Liquid	166	1	10	23	73
Apples	Ground	Liquid	164	1	5	21	72
Peaches	Ground	Liquid	235	2	8	21	46
Beans (unspecified type)	Ground	Liquid	1	20	20	20	20
Broccoli	Ground	Liquid	3899	0	11	20	162
Nectarines	Ground	Liquid	181	1	9	20	47
Pears	Ground	Liquid	11	1	2	20	35
Turnips	Ground	Liquid	13	8	10	20	25
Broccoli	Other	Liquid	22	5	10	19	36
Sunflowers	Ground	Liquid	3	8	10	18	18
Cauliflower	Ground	Liquid	1125	1	10	16	36
Peas	Ground	Liquid	33	3	10	16	19
Beans (succulent)	Ground	Liquid	12	4	10	15	18
Cherries	Ground	Liquid	34	1	5	15	20
Tangerines	Other	Liquid	1	15	15	15	15

Crop[c]	Application Method[d]	Product Applied[e]	Sample Size	Acres treated per application per day			
				Minimum	50th Percentile	90th Percentile	Maximum
Broccoli	Air	Liquid	6	5	7	14	14
Cabbage	Ground	Liquid	381	1	6	14	27
Cauliflower	Air	Liquid	1	13	13	13	13
Collards	Ground	Liquid	10	5	9	12	13
Grapefruit	Other	Liquid	1	12	12	12	12
Kale	Ground	Liquid	70	0	2	12	15
Pecans	Air	Liquid	2	11	11	11	11
Beans (succulent)	Air	Liquid	1	10	10	10	10
Grapefruit	Ground	Liquid	109	0	5	10	46
Lettuce (leaf)	Ground	Liquid	1	10	10	10	10
Limes	Ground	Liquid	3	1	2	6	6
Rappini	Ground	Liquid	103	1	5	6	9
Bok Choy (cabbage)	Air	Liquid	1	3	3	3	3
Bok Choy	Ground	Liquid	249	0	1	3	5
Cabbage, Chinese (Nappa)	Ground	Liquid	187	1	2	3	5
Kumquats	Ground	Liquid	1	2	2	2	2
Radishes	Ground	Liquid	191	1	1	2	3
Grapes (wine)	Ground	Low VOC	367	3	42	212	560
Sorghum (Milo)	Air	Low VOC	9	38	76	115	115
Prunes (dried plums)	Ground	Low VOC	8	7	25	114	114
Corn (forage/fodder)	Ground	Low VOC	33	2	50	110	230
Citrus (unspecified type)	Ground	Low VOC	14	1	10	102	150
Alfalfa	Ground	Low VOC	73	3	40	100	150
Lemons	Air	Low VOC	2	5	53	100	100
Alfalfa	Air	Low VOC	473	1	52	97	319
Almond	Ground	Low VOC	231	3	20	90	470
Corn (forage/fodder)	Air	Low VOC	210	3	38	84	262
Grapes (unspecified type)	Ground	Low VOC	68	3	40	80	301
Cotton	Air	Low VOC	6	10	30	76	76
Walnuts	Air	Low VOC	90	5	21	76	163
Walnuts	Ground	Low VOC	430	2	20	76	200
Wheat (forage/fodder)	Air	Low VOC	3	25	65	66	66
Strawberries	Ground	Low VOC	70	0	28	60	324
Almond	Air	Low VOC	2	8	31	54	54
Asparagus	Air	Low VOC	47	1	21	53	125
Asparagus	Ground	Low VOC	62	4	24	53	471
Sunflowers	Air	Low VOC	3	10	10	50	50
Turf/Sod	Ground	Low VOC	7	10	30	50	50
Lemons	Ground	Low VOC	229	1	10	45	126
Oranges	Air	Low VOC	2	10	28	45	45

