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

OFFICE OF
CHEMICAL SAFETY AND
POLLUTION PREVENTION

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November 6, 2012

MEMORANDUM

SUBJECT: Evaluation of Direct Flux Measurement of Chlorpyrifos and Chlorpyrifos-Oxon Emissions Following Applications of Lorsban Advanced Insecticide to Alfalfa (MRID 48883201)

TO: Joel Wolf, Chemical Review Manager
Pesticide Re-Evaluation Division (7508P)

FROM: Rochelle F.H. Bohaty, PhD, Chemist Rochelle F H Bohaty 11/6/12
Environmental Risk Branch III
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Chuck Peck, MS, Environmental Engineer 6 Nov 2012
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THRU: Dana Spatz, Branch Chief 11/6/12
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Dow AgroSciences LLC submitted one study investigating the off-gassing rates of chlorpyrifos and chlorpyrifos-oxon following application of Lorsban Advanced Insecticide (Reg. No. 62719-591) to alfalfa via broadcast application. The study is scientifically sound; however, there are several questions concerning the interpretation and representation of this study and potential exposure, when all registered chlorpyrifos formulations and uses are considered. For example, the formulation (Lorsban Advance) used in this study is reportedly a low VOC (volatile organic compounds) product suggesting that the use of the flux rates determined in this study may underestimate the potential exposure resulting from the use of other non-low VOC formulations. In addition, extrapolation of the flux rates determined in this study for alfalfa to other uses (*e.g.*, citrus, strawberries, grapes, etc.) may not represent actual flux rates for these crops due to the physical differences in the crop canopy and field design as well as agronomic practices.

Data Requirement	Guideline Number	MRID	Study Classification[1]	Remarks
Field Volatility	835.8100	47473318	48883201 Acceptable	While this study is acceptable, there are several reviewer comments that should be considered in the interpretation and representation of this study, which are summarized in the final DER. In addition, EPA noted one error concerning the total oxon chlorpyrifos equivalents in the final report submitted to EPA; however, this error does not alter the study classification and is not expected to substantially impact the conclusions of the study.

[1]OPPIN Classifications: Acceptable/Guideline; Acceptable/Non-Guideline; Cited; Confirmatory; Decision Deferred; Extraneous submission; In Review; No Decision; Partially Acceptable; Supplemental: Unacceptable/Guideline; Unacceptable/Non-Guideline; Upgradeable.

DATA EVALUATION RECORD

STUDY TYPE: Direct Flux Measurement of Chlorpyrifos and Chlorpyrifos-Oxon Emissions Following Applications of Lorsban Advanced Insecticide to Alfalfa

GUIDELINE: 835.8100

PC CODE: 059101

TEST MATERIAL Lorsban Advanced Insecticide (Reg. No. 62719-591) is a liquid formulation containing 3.66 lb ai/gal (439 g ai/L; 40.2% w/w) active ingredient, chlorpyrifos.

SYNONYMS: Chlorpyrifos; O,O-diethyl O-(3,5,6-trichloro-2-pyridinyl) phosphorothioate, CAS No. 2921-88-2.

CITATION:

Study Authors: Aaron Rotondaro and Patrick Havens
Title: Direct Flux Measurement of Chlorpyrifos and Chlorpyrifos-Oxon Emissions Following Applications of Lorsban Advanced Insecticide to Alfalfa
Study Report Date: July 6, 2012
Analytical Laboratory: Dow AgroSciences LLC
9330 Zionsville Road
Indianapolis, IN 46268-1054
Testing Facility: Paragon Research Services, Inc.
6773 Woodcliff Circle
Zionsville, IN 46077-9173
Identifying Codes: Study No. 110469

SPONSOR: Dow AgroSciences LLC
9330 Zionsville Road
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CLASSIFICATION: This study is **acceptable**.

EPA Reviewer: Chuck Peck
ERB4, EFED
Signature: [signature]
Date: 6 NOV 2012

EPA Reviewer: Rochelle Bohaty
ERB3, EFED
Signature: Rochelle H Bohaty
Date: Nov. 6, 2012

EXECUTIVE SUMMARY:

This study was conducted to evaluate off-gassing rates of chlorpyrifos and total toxic residues (chlorpyrifos and chlorpyrifos-oxon) following application of Lorsban Advanced Insecticide to alfalfa via broadcast application.

The test substance used in this study was Lorsban Advanced Insecticide, a liquid formulation containing 3.66 lb/gal chlorpyrifos as the active ingredient. Using a tractor-mounted ground boom, a single foliar broadcast application of the test substance was made to one 7.59 acre field in Los Banos, California at a

target rate of 2 pints product/acre (0.878 lb ai/A) in approximately 20 GPA of water. A buffer (BU-pH-ER)[1] was added to the water to reduce the pH of the spray solution from 7.0 to 5.5. The actual application rate was reported as 0.811 lb ai/acre. The application was made on September 9, 2011 between 9:10 – 10:40 am using a ground broadcast method (tractor mounted sprayer). The boom height was 20 inches above the crop canopy. The alfalfa was cut 14 days prior to application. The crop height was 10 inches at the time of application; the alfalfa field had just dried after irrigation.

Air sampling was conducted for three days during and after the application and was performed using SKC 226-52 XAD-2 sampling tubes, Tygon tubing, and SKC air sampling pumps set to a flow rate of 1 L/min. 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 which measured 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. Soil samples were collected one day prior to application from four locations across the plot at depths of 0-6", 6-12", 12-18", and 18-24". These pre-application soil samples were analyzed for texture, bulk density, CEC, pH, maximum water holding capacity, organic matter, and soil moisture by Agvise Laboratories. The soil texture was classified as clay loam (no soil series data reported). The organic matter ranged from 0.82-2.1%. The soil pH increased as depth increased ranging from 7.7-8.4.

The samples were analyzed for residues of chlorpyrifos, chlorpyrifos-oxon, and 3,5-6 tricloropyridinol (TCP) using Dow AgroScience Analytical Method "Determination of Residues of Chlorpyrifos in Air Sampling Tubes by High Performance Liquid Chromatography with Mass Spectrometry Detection." The limit of quantification (LOQ) was 2 ng per tube. Field fortification was conducted during two sampling periods, using three different fortification levels. Air concentrations were calculated in terms of $\mu g/m^3$.

Flux rates for chlorpyrifos and total residues in $\mu g/m^2$-s for the first period when the application was in progress (Sampling Period 1) were calculated using the Indirect Flux Method. Flux rates for the other sampling periods were calculated using both the Integrated Horizontal Flux (IHF) method and the Aerodynamic (AD) method. Total toxic residues are defined as the sum of the chlorpyrifos concentration and the oxon concentration which has been corrected using the relative potency factor (RPF) of 12.[2]

The samples were corrected using the average field fortification recoveries. Residues ≤0.275 µg were corrected for the average low level field fortification recovery (81.1% for chlorpyrifos and 86.7% for the total toxic residues), residues >1.25 µg were corrected for the average high level field fortification recovery (82.0% for chlorpyrifos and 84.5% for total toxic residues), and residues between 0.275 and 1.25 µg were corrected for the average mid-level field fortification recovery (75.3% for chlorpyrifos and 79.6% for total toxic residues). Residues were also corrected separately for the storage stability recoveries. Residues ≤0.275 µg were corrected for the average low level storage stability recovery (91.6% for chlorpyrifos and total toxic residues), residues >1.25 µg were corrected for the average high level storage stability recovery (94.2% for chlorpyrifos and total toxic residues), and residues between

1 BU-pH-ER is a spray adjuvant designed to improve the effectiveness of certain agricultural chemicals by reducing the pH of higher alkaline water and contains phosphoric acid, propylene glycol, casuistic soda as well as other constituents.
2 Email from Wade Britton (OPP/HED) to Rochelle Bohaty (OPP/EFED) September 10, 2012.

0.275 and 1.25 µg were corrected for the average mid-level storage stability recovery (97.3% for chlorpyrifos and total toxic residues). Values reported as below the LOQ were assigned a value of ½ LOQ.

Reviewer-estimated flux rate values using the Indirect Method for Period 1 (application period) were 0.22 µg/m^2-s (field fortification correction) and 0.20 µg/m^2-s (storage stability correction) for chlorpyrifos and 0.46 µg/m^2-s (field fortification correction) and 0.52 µg/m^2-s (storage stability correction) for total toxic residues. The r^2 values for all of the regressions were above 0.81. The reviewer-estimated flux rate values for chlorpyrifos compare well with the study author's results even though the study authors did not correct for field fortification and storage stability.

The chlorpyrifos flux calculated for the first period after application using the AD method was 0.824 µg/m^2-s (field fortification correction) and 0.717 µg/m^2-s (storage stability correction). The flux then declined over the next 24 hours, followed by a second smaller peak of 0.081 µg/m^2-s (field fortification) and 0.070 µg/m^2-s (storage stability; Sampling Period 5). Flux generally continued to decrease over the remainder of the study and was 0.002 µg/m^2-s by the last sampling interval.

The chlorpyrifos flux calculated for the first period after application using the Indirect Method was 0.591 µg/m^2-s (field fortification correction) and 0.515 µg/m^2-s (storage stability correction). The highest flux was observed during the subsequent period (Period 2) at a considerably higher level of 0.759 µg/m^2-s (field fortification) and 0.660 µg/m^2-s (storage stability). The flux then declined over the next 24 hours, followed by a second smaller peak of 0.167 µg/m^2-s (field fortification) and 0.145 µg/m^2-s (storage stability; Sampling Period 6). Flux generally continued to decrease over the remainder of the study and was 0.004-0.005 µg/m^2-s by the last sampling interval.

The reviewer-estimated flux rates for chlorpyrifos using the AD method were comparable to those estimated by the study author. The reviewer-estimated flux rate values for chlorpyrifos using the IHF method were much higher than those estimated by the study author. A review of the study author's calculations indicated that Zp (height of plume) was truncated at 150 cm, which in turn yielded lower flux rate estimates. The reviewer's calculations were based on Z_p (the height of the plume top in units of meters; see equations in the **Flux Calculations** section of this document). The flux trends exhibited by both those estimated by the reviewer and those by the study authors were very similar.

In this study approximately 29% of the applied chlorpyrifos was observed to volatilize off the field during the first 24 hours following application.

The total toxic residue flux calculated for the first period after application using the AD method was 1.102 µg/m^2-s (field fortification correction) and 0.989 µg/m^2-s (storage stability correction). The flux then declined over the next 24 hours, followed by a second smaller peak of 0.186 µg/m^2-s (field fortification) and 0.167 µg/m^2-s (storage stability; Sampling Period 6). Two smaller peaks occurred at 0.034 µg/m^2-s (field fortification) and 0.028 µg/m^2-s (storage stability; Sampling Period 8) and at 0.052 µg/m^2-s (field fortification) and 0.034 µg/m^2-s (storage stability; Sampling Period 10). Flux was 0.002-0.003 µg/m^2-s by the last sampling interval.

The total toxic residue flux calculated for the first period after application using the Indirect Method was 0.791 µg/m^2-s (field fortification correction) and 0.710 µg/m^2-s (storage stability correction). The highest flux was observed during the subsequent period (Period 2) at a considerably higher level of 1.27 µg/m^2-s (field fortification) and 1.14 µg/m^2-s (storage stability). The flux then declined over the next 24 hours, followed by a second smaller peak of 0.384 µg/m^2-s (field fortification) and 0.345 µg/m^2-s (storage stability; Sampling Period 6). Two smaller peaks occurred at 0.057 µg/m^2-s (field fortification) and 0.046 µg/m^2-s (storage stability; Sampling Period 8) and at 0.038 µg/m^2-s (field fortification) and 0.074 µg/m^2-s

(storage stability; Sampling Period 10). Flux was 0.007-0.010 µg/m^2-s by the last sampling interval.

COMPLIANCE:

Signed and dated GLP, Quality Assurance, and Data Confidentiality statements were provided. The study sponsor waived claims of confidentiality within the scope of FIFRA Section 10 (d)1(A), (B), or (C). The Study Report indicated that the study was conducted under EPA Good Laboratory Practice Standards (40 CFR Part 160) and OECD ENV/MC/CHEM (98)17, with the following exceptions: GPS coordinates were collected with a non-GLP compliant instrument; the crop history and chlorpyrifos use were obtained from the grower; sunrise/sunset and cloud cover information were obtained from the National Climate Data Center. None of the noted field phase GLP deviations had any impact on the validity of the study.

I. MATERIALS AND METHODS

A. MATERIALS:

1. Test Material:

Formulation:	The test substance is Lorsban Advanced Insecticide (Reg. No. 62719-591), a liquid formulation containing 3.66 lb ai/gal (439 g ai/L; 40.2% w/w) chlorpyrifos as the active ingredient.
Lot/Batch #:	A lot number for the test substance was not provided. Lot numbers for the reference substances were: MM 930503-17 (chlorpyrifos reference substance); YC2-106153-76 (chlorpyrifos-oxon reference substance); and 597-F0580-42A (TCP reference substance).
Formulation guarantee:	The Certificate of Analysis for the test product was not provided.
Purity:	Reference standard of chlorpyrifos was analyzed and found to have a purity of 99.8% (expiration date not reported). Reference standard of chlorpyrifos-oxon was analyzed and found to have a purity of 98% (expiration date not reported). Reference standard of TCP was analyzed and found to have a purity of 100% (expiration date not reported). The stable isotope internal standard of chlorpyrifos was analyzed and found to have a purity of 100% (expiration date 3/17/10). The stable isotope internal standard of chlorpyrifos-oxon was analyzed and found to have a purity of 95% (expiration date not reported).
CAS No. (s):	2921-88-2
Storage conditions:	Formulation was stored at ambient temperatures, ranging from 19 to 34ºC.

2. Relevance of Test Material to Proposed Formulation(s):

The test product used in this study was Lorsban Advanced Insecticide, containing 3.66 lb ai/gal (40.2% w/w) chlorpyrifos. A label was not provided with the study report but the reviewer was able to locate a label on EPA's Pesticide Product Label System (PPLS) website. The test product formulation appears to be the same as that listed in the label. Discussion of the uncertainties associated with the formulation used in this study is provided in the **Reviewer's Comments** (**RC 1**) section of this document.

B. STUDY DESIGN:

The study protocol was provided in advance and also included in the study report. EPA provided comments on the protocol; however, these comments arrived after the study had already started. Many of EPA's comments were addressed in the study and the study authors provided a response to each comment in the study report. There were eight amendments and three deviations from the protocol. Protocol amendments involved: 1) removing Appendix B, 2) changing the foliage sample size from 1 kg to 0.5 kg, 3) changing the meteorological monitoring heights for relative humidity, solar radiation, and barometric pressure and adding the use of a buffer to lower pH in the spray solution, 4) providing the name and address of the principal analyst, 5) providing the details of the laboratory stability study and changing the name of the principal investigator, 6) supplying supplemental information to the protocol regarding the analytical method, 7) authorization to reactivate the study on the master schedule to allow it to be amended to change an incorrect field fortification, and 8) authorization to reactivate the study on the master schedule to allow it to be amended to change an incorrect chain of custody date. Protocol deviations involved: 1) the front and back sections of the first two air sampling tubes were analyzed separately instead of the first four tubes as called for in the protocol and analytical set recoveries were not calculated for each analytical set, 2) the air temperature was collected at 1.7 m, and 3) the leaf area index was not collected according to the protocol (see **RC 2**).

The study author stated that none of the deviations had any negative effect on the overall study objectives.

1. Site Description:

Test location: The study was conducted on a 7.59 acre (575 ft x 575 ft) field in Los Banos, California. The plot had established alfalfa that was in its fourth year of production. The plot area was flat and was free of obstacles around the edges. The location of the field is shown in **Figure 1** (provided at the end of this report).

Meteorological Data: Meteorological conditions during application and monitoring were typical for the region and season that the application was made. The air temperature and wind were moderate with daily maximum air temperatures that ranged from the high 20's to the low 30's (°C). No precipitation occurred during the course of the study.

Meteorological equipment was established within 4 meters of the treated area. The wind monitor orientation was set to true North; the field orientation was approximately 15 degrees east of North. Details of the sensor heights and the meteorological parameters for which data were collected are illustrated in **Table 1**. The location of the meteorological equipment is shown in **Figure 2** (provided at the end of this report)..

Irrigation during the study was not discussed in the study report. Prior to application, the alfalfa field was irrigated and dried.

Table 1. Summary of Meteorological Parameters Measured in the Field		
Parameter	**Monitoring height (m)**	**Averaging Period**
Wind speed/Wind direction[1]	0.15, 0.33, 0.55, & 0.9	1 minute, hourly
Ambient air temperature[1]	0.15, 0.33, 0.55, & 0.9	1 minute, hourly
Relative humidity	1.7	hourly
Solar radiation	1.7	hourly
Precipitation	1.8	hourly
Barometric pressure	0.9	hourly

1. While the protocol and study indicated that wind speed and temperature would be collected at 1.8 m, data were only provided for up to 0.9 m in the final report.