Crop[c]	Application Method[d]	Product Applied[e]	Sample Size	Acres treated per application per day			
				Minimum	50th Percentile	90th Percentile	Maximum
Apples	Ground	Low VOC	21	1	18	43	80
Brussels sprouts	Ground	Low VOC	42	2	8	40	52
Corn (human consumption)	Ground	Low VOC	5	2	8	40	40
Oranges	Ground	Low VOC	758	1	17	40	248
Tangerines	Ground	Low VOC	61	2	12	40	157
Peas	Ground	Low VOC	7	7	12	38	38
Cotton	Ground	Low VOC	1	36	36	36	36
Sweet potatoes	Ground	Low VOC	4	10	20	34	34
Almond	Other	Low VOC	1	32	32	32	32
Beans (succulent)	Ground	Low VOC	56	3	20	31	50
Tangelo	Ground	Low VOC	26	5	10	31	42
Peaches	Ground	Low VOC	16	2	10	24	40
Beans (dried)	Ground	Low VOC	16	10	14	21	25
Broccoli	Other	Low VOC	35	3	15	20	25
Grapes (unspecified type)	Other	Low VOC	1	20	20	20	20
Grapefruit	Ground	Low VOC	27	2	6	20	26
Onions (dry)	Ground	Low VOC	1	20	20	20	20
Pecans	Ground	Low VOC	8	12	19	20	20
Strawberries	Air	Low VOC	3	5	7	18	18
Broccoli	Ground	Low VOC	1061	0	10	17	29
Cauliflower	Ground	Low VOC	145	1	10	17	25
Plums	Ground	Low VOC	13	2	7	17	30
Pomelo	Ground	Low VOC	10	1	6	16	20
Broccoli	Air	Low VOC	3	12	12	13	13
Cauliflower	Other	Low VOC	2	5	8	11	11
Nectarines	Ground	Low VOC	9	2	5	11	11
Oranges	Other	Low VOC	2	10	10	10	10
Radishes	Ground	Low VOC	65	3	5	7	9
Cabbage	Ground	Low VOC	94	1	4	5	13
Sunflowers	Ground	Low VOC	1	5	5	5	5
Bok Choy	Ground	Low VOC	38	1	2	3	3
Cabbage, Chinese (Nappa)	Ground	Low VOC	12	1	1	2	2
Kale	Ground	Low VOC	6	1	2	2	2
Kale	Other	Low VOC	1	2	2	2	2
Citrus (unspecified type)	Ground	Granular	35	15	80	240	240
Corn (forage/fodder)	Ground	Granular	121	6	40	89	192
Walnuts	Ground	Granular	10	5	24	82	99
Lemons	Ground	Granular	16	1	5	80	85
Strawberries	Ground	Granular	7	4	14	71	71
Tangerines	Ground	Granular	24	1	14	69	88

Crop[c]	Application Method[d]	Product Applied[e]	Sample Size	Acres treated per application per day			
				Minimum	50th Percentile	90th Percentile	Maximum
Sweet potatoes	Ground	Granular	93	4	19	60	104
Oranges	Ground	Granular	198	0	19	58	240
Tangerines	Other	Granular	1	48	48	48	48
Broccoli	Other	Granular	15	1	10	40	40
Cauliflower	Other	Granular	18	8	15	40	40
Corn (human consumption)	Ground	Granular	119	2	16	40	48
Onions (dry)	Ground	Granular	39	3	24	40	180
Cauliflower	Air	Granular	6	4	9	35	35
Broccoli	Air	Granular	119	1	11	28	45
Broccoli	Ground	Granular	9847	0	10	19	161
Cabbage	Ground	Granular	1012	1	8	19	53
Cauliflower	Ground	Granular	3542	0	10	16	276
Mustard	Ground	Granular	13	6	14	15	16
Brussels sprouts	Ground	Granular	412	1	8	14	44
Collards	Ground	Granular	27	3	9	14	16
Rappini	Ground	Granular	56	1	5	12	20
Grapefruit	Ground	Granular	38	0	3	10	23
Oranges	Other	Granular	1	10	10	10	10
Turf/Sod	Ground	Granular	1	10	10	10	10
Peas	Ground	Granular	3	6	7	9	9
Cabbage	Other	Granular	2	8	8	8	8
Lettuce (leaf)	Ground	Granular	3	3	4	8	8
Cabbage	Air	Granular	3	5	6	7	7
Canola (rapeseed)	Ground	Granular	4	4	6	7	7
Cabbage, Chinese (Nappa)	Ground	Granular	1471	0	4	6	15
Kale	Ground	Granular	137	0	1	4	10
Bok Choy	Ground	Granular	751	0	2	3	8
Alfalfa	Ground	Granular	1	2	2	2	2
Radishes	Ground	Granular	81	0	0	1	24
Turnips	Ground	Granular	85	0	0	1	2

a. Data are for use in the years 2006 through 2010. The table shows data grouped first by "product applied" and within these groups, sorted by the 90th percentile application rate (in descending order--high to low].
b. "Product" is referred to as "form" in the CDPR database.
c. Crop names are shown as reported in the CDPR database (see the "Data and Scope' section above for further discussion).
d. "Other" application methods may include one or more of the following, as described by CDPR: chemigation, paints, dips, or other non-tractor ground-based methods.
e. "Liquid" products correspond to the "regular" – non-low VOC – products