Soil Sampling: Soil samples were collected one day prior to application from four locations across the plot at depths of 0-6", 6-12", 12-18", and 18-24". Soil samples were analyzed for texture, bulk density, CEC, pH, maximum water holding capacity, organic matter, and soil moisture by Agvise Laboratories. Soil properties are provided in **Table 2**.

Table 2. Summary of Soil Analysis				
Depth (in)	**0 to 6**	**6 to 12**	**12 to 18**	**18 to 24**
USDA Texture Class	Clay Loam	Clay Loam	Clay Loam	Clay Loam
USDA Sand (%)	31	29	31	33
USDA Silt (%)	34	36	34	28
USDA Clay (%)	35	35	35	39
Bulk Density, disturbed (gm/cc)	1.18	1.22	1.20	1.23
Cation Exchange Capacity (meq/100 g)	23.2	23.7	23.7	25.5
pH (1:1 soil:water ratio)	7.7	8.1	8.2	8.4
Maximum Water Holding Capacity (g/100 g)	45.4	38.5	36.8	39.1
Moisture (% @ 1/3 bar)	26.0	27.7	27.3	28.9
Moisture (% @ 15 bar)	14.8	16.0	16.2	16.2
Moisture before monitoring (%)	15.6	19.5	21.7	21.8
Organic Matter (%)	2.1	1.7	1.2	0.82

2. Surface Monitored:

Plant Species: Alfalfa: AmeriStand 802 variety. Discussion of the uncertainties associated with the crop used in this study is provided in the **Reviewer's Comments** (**RC 3**) section of this document

Residential or Public Area: The field site was representative of current commercial practice in the California Central Valley. Discussion of the uncertainties associated with the site used in this study is provided in the **Reviewer's Comments** (**RC 4**) section of this document

3. Physical State of Formulation as Applied:

Lorsban Advanced Insecticide (US EPA Reg. No. 62719-591) is a liquid formulation (water emulsion/emulsifiable concentrate) containing 3.66 lb ai/gal (439 g ai/L; 40.2% w/w) of the active ingredient chlorpyrifos.

4. Application Details:

Application rate(s):	The target application rate was 2 pints product/A (0.878 lb ai/A). The actual application rate was 0.811 lb ai/A (92.5% of the target rate). The maximum label rate for alfalfa is 2 pints ai/A (0.878 lb ai/A).
Application Regime:	One broadcast spray application was made on September 9, 2011 between 9:10 and 10:40 am. The alfalfa was cut 14 days prior to application. The crop height was 10 inches at the time of application; the alfalfa field had just dried after irrigation.
Spray Volume:	A spray volume of approximately 20 gallons per acre (GPA) was used for the application. A buffer (BU-pH-ER)[1] was added to the water to reduce the pH of the spray solution from 7.0 to 5.5.
Application Equipment:	A Massy Ferguson 2405 tractor-mounted boom sprayer equipped with 15 teejet nozzles spaced 20 inches apart. The boom height was 20 inches above the crop.
Equipment Calibration Procedures:	According to the study protocol, equipment calibration results will be recorded in the field raw data notebook. No further equipment calibration details were provided in the Study Report.

5. Flux Air Sampling Procedures:

Method and Equipment:	For the first flux period (during application), eight off-field monitoring stations were placed uniformly around the field in eight directions at approximately 30 m from the field edges (**Figure 2**). The sampling height of the off-field monitors was 1.5 m. The on-site profile monitoring station (located approximately at the center of each field) measured concentrations at heights of 15, 33, 55, 90, and 150 cm. Sampling using on-site samplers began less than 2 hours after the center of the plot was treated and was continued for the remainder of the study. Air sampling was performed using SKC 226-52 XAD-2 resin sampling tubes, Tygon tubing, and SKC air sampling pumps using a flow rate of 1 L/min during the duration of the study. The sorbent tubes were covered with a PVC tube to protect them from sunlight.
Sampling Procedure:	The flow rate was measured at the beginning and end of each monitoring period and recorded. The tubes were removed, capped, and placed in pre-labeled re-sealable bags. Samples were stored frozen (temperature not reported) prior to shipment.
Replicates:	Air samples were collected from the eight off-field monitoring stations during the application. The air flow was started just prior to application and was concluded after the application was complete. Air samples were collected from the on-field profile monitoring stations approximately 24 hours prior to application. Following application, 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. Single replicates were collected at each sampling station from each sampling period.

6. Sample Handling:

The samples were maintained frozen (temperature not reported) at the field facilities until they were shipped frozen via FedEx to Dow AgroSciences for analysis. Samples were received at the analytical facility on September 13, 2011 through September 15, 2011 and were stored at approximately -20 ºC until extraction. The maximum length of frozen storage for the samples from sample collection to analysis was 285 days. Sample extracts were stored 0-8 days prior to analysis and storage conditions for the extracts were not reported.

7. Analytical Methodology:

Extraction method: The contents of each OSHA Versatile Sampler (OVS) tube were divided into two separate samples. The front section (polytetrafluoroethylene [PTFE] retainer ring, glass fiber filter, 270 mg of XAD-2 sorbent, and the foam separator plug) and the back section (140 mg of XAD-2 sorbent and a foam retention plug). Front and back section samples were initially analyzed separately. Since residue levels of the back sections were non-detectable or relatively inconsequential, the remainder of the samples were analyzed together to represent one sample.

Residues of chlorpyrifos, chlorpyrifos-oxon, and 3,5-6 tricloropyridinol (TCP) were extracted from the air sampling tubes by sonicating and shaking with an acetonitrile/methanol solution (1:1, v:v). Samples were either diluted or concentrated prior to being brought to a final volume of 1.0 mL using an aqueous 0.2% acetic acid solution. 50 µL of a mixed internal standard solution containing 0.1 µg/mL of chlorpyrifos-d10 and 0.1 µg/mL of 3,5,6-trichloropyridin-2-ol-1-^{15}N-2,6-^{13}C was added to each sample and calibration standard. The solution was mixed and analyzed using LC-MS/MS.

Detection methods: The air sampling tube extracts were analyzed for chlorpyrifos, chlorpyrifos-oxon, and TCP by liquid chromatography with positive-ion electrospray tandem mass spectrometry. A summary of the LC-MS/MS conditions are shown in **Table 3**.

Table 3. Typical HPLC/MS/MS Instrument Parameters				
Instrument:	Agilent Model 1200			
Column:	Phenomenex Luna C-18, 50 x 2.0 mm, 5 µm			
Injection Volume:	20 µl			
Mobile Phase A: Mobile Phase B:	Water containing 0.1% acetic acid Acetonitrile containing 0.1% acetic acid			
Flow Rate:	0.40 mL/min			
Steps	Time (min)	Flowrate (mL/min)	Phase A	Phase B
	4:00	0.4	75	25
	0:00	0.4	75	25
	10:00	0.4	0	100
Expected Retention Times	Not reported.			
Ionization Mode:	Positive			
Transitions:	Chlorpyrifos Chlorpyrifos-oxon TCP Chlorpyrifos-d10 TCP [M+3]	350.0→197.8 and 349.9→97.0 334.1→277.9 and 334.1→197.8 198.0→134.0 and 198.0→107.0 359.9→198.9 202.9→109.1		

Method validation: A separate method validation study was not conducted prior to the start of the study. The analytical method was validated concurrently by analyzing an appropriate number of air sampling tubes spiked individually at the limit of quantification (LOQ), the limit of detection (LOD), and concentrations high enough to cover the high-end of the expected residues. The LOQ was 2 ng per tube. The LOD was 0.65 ng per tube.

Instrument performance: A series of calibration standards were injected with each set to quantify residues in the samples. These calibration standards generated a linear plot of chlorpyrifos, chlorpyrifos-oxon, or TCP versus area with 1/x weighting.

Quantification: Quantitation of residues in all samples was achieved by using a calibration curve for each of the reference substances at multiple concentrations.

8. Quality Control:

Lab Recovery: Analytical method performance was monitored through concurrent analysis of freshly fortified control samples. Control air sampling tube samples were fortified with chlorpyrifos at concentrations of 2, 500, 2000, 3000, and 6500 ng/tube and with chlorpyrifos-oxon and TCP at concentrations of 2, 500, and 2000 ng/tube. Individual concurrent laboratory recoveries ranged from 58% to 99% with an overall mean recovery of 83.7% ± 7.82% (n= 32) for chlorpyrifos, from 61% to 104% with an overall mean recovery of 78.5% ± 11.3% (n= 22) for chlorpyrifos-oxon, and from 61% to 108% with an overall mean recovery of 89.5% ± 12.1% (n= 22) for TCP.

Field blanks: During the day before the application, background sampling was conducted for approximately 12 hours at two off-field sample locations.

Background chlorpyrifos and chlorpyrifos-oxon concentrations were not detected.

Triplicate field blanks were weathered with the 6-hr and 12-hr field fortification spikes. Residues of chlorpyrifos and chlorpyrifos-oxon were not detected.

Field Fortifications: Fortified samples were prepared in the analytical laboratory and shipped to the field prior to the application. Spikes were prepared in triplicate at loading levels that approximate the levels anticipated on the air samples. The solid sorbent tubes were fortified with chlorpyrifos and chlorpyrifos-oxon at 50, 500, and 2,000 ng/tube. Air was drawn through the spiked tubes at similar flow rates and sampling durations (6 and 12 hours) as used for the collection of the on-field air monitoring samples. Field spikes were handled, stored, shipped and analyzed in the same manner as all other samples. The field fortification experiments were conducted during Periods 5 and 7 for chlorpyrifos and Periods 5 and 9 for chlorpyrifos-oxon.

Table 4 provides a summary of the field fortification recoveries. While some individual field fortification samples indicated low recoveries the overall averages were between 70 and 120 % (generally acceptable range criteria). The overall average recoveries for chlorpyrifos were 81.1%, 75.3%, and 82.0% at the 0.05, 0.5, and 2.00 µg fortification levels, respectively. The overall average recoveries for total toxic residues were 86.7%, 79.6%, and 84.5% at the 0.05, 0.5, and 2.00 µg fortification levels, respectively.

The field fortification levels bracketed the expected residues in the field.

Table 4. Summary of Field Fortification Recoveries

Analyte	Trapping Interval (hr)[1]	Fortification Level (µg/sample)	n	Range of Recoveries[1] (%)	Average Recovery ± Standard Deviation (%)	Overall Average Percent Recovery ± Standard Deviation (%)		
						Low Level	Mid Level	High Level
Chlorpyrifos	6	0.05	3	76.5-98.0	87.0 ± 10.8	81.1 ± 9.84	75.3 ± 13.4	82.0 ± 4.11
		0.50	3	49.1-77.4	66.9 ± 15.5			
		2.00	3	74.8-83.9	79.7 ± 4.59			
	12	0.05	3	71.2-80.6	75.3 ± 4.83			
		0.50	3	81.6-85.5	83.6 ± 1.95			
		2.00	3	82.1-86.8	84.2 ± 2.38			
Total Toxic Residues[2]	6	0.05	3	82.8-104	92.6 ± 10.9	86.7 ± 9.98	79.6 ± 12.6	84.5 ± 3.43
		0.50	3	54.5-83.3	72.6 ± 15.8			
		2.00	3	78.7-85.3	82.6 ± 3.46			
	12	0.05	3	77.5-86.9	80.9 ± 5.24			
		0.50	3	85.0-88.2	86.6 ± 1.60			
		2.00	3	84.1-89.2	86.4 ± 2.60			

[1] Presented values represent "with flow" samples.
[2] Total toxic residues = chlorpyrifos + total oxon. The chlorpyrifos and oxon values are from the chlorpyrifos field

fortification samples.

Travel Recovery: Travel recovery samples were not used in this study.

Application Verification: Tank mix samples were not collected for this study. However, the application rate was confirmed using monitoring pads. Prior to application, at least 12 filter pads, measuring 301.4 cm^2, were placed in shallow foil pans that were put on supports immediately above the plant canopy. Immediately following application, the pads were collected, individually bagged, and stored frozen. The filter pad samples ranged from 1,398 to 4,341 µg/sample and averaged 2,751 µg/sample. This corresponds to 0.878 lb ai/A, which is 92.5% of the target application rate.

Storage Stability: Sorbent tubes were prepared and spiked chlorpyrifos, oxon, or TCP at 50, 500, and 2,000 ng/tube. The samples were aged in a laboratory hood at ambient conditions for 6 and 12 hours with airflow at 1 L/min. TCP was stable in the sorbent tubes. Oxon was not stable showing substantial conversion to TCP. Chlorpyrifos was not stable showing conversion to oxon. The petitioner used a simple linear regression of % conversion vs. time to correct the chlorpyrifos concentrations. See **APPENDIX G** for a more thorough discussion of the correction factor development.

Table 5 provides a summary of the storage stability recoveries.

Table 5. Summary of Storage Stability Recoveries

Analyte	Trapping Interval (hr)[1]	Fortification Level (µg/sample)	n	Range of Recoveries [1] (%)	Average Recovery ± Standard Deviation (%)	Overall Average Percent Recovery ± Standard Deviation (%)		
						Low Level	Mid Level	High Level
Chlorpyrifos	6	0.05	3	81.0-91.9	86.6 ± 5.45	91.6 ± 6.61	97.3 ± 10.1	94.2 ± 3.25
		0.50	3	89.6-92.7	91.3 ± 1.58			
		2.00	3	91.3-93.4	92.5 ± 1.10			
	12	0.05	3	95.5-98.6	96.7 ± 1.69			
		0.50	3	89.7-112	103 ± 11.9			
		2.00	3	91.7-100	95.8 ± 4.15			
Total Toxic Residues[2]	6	0.05	3	81.0-91.9	86.6 ± 5.45	91.6 ± 6.61	97.3 ± 10.1	94.2 ± 3.25
		0.50	3	89.6-92.7	91.3 ± 1.58			
		2.00	3	91.3-93.4	92.5 ± 1.10			
	12	0.05	3	95.5-98.6	96.7 ± 1.69			
		0.50	3	89.7-112	103 ± 11.9			
		2.00	3	91.7-100	95.8 ± 4.15			

[1] Presented values represent "with flow" samples.
[2] Total toxic residues = chlorpyrifos + total oxon. The chlorpyrifos and oxon values are from the chlorpyrifos storage stability samples. *Note:* storage stability recoveries for chlorpyrifos were calculated from total residues because oxon contributions were minimal.

Breakthrough: Front and back sections were initially analyzed separately. As residue levels in the back sections were nondetectable, breakthrough analysis

was discontinued.

C. FLUX CALCULATIONS:

Flux rates for Sampling Period 1 were calculated using the Indirect Flux Method. Flux rates for the remaining sampling periods were calculated using the Integrated Horizontal Flux (IHF) Method and the Aerodynamic (AD) Method. A brief description of these methods is given below.

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)

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

if R_i <0 (for Convective/Unstable IBL)

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

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.

II. RESULTS AND CALCULATIONS

Chlorpyrifos and Total Toxic Residue Concentrations

Air samples were corrected using the average field fortification recoveries. Residues ≤0.275 µg were corrected for the average low level field fortification recovery (81.1% for chlorpyrifos and 86.7% for the total toxic residues), residues >1.25 µg were corrected for the average high level field fortification recovery (82.0% for chlorpyrifos and 84.5% for total toxic residues), and residues between 0.275 and 1.25 µg were corrected for the average mid level field fortification recovery (75.3% for chlorpyrifos and 79.6% for total toxic residues). Residues were also corrected in a separate analysis for the storage stability recoveries. Residues ≤0.275 µg were corrected for the average low level storage stability recovery (91.6% for chlorpyrifos and total toxic residues), residues >1.25 µg were corrected for the average high level storage stability recovery (94.2% for chlorpyrifos and total toxic residues), and residues between 0.275 and 1.25 µg were corrected for the average mid-level storage stability recovery (97.3% for chlorpyrifos and total toxic residues). Values reported as below the LOQ were assigned a value of ½ LOQ. Total toxic residues were estimated by summing the chlorpyrifos concentration and oxon

concentration which was corrected using the relative potency factor (RPF of 12X)[2].

Flux Rate Estimates

Reviewer-estimated flux rate values using the Indirect Method for Period 1 (application period) were 0.22 µg/m^2-s (field fortification correction) and 0.20 µg/m^2-s (storage stability correction) for chlorpyrifos and 0.46 µg/m^2-s (field fortification correction) and 0.52 µg/m^2-s (storage stability correction) for total toxic residues. The r^2 values for all of the regressions were above 0.81. Calculations are provided in **APPENDIX A**.