APPENDIX C

FLUX CALCULATIONS

1. Flux determination using the Indirect Method (IM):

The indirect method, commonly referred to as the "back calculation" method, was the technique employed for estimating flux rates from fields during application. In the indirect method, air samples are collected at various locations outside the boundaries of a treated field. Meteorological conditions, including air temperature, wind speed, and wind direction, are also collected for the duration of the sampling event. The dimensions and orientation of the treated field, the location of the samplers, and the meteorological information is used in combination with the ISCST3 dispersion model (Version 02035) and a unit flux rate of 0.001 µg/m2•s to estimate concentrations at the sampler locations. Since there is a linear relationship between flux and the concentration at a given location, the results from the ISC model runs are compared to those concentrations actually measured and a regression is performed, using the modeled values along the x-axis and the measured values along the y-axis. If the linear regression does not result in a statistically significant relationship, the regression may be rerun forcing the intercept through the origin, or the ratio of averages between the monitored to modeled concentrations may be computed, removing the spatial relationship of the concentrations. The indirect method flux back calculation procedure is described in detail in Johnson *et al.*, 1999.

2. Flux determination using the integrated horizontal flux (IHF) method:

The integrated horizontal flux method, also referred to as the "mass balance" method, was the technique employed for estimating flux rates from fields following application. In the integrated horizontal flux method, a mast is erected in the middle of the treated field and concentration samples are typically collected at four or five different heights, ranging from approximately 0.5 to 5 feet. Likewise, wind speed data are collected at a variety of heights. A log-linear regression is performed relating the natural logarithm of the sample height to the air concentration and wind speed following the log law relationships for the atmospheric boundary layer. These relationships are then incorporated into an equation to estimate flux. The methods to estimate flux and related equations are presented in Majewski *et al.*, 1990. The equation for estimating flux using the integrated horizontal flux method is the following expression:

$$P = \frac{1}{x}\int_{Z_0}^{Z_p} \bar{c}\,\bar{u}\,dz$$

where P is the volatile flux in units of µg/m^2·s, $\bar{c}$ is the average pesticide residue concentration in units of µg/m^3 at height Z in units of meters, $\bar{u}$ is the wind speed in units of m/s at height Z, x is the fetch of the air trajectory blowing across the field in units of meters, Z_0 is the aerodynamic surface roughness length in units of meters, Z_p is the height of the plume top in units of meters, and dz is the depth of an incremental layer in units of meters. Following trapezoidal integration, the above equation is simplified as follows (Yates, 1996):

$$P = \frac{1}{x}\sum_{Z_0}^{Z_p} (A * Ln(z) + B) * (C * Ln(z) + D)dz$$

where A is the slope of the wind speed regression line by ln(z), B is the intercept of the wind speed regression line by ln(z), C is the slope of the concentration regression by ln(z), D is the intercept of the concentration regression by ln(z), z is the height above ground level. Z_p can be determined from the following equation:

$$Z_P = \exp\left[\frac{(0.1 - D)}{C}\right]$$

The minimum fetch requirement of 20 meters for this method to be valid was satisfied at all times. The raw wind speed and wind direction data at varying heights were averaged for the concentration sampling durations. The wind direction values were used to calculate a fetch at every minute, which then was averaged for the concentration sampling periods. Finally, the period averaged wind speed values were used along with the natural logarithm of the height measurements to calculate regression coefficients (slope, intercept, and r^2) for each period. Period averaged meteorological parameters for each field and the meteorological regression coefficients are shown in Appendix B.

3. <u>Flux determination using the Aerodynamic Method (AD)</u>:

The aerodynamic method, also referred to as the "flux-gradient" method, was the technique employed for estimating flux rates from fields following application. In the aerodynamic method, a mast is erected in the middle of the treated field and concentration samples are typically collected at four or five different heights, ranging from 0.5 to 10 feet. Likewise, temperature and wind speed data are collected at a variety of heights. A log-linear regression is performed relating the natural logarithm of the sample height to the concentration, temperature, and wind speed. These relationships are then incorporated into an equation to estimate flux. These methods to estimate flux and related equations are presented in Majewski *et al.*, 1990. The equation for estimating flux using the aerodynamic method is Thornthwaite-Holzman Equation which is shown in the following expression:

$$P = \frac{k^2(\Delta\bar{c})(\Delta\bar{u})}{\phi_m\phi_p[\ln\left(\frac{z_2}{z_1}\right)]^2}$$

where P is the flux in units of $\mu g/m^2 \cdot s$, k is the von Karman's constant (dimensionless ~0.4), $\Delta\bar{c}$ is the vertical gradient pesticide residue concentration in air in units of $\mu g/m^3$ between heights z_{top} and z_{bottom} in units of meters, $\Delta\bar{u}$ is the vertical gradient wind speed in units of m/s between heights z_{top} and z_{bottom}, and ϕ_m and ϕ_p are the momentum and vapor stability correction terms respectively. Following the conditions expected in the neutrally stable internal boundary layer characterized by an absence of convective (buoyant) mixing but mechanical mixing due to wind shear and frictional drag, a log-linear regression is performed relating the natural logarithm of the sample height to the concentration, temperature, and wind speed. The adjusted values of the concentration, temperature, and wind speed from this regression is incorporated into the equation above to arrive at the following equation, which is ultimate used to compute the flux.

$$Flux = \frac{-(0.42)^2(c_{ztop} - c_{zbottom})(u_{ztop} - u_{zbottom})}{\phi_m\phi_p \ln\left(\frac{z_{top}}{z_{bottom}}\right)^2}$$

where ϕ_m and ϕ_p are internal boundary layer (IBL) stability correction terms determined according to the following conditions based on the calculation of the Richardson number, R_i:

$$\textit{Equation } x_3 \qquad R_i = \frac{(9.8)(z_{top} - z_{bottom})(T_{ztop} - T_{zbottom})}{\left[\left(\frac{T_{ztop} + T_{zbottom}}{2}\right) + 273.16\right] + \left(u_{ztop} - u_{zbottom}\right)^2}$$

where T_{ztop} and $T_{zbottom}$ are the regressed temperatures at the top and bottom of the vertical profile in units of °C.

if R_i >0 (for Stagnant/Stable IBL)

$\phi_m = (1 + 16R_i)^{0.33}$ *and* $\phi_p = 0.885(1 + 34R_i)^{0.4}$

if R_i <0 (for Convective/Unstable IBL)

$\phi_m = (1 - 16R_i)^{-0.33}$ *and* $\phi_p = 0.885(1 - 22R_i)^{-0.4}$

The minimum fetch requirement that the fetch is 100 times the highest height of the air sampler for this method to be valid was not satisfied at all times. The raw wind speed and temperature data at varying heights were averaged for the concentration sampling durations. The period averaged wind speed and temperature values were used along with the natural logarithm of the height measurements to calculate regression coefficients (slope, intercept, and r^2) for each period. Meteorological parameters for each averaging period and the regression coefficients are shown in Appendix D. The aerodynamic method used to estimate flux and related equations are presented in Majewski *et al.*, 1990.

APPENDIX D

CURRENT CHLORPYRIFOS BUFFERS RESTRICTIONS

Table D.1. Chlorpyrifos Buffer Distances for Aquatic Sites

Application Method	Required Buffer Zone (feet)
Groundboom	25
Chemigation	25
Airblast	50
Aerial (fixed wing or helicopter)	150

Table D.2. Chlorpyrifos Human Health Spray Drift Buffer Zones for Sensitive Sites

Application rate (lb ai/A)	Nozzle Droplet Type	Required Setback (Buffer Zones) (feet)		
		Aerial	Airblast	Ground
>0.5 - 1	coarse or very coarse	10	10	10
>0.5 - 1	medium	25	10	10
>1 - 2	coarse or very coarse	50	10	10
>1 - 2	medium	80	10	10
>2 - 3	coarse or very coarse	80[a]	10	10
>2 - 3	medium	100[a]	10	10
>3 - 4	medium or coarse	NA[b]	25	10
>4	medium or coarse	NA	50	10

a. Aerial application of greater than 2 lb ai/A is only permitted for Asian Citrus Psylla control, up to 2.3 lb ai/A.
b. NA is not allowed.

Table D.3. Granular Applications Chlorpyrifos Buffer Zones for Sensitive Sites

Application Rate (lb a.i./A)	Required Setback (Buffer Zones) (feet)	
	Aerial	Ground[a]
>0.5 - 1	25	10
>1 - 2	Not allowed	10
>2 - 3	Not allowed	10
>3 - 4	Not allowed	10
>4	Not allowed	10

a. The required buffer zones for ground application apply to applications made via spreaders.