Chlorpyrifos

The reviewer-estimated flux rate values for chlorpyrifos are presented in **Table 6** for AD Flux and **Table 7** for IHF along with those estimated by the study author. Regression results for the sampler concentrations are provided in **APPENDICES C** (IHF) and **E** (AD).

The chlorpyrifos flux calculated for the first period after application using the AD method was 0.824 µg/m^2-s (field fortification correction) and 0.717 µg/m^2-s (storage stability correction). The flux then declined over the next 24 hours, followed by a second smaller peak of 0.081 µg/m^2-s (field fortification) and 0.070 µg/m^2-s (storage stability; Sampling Period 5). Flux generally continued to decrease over the remainder of the study and was 0.002 µg/m^2-s by the last sampling interval.

The chlorpyrifos flux calculated for the first period after application using the Indirect Method was 0.591 µg/m^2-s (field fortification correction) and 0.515 µg/m^2-s (storage stability correction). The highest flux was observed during the subsequent period (Period 2) at a considerably higher level of 0.759 µg/m^2-s (field fortification) and 0.660 µg/m^2-s (storage stability). The flux then declined over the next 24 hours, followed by a second smaller peak of 0.167 µg/m^2-s (field fortification) and 0.145 µg/m^2-s (storage stability; Sampling Period 6). Flux generally continued to decrease over the remainder of the study and was 0.004-0.005 µg/m^2-s by the last sampling interval.

Table 6. Estimated Flux Rates for Chlorpyrifos Using AD Method

Period	Sample Start Times	Sample End Times	Duration (hh:mm)	Estimated Flux FF (µg/m^2-s)	Estimated Flux SS (µg/m^2-s)	Study Author Estimated Flux (µg/m^2-s)
2	9/9/2011 10:45	9/9/2011 13:00	2.25	0.824	0.717	0.657
3	9/9/2011 13:00	9/9/2011 19:00	6.00	0.260	0.227	0.204
4	9/9/2011 19:00	9/10/2011 1:00	6.00	0.038	0.033	0.035
5	9/10/2011 1:00	9/10/2011 7:00	6.00	0.026	0.024	0.022
6	9/10/2011 7:00	9/10/2011 19:00	12.00	0.081	0.070	0.068
7	9/10/2011 19:00	9/11/2011 7:00	12.00	0.012	0.007	0.008
8	9/11/2011 7:00	9/11/2011 19:00	12.00	0.020	0.016	0.015
9	9/11/2011 19:00	9/12/2011 7:00	12.00	0.007	0.004	0.005
10	9/12/2011 7:00	9/12/2011 19:00	12.00	0.018	0.011	0.012
11	9/12/2011 19:00	9/13/2011 7:00	12.00	0.002	0.002	0.002

Table 7. Estimated Flux Rates for Chlorpyrifos Using IHF Method

Period	Sample Start Times	Sample End Times	Duration (hh:mm)	Estimated Flux FF ($\mu g/m^2$-s)	Estimated Flux SS ($\mu g/m^2$-s)	Study Author Estimated Flux ($\mu g/m^2$-s)
2	9/9/2011 10:45	9/9/2011 13:00	2.25	0.591	0.515	0.161
3	9/9/2011 13:00	9/9/2011 19:00	6.00	0.759	0.660	0.221
4	9/9/2011 19:00	9/10/2011 1:00	6.00	0.171	0.149	0.052
5	9/10/2011 1:00	9/10/2011 7:00	6.00	0.054	0.038	0.027
6	9/10/2011 7:00	9/10/2011 19:00	12.00	0.167	0.145	0.051
7	9/10/2011 19:00	9/11/2011 7:00	12.00	0.021	0.034	0.009
8	9/11/2011 7:00	9/11/2011 19:00	12.00	0.033	0.024	0.009
9	9/11/2011 19:00	9/12/2011 7:00	12.00	0.006	0.008	0.004
10	9/12/2011 7:00	9/12/2011 19:00	12.00	0.012	0.017	0.006
11	9/12/2011 19:00	9/13/2011 7:00	12.00	0.005	0.004	0.002

The reviewer-estimated flux rates for chlorpyrifos using the AD method were comparable to those estimated by the study author. The reviewer-estimated flux rate values for chlorpyrifos using the IHF method were much higher than those estimated by the study author. A review of the study author's calculations indicated that Zp (height of plume) was truncated at 150 cm, which in turn yielded lower flux rate estimates. The flux trends exhibited by both those estimated by the reviewer and those by the study author were very similar.

Chloropyrifos-oxon

The reviewer examined the flux rate values for oxon only; however, attempts at conducting a regression analysis for the residues generated poor fitting results. The study authors also completed this analysis and are consistent with EPA's analysis. It is unclear if the oxon residues are a result of oxon flux off the field or from transformation of chlorpyrifos in the air or on the tube. As a result, the reviewer decided to examine total toxic residues together (see section below as well as **RC 6**).

Total Toxic Residues

The reviewer estimated flux rate values for total toxic residues are presented in **Table 8** for AD Flux and **Table 9** for IHF along with those estimated by the study author. Regression results for the sampler concentrations are provided in **APPENDICES C** (IHF) and **E** (AD).

Initial attempts at conducting a regression analysis for the total toxic residues generated poor fitting results (*e.g.*, $r^2<0.2$). In general, the oxon concentrations did not follow a decreasing trend with height like the chlorpyrifos concentrations, resulting in poor 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 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. The mass of the oxon was then multiplied by the RPF $(12X)^2$ and added to the chlorpyrifos mass and divided by the volume of air sampled to estimate the total toxic residues at each height.

An example calculation is provided below for sampling Period 2. The total oxon mass is 0.397 µg and the total chlorpyrifos mass is 12.571 µg, resulting in a conversion factor of 0.031581. This conversion factor

is then applied to each of the chlorpyrifos samples to estimate a revised oxon amount. The revised oxon amount is then multiplied by the RPF (12) [2] and added to the chlorpyrifos mass to estimate the total toxic residue. This total toxic residue mass was divided by the sampler flowrate and length of sampling time for each sampler (131-133 minutes) to arrive at the total toxic residue concentration at each sampler height.

Period	Sampler	Sampler Flowrate (L/min)	Chlorpyrifos (µg)	Oxon (µg)	Revised Oxon (µg)	Total Toxic Residue (µg)	Total Toxic Residue (µg/m^3)
2	A1 (15 cm)	1.076	3.630	0.082	0.115	5.01	35.54
	B1 (33 cm)	1.047	2.901	0.082	0.092	4.005	29.20
	C1 (55 cm)	1.029	2.473	0.083	0.078	3.409	25.10
	D1 (90 cm)	1.081	2.097	0.086	0.066	2.889	20.25
	E1 (150 cm)	1.043	1.470	0.064	0.046	2.022	14.58

These concentrations were then corrected for field fortification or storage stability recoveries and used to estimate the regression for total toxic residues to be used in both the AD and IHF methods. The calculation of the revised total toxic residues is provided in **APPENDIX F**.

The total toxic residue flux calculated for the first period after application using the AD method was 1.102 µg/m^2-s (field fortification correction) and 0.989 µg/m^2-s (storage stability correction). The flux then declined over the next 24 hours, followed by a second smaller peak of 0.186 µg/m^2-s (field fortification) and 0.167 µg/m^2-s (storage stability; Sampling Period 6). Two smaller peaks occurred at 0.034 µg/m^2-s (field fortification) and 0.028 µg/m^2-s (storage stability; Sampling Period 8) and at 0.052 µg/m^2-s (field fortification) and 0.034 µg/m^2-s (storage stability; Sampling Period 10). Flux was 0.002-0.003 µg/m^2-s by the last sampling interval.

The total toxic residue flux calculated for the first period after application using the Indirect Method was 0.791 µg/m^2-s (field fortification correction) and 0.710 µg/m^2-s (storage stability correction). The highest flux was observed during the subsequent period (Period 2) at a considerably higher level of 1.27 µg/m^2-s (field fortification) and 1.14 µg/m^2-s (storage stability). The flux then declined over the next 24 hours, followed by a second smaller peak of 0.384 µg/m^2-s (field fortification) and 0.345 µg/m^2-s (storage stability; Sampling Period 6). Two smaller peaks occurred at 0.057 µg/m^2-s (field fortification) and 0.046 µg/m^2-s (storage stability; Sampling Period 8) and at 0.038 µg/m^2-s (field fortification) and 0.074 µg/m^2-s (storage stability; Sampling Period 10). Flux was 0.007-0.010 µg/m^2-s by the last sampling interval.

Table 8. Estimated Flux Rates for Total Toxic Residue Using AD Method*

Period	Sample Start Times	Sample End Times	Duration (hh:mm)	Estimated Flux FF (µg/m^2-s)	Estimated Flux SS (µg/m^2-s)
2	9/9/2011 10:45	9/9/2011 13:00	2.25	1.102	0.989
3	9/9/2011 13:00	9/9/2011 19:00	6.00	0.436	0.391
4	9/9/2011 19:00	9/10/2011 1:00	6.00	0.044	0.039
5	9/10/2011 1:00	9/10/2011 7:00	6.00	0.033	0.031
6	9/10/2011 7:00	9/10/2011 19:00	12.00	0.186	0.167
7	9/10/2011 19:00	9/11/2011 7:00	12.00	0.020	0.014
8	9/11/2011 7:00	9/11/2011 19:00	12.00	0.034	0.028
9	9/11/2011 19:00	9/12/2011 7:00	12.00	0.007	0.005
10	9/12/2011 7:00	9/12/2011 19:00	12.00	0.052	0.034

Table 8. Estimated Flux Rates for Total Toxic Residue Using AD Method*					
Period	**Sample Start Times**	**Sample End Times**	**Duration (hh:mm)**	**Estimated Flux FF ($\mu g/m^2$-s)**	**Estimated Flux SS ($\mu g/m^2$-s)**
11	9/12/2011 19:00	9/13/2011 7:00	12.00	0.003	0.002

* The study author did not estimate total toxic residue flux rates, instead the study author calculated flux rates for the chlorpyrifos-oxon alone.

Table 9. Estimated Flux Rates for Total Toxic Residue Using IHF Method					
Period	**Sample Start Times**	**Sample End Times**	**Duration (hh:mm)**	**Estimated Flux FF ($\mu g/m^2$-s)**	**Estimated Flux SS ($\mu g/m^2$-s)**
2	9/9/2011 10:45	9/9/2011 13:00	2.25	0.791	0.710
3	9/9/2011 13:00	9/9/2011 19:00	6.00	1.270	1.140
4	9/9/2011 19:00	9/10/2011 1:00	6.00	0.197	0.176
5	9/10/2011 1:00	9/10/2011 7:00	6.00	0.064	0.049
6	9/10/2011 7:00	9/10/2011 19:00	12.00	0.384	0.345
7	9/10/2011 19:00	9/11/2011 7:00	12.00	0.047	0.067
8	9/11/2011 7:00	9/11/2011 19:00	12.00	0.057	0.046
9	9/11/2011 19:00	9/12/2011 7:00	12.00	0.007	0.009
10	9/12/2011 7:00	9/12/2011 19:00	12.00	0.038	0.074
11	9/12/2011 19:00	9/13/2011 7:00	12.00	0.007	0.010

* The study author did not estimate total toxic residue flux rates, instead the study author calculated flux rates for the chlorpyrifos-oxon alone.

III DISCUSSION:

Flux rates for chlorpyrifos and total toxic residues started off low, but reached a peak in the second or third sampling period, depending on the method used to estimate flux rates, and then generally decreased, with other lower subsequent peaks that occurred during daytime hours of Days 2, 3, and 4.

Log-normal regressions developed for wind speed, temperature, and concentration data versus the log-normal estimates for height usually provided good fits, with most r^2 estimates above 0.9.

IV REVIEWER'S COMMENTS:

1 While Lorsban Advanced may be an end-use emulsifiable concentrate (water emulsion) used on a range of crops including alfalfa and is a preferred chlorpyrifos liquid formulation sold by Dow AgroSciences it may not represent the preferred formulation by applicators. In addition, Lorsban Advance is reported to be a low VOC (a low volatility formulation); therefore, the observed flux rates reported in this study may not represent the potential flux for other formulations and the results could under predict the potential exposure from other chlorpyrifos formulations. California is currently the only state actively working to reduce pesticide VOC; therefore, it is not expected the Lorsban Advance and other low VOC formulations dominate the market. Additional information on the use of Lorban Advance and other low VOC formulations compared to other "regular/non-low VOC" would be helpful to determine the representative nature of the selected formulation.

2 The study protocol indicated that the leaf area index would be reported. Although reporting the leaf is not a critical component of this study and does not affect the results and conclusions of this

study, not having the leaf area index for the studied crop limits the comparative value of this study to other crops.

3 The maximum single application rate for alfalfa (1 lb ai/a; 4 lb ai/a per year) is higher than the 0.878 lb ai/a used in this study. In addition, these rates are substantially lower than current maximum single applications for grapes (33.3 lb ai/a; 33.3 lb ai/a per year) permitted on currently labeled chlorpyrifos products. In addition to grapes, several other uses also have maximum single application rates substantially higher than alfalfa including citrus (6 lb ai/a; 10.5 lb ai/a per year), mint (2.0 ai/a; 6 lb ai/a per season), and turf (4.0 lb ai/a; no yearly application restriction).

Field volatility studies are typically conducted similar to terrestrial field dissipation studies (OCSPP 835.6100); therefore, the maximum single application rate of all uses is normally recommended. To address this uncertainty, additional studies may be necessary to evaluate flux rates under different cropping conditions and application rates.

4 In addition to temperature, environmental factors such as humidity and rainfall may influence the amount of chlorpyrifos and chlorpyrifos-oxon observed in air samples. While the temperature throughout the 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 this study, conducted in the central valley of California, compare to the results that may be obtained for other sites in the US. To address this uncertainty, additional studies may be necessary to evaluate flux rates under different environmental conditions in different regions of the country.

5 The total oxon chlorpyrifos equivalents for the 12-hour 500 ug sample (pg. 118 of report) were not consistent with the other data. Either the corrected concentrations are too high or the raw data is reported incorrectly. The reviewer thinks the corrected equivalents should be down around 2% based on examination of the molecular weight conversion. This error was confirmed with the study authors; however, a corrected report has not been provided. If this is the case, the oxon concentration would be slightly less than currently calculated. This is not expected to have a substantial impact on the total toxic residue concentrations and the calculated flux rates because the oxon concentrations are low and the change in the correction factor is not expected to be great (>5%).

6 It is unclear if the oxon residues observed in this study are a result of oxon flux off the field or from transformation of chlorpyrifos in the air or on the tube. As a result, the reviewer decided to examine total toxic residues (chlorpyrifos and chlorpyrifos-oxon) together. The study authors did not complete this analysis. This is thought to be a reasonable approach to account for any toxic residues that may end up in air as a result of chlorpyrifos applications independent of the route of oxon formation.

V CONCLUSION:

Despite issues with oxon recoveries during the study, the data and the flux rate estimates derived from the data appear to be scientifically sound. This study is classified as acceptable.

V REFERENCES:

Johnson, B., Barry, T., and Wofford P. 1999. Workbook for Gaussian Modeling Analysis of Air Concentrations Measurements. State of California Environmental Protection Agency, Department of Pesticide Regulation. Sacramento, CA.

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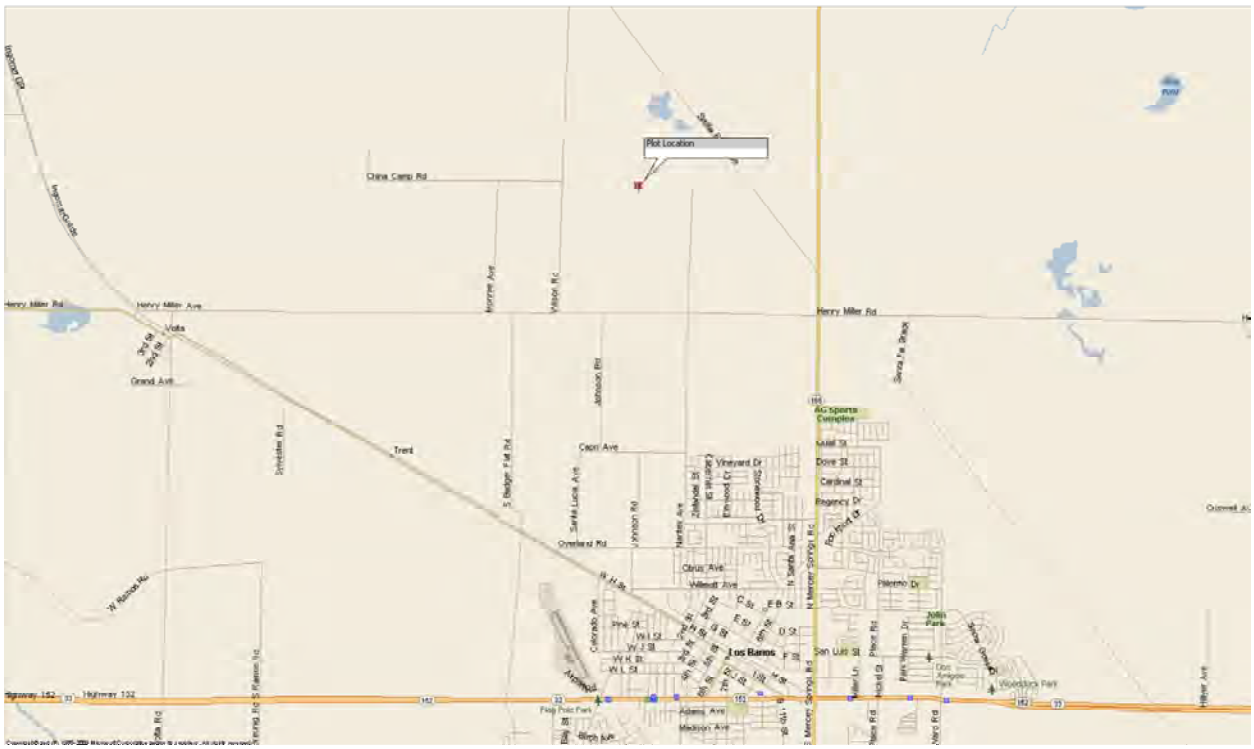

Figure 1. Location of Field in California

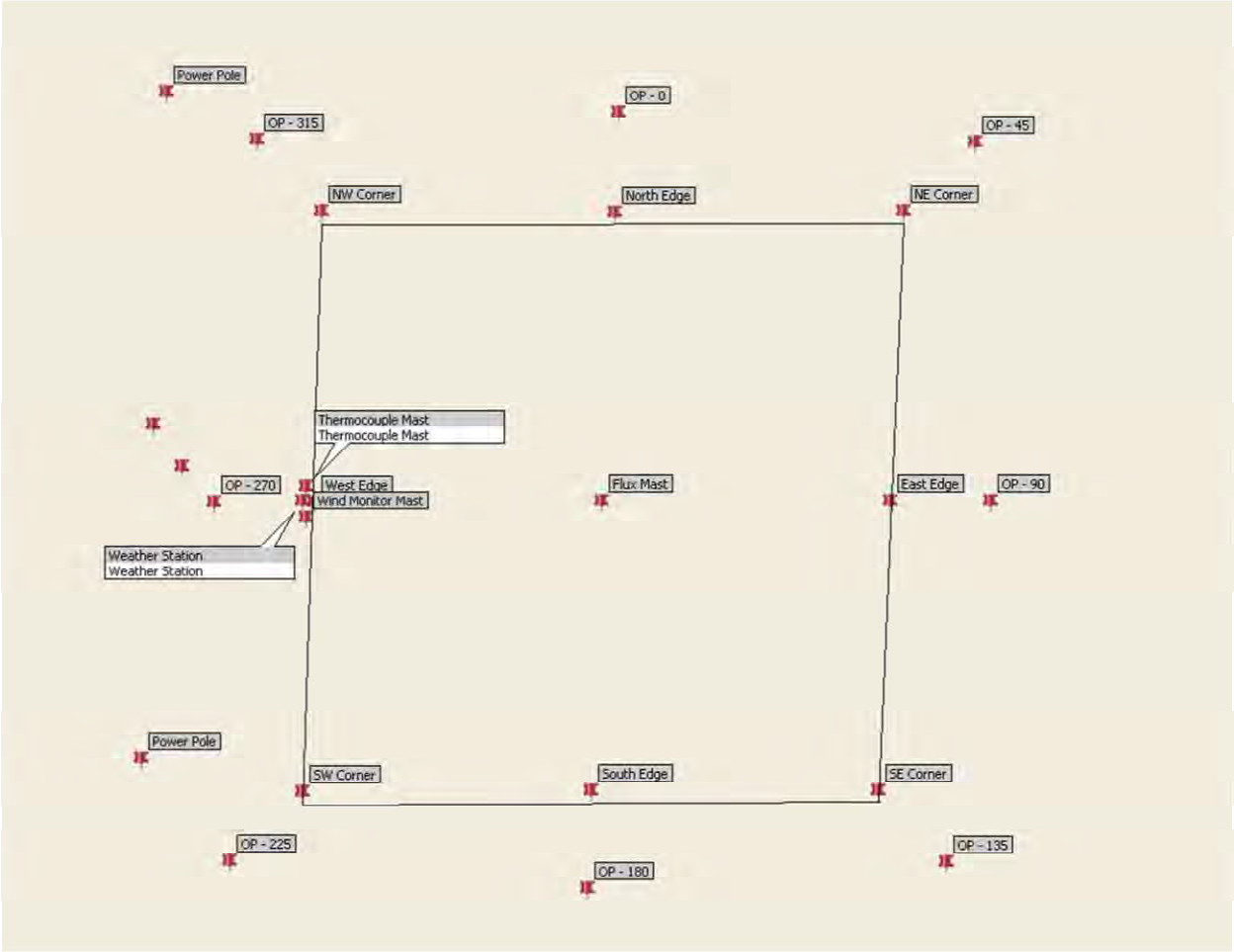

Figure 2. Air Quality and Meteorological Monitoring Stations

COMPLIANCE CHECKLIST

Applicable Checklist Items Taken from:

FIELD VOLATILITY STUDIES

- *Investigators should submit protocols for review purposes prior to the inception of the study*. This criterion was met. A protocol was provided in the study report and was submitted prior to the inception of the study. Comments provided by EPA on the protocol were also addressed in the study report.

- *Expected deviations from GLPs should be presented concurrently with any protocol deviations and their potential study impacts*. This criterion was met.

- *The test substance must be the typical end use product of the active ingredient*. This criterion was met.

- *The production of metabolites, breakdown products, or the presence of contaminants of potential toxicologic concern, should be considered on a case-by-case basis*. This criterion was met. Samples were analyzed for chlorpyrifos-oxon and TCP.

- *The application rate should be the maximum rate specified on the label. If multiple applications are made, the minimum allowable interval between applications should be used.* This criterion was met.

- *The percentage of active ingredient and formulation type should be reported. Properties of the pesticide (i.e., vapor pressure, water solubility, adsorption to soil, and texture) should also be addressed*. This criterion was met.

- *The study should be conducted domestically (USA). The site should be typical in geography, topography, soil type, season, and meteorology of those sites with intended use patterns. The use of two or more topographically and meteorologically diverse sites is recommended in order to ascertain the effects of these variables on spray drift*. These criteria were partially met. The study was conducted on a representative field in California. However, only one test site was used.

- *Field data should be documented, including area description, meteorological conditions, application data, and equipment information. Volatility (g/ha/day), air concentrations (µg/m^3), and vapor pressure (mm Hg or equivalent) should also be reported*. These criteria were partially met. Volatility and vapor pressure data were not provided.

- *Appropriate air sampling media should be selected. The medium should entrap a high percentage of the chemical passing through it, and it should allow the elution of a high percentage of the entrapped chemical for analysis. A trapping efficiency test for the monitoring media chosen must be documented*. These criteria were partially met. An appropriate air sampling media was selected. However, a trapping efficiency test was not performed.

- *Air monitoring techniques area (i.e., stationary) should contain sufficient samples to characterize the likely range of possible exposure concentrations, and to ensure that the reentry and/or bystander scenarios can be adequately addressed. Stationary samples should be collected from the center of treated fields and from at least 4 other locations, preferably at the cardinal compass*

points from the center location and at representative distances to reflect buffer zones. Air samplers should be placed at a height that is representative of the breathing zone of potentially exposed individual (i.e. 2 to 3 feet for workers removing tarps, 4 to 5 feet for bystanders downwind, etc.) At least three downwind collection sites should be used. If homes or structures are present, representative samples should be taken within the structure to establish buffer zones. These criteria were met.

- *The duration of the sampling interval and air flow rates should be maximized within the appropriate flow rate range to increase the potential for capturing enough residues to be quantifiable*. This criterion was met. The flow rate was maintained at 1 L/min (appropriate range for gaseous residue).

- *A sufficient number of replicates should be generated to address the exposure issues associated with the population of interest*. This criterion was met.

- *Air samples should be monitored for residues at intervals which increase with time after application. Sampling should be continued until the nature of the dissipation curve has been clearly established*. This criterion was met.

- *A monitoring pump capable of producing airflow of at least 2 L/min. should be used and its batteries should be capable of sustaining maximum airflow for at least 4 hours without recharging. Airflow should be measured at the beginning and end of the exposure period*. These criteria were met. The pumps were operated at airflow appropriate for the monitoring of gases and were sampled for intervals ranging from 6 to 12 hours. Airflow was monitored before and after the exposure period to ensure proper operation.

- *Field calibration of air monitors should be performed at the beginning and end of the sampling period*. This criterion was met.

- *An adequate number of field blanks should be analyzed for contamination. If an appropriate analytical method had not been established (i.e by NIOSH or OSHA), field fortification samples should be analyzed for correction of residue losses occurring during the sampling period. When appropriate, fortified samples and blanks should be fortified at the expected residue level of the actual field samples. Fortified blanks should be exposed to the same weather conditions*. These criteria were met.

- *Retention and breakthrough studies should be performed under conditions similar to those anticipated in the field phase of the study to ensure that collected material is not lost from the medium during sampling. It is recommended that at least one test be carried out where the initial trap contains 10x the highest amount of residue expected in the field*. These criteria were not met.

- *Samples should be stored in a manner that will minimize deterioration and loss of analytes between collection and analyses. Storage stability samples should be extracted and analyzed immediately before and at appropriate periods during storage. The time periods for storage should be chosen so that the longest interval corresponds to the longest projected storage period for field samples*. These criteria were met.

- *If exposed media are to be stored prior to extraction, storage media/containers should be made of appropriate material that protects against contamination and that does not interfere with analysis*. These criteria were met.

- *Validated analytical methods of sufficient sensitivity are needed. The method must be specific for the analyte of interest. Information on method efficiency (residue recovery) and limit of quantification (LOQ) should be provided*. This criterion was met.

- *Analysis methods should be documented and appropriate. The analytical procedure must be capable of measuring exposure to 1µg/hr (or less, if the toxicity of the material under study warrants greater sensitivity).* Not applicable.

- *Method accuracy should range between 70 and 120 percent. Precision values should be less than or equal to 20 percent (coefficient of variation). The extraction efficiency of laboratory fortified controls is considered acceptable if the lower limit of the 95% confidence interval is greater than 75%, unless otherwise specified by the Agency*. These criteria were met

- *Information on recovery samples must be included in the study report. A complete set of field recoveries should consist of at least one blank control sample and three or more each of a low-level and high-level fortification. These fortifications should be in the range of anticipated residue levels in the field study. Total recovery from field-fortified samples must be greater than 50% for the study*. These criteria were met.

- *Raw residue data must be corrected if appropriate recovery values are less than 90 percent*. This criterion was not met. The study authors did not correct for field recoveries. However, the petitioner used a simple linear regression of % conversion vs. time to correct the chlorpyrifos concentrations.

- *Residues should be reported as µg pesticide active ingredient per sample and as an airborne concentration (µg/m3). Distributional data should be reported, to the extent possible*. This criterion was met.

- *A sample history sheet must be prepared by the laboratory upon receipt of the samples*. This criterion was met.

APPENDIX A

Indirect Method Regression Analysis

Indirect Regression Analysis for Chlorpyrifos (Adjusted for Field Fortification)

Location	Measured concentration (µg/m3)	Modeled concentration (µg/m3)
OP - 0	0	0.000
OP - 45	0	0.000
OP - 90	1.67721	1.381
OP - 135	7.75345	2.208
OP - 180	11.41688	2.315
OP - 225	0.01814	0.019
OP - 270	0.00008	0.000
OP - 315	0	0.000
	Linear Regression	
	0.219083	0.168975
	0.036237	0.178115
	0.858993	0.427006
	36.55118	6
	Least Squares Regression	
	0.237325	0
	0.030495	#N/A
	0.896401	0.423945
	60.56806	7
Is LR Slope Sig.?	Yes	
Is LR Intercept Sig.?	No	
Is Intercept < 25 Per.	No	
Is LSR Slope Sig.?	Yes	
Flux	**0.22**	
Flux source	Linear Regression	

Indirect Regression Analysis for Chlorpyrifos (Adjusted for Storage Stability)

Location	Measured concentration (µg/m3)	Modeled concentration (µg/m3)
OP - 0	0	0.000
OP - 45	0	0.000
OP - 90	1.67721	1.223
OP - 135	7.75345	1.955
OP - 180	11.41688	2.050
OP - 225	0.01814	0.016
OP - 270	0.00008	0.000
OP - 315	0	0.000
	Linear Regression	
	0.194014	0.14964
	0.032091	0.157734
	0.858993	0.378145
	36.55118	6
	Least Squares Regression	
	0.210169	0
	0.027005	#N/A
	0.896401	0.375435
	60.56806	7
Is LR Slope Sig.?	Yes	
Is LR Intercept Sig.?	No	
Is Intercept < 25 Per.	No	
Is LSR Slope Sig.?	Yes	
Flux	**0.194**	
Flux source	Linear Regression	

Indirect Regression Analysis for Total Residues (Adjusted for Field Fortification)

Location	Measured concentration (µg/m3)	Modeled concentration (µg/m3)
OP - 0	0	0
OP - 45	0	0
OP - 90	1.67721	3.244886
OP - 135	7.75345	4.758321
OP - 180	11.41688	4.799108
OP - 225	0.01814	0.018528
OP - 270	0.00008	0
OP - 315	0	0
	Linear Regression	
	0.458671	0.406291
	0.087951	0.432297
	0.819261	1.036372
	27.19712	6
	Least Squares Regression	
	0.502534	0
	0.073923	#N/A
	0.868456	1.027697
	46.21409	7
Is LR Slope Sig.?	Yes	
Is LR Intercept Sig.?	No	
Is Intercept < 25 Per.	No	
Is LSR Slope Sig.?	Yes	
Flux	**0.459**	
Flux source	Linear Regression	

Indirect Regression Analysis for Total Residues (Adjusted for Storage Stability)

Location	Measured concentration (µg/m3)	Modeled concentration (µg/m3)
OP - 0	0	0
OP - 45	0	0
OP - 90	1.67721	3.788345
OP - 135	7.75345	5.4658
OP - 180	11.41688	5.469314
OP - 225	0.01814	0.016408
OP - 270	0.00008	0
OP - 315	0	0
	Linear Regression	
	0.5238	0.476299
	0.103276	0.507624
	0.810866	1.21696
	25.72351	6
	Least Squares Regression	
	0.575221	0
	0.086785	#N/A
	0.862561	1.206517
	43.93151	7
Is LR Slope Sig.?	Yes	
Is LR Intercept Sig.?	No	
Is Intercept < 25 Per.	No	
Is LSR Slope Sig.?	Yes	
Flux	**0.524**	
Flux source	Linear Regression	

APPENDIX B

Integrated Horizontal Flux Method Meteorological Calculations

IHF Method Meteorological Parameters for Chlorpyrifos and Total Residues

Period	Start		End		Duration (hours)	Period Averaged Wind Speed m/s				Regression Coefficients			Fetch
	Date	Time	Date	Time		15 cm	33 cm	55 cm	90 cm	Slope	Intercept	R^2	(m)
2	9/9/2011	10:45	9/9/2011	13:00	2.25	0.44	0.56	0.63	0.74	0.16	0.74	0.99	104.5
3	9/9/2011	13:00	9/9/2011	19:00	6.00	0.79	1.11	1.23	1.59	0.42	1.57	0.96	87.7
4	9/9/2011	19:00	9/10/2011	1:00	6.00	0.31	0.44	0.57	0.74	0.23	0.73	0.96	91.2
5	9/10/2011	1:00	9/10/2011	7:00	6.00	0.23	0.36	0.48	0.62	0.22	0.62	0.98	93.9
6	9/10/2011	7:00	9/10/2011	19:00	12.00	0.55	0.76	0.94	1.14	0.33	1.15	0.99	99.3
7	9/10/2011	19:00	9/11/2011	7:00	12.00	0.92	1.18	1.40	1.69	0.43	1.69	0.98	88.0
8	9/11/2011	7:00	9/11/2011	19:00	12.00	0.60	0.83	0.97	1.17	0.31	1.18	0.99	99.3
9	9/11/2011	19:00	9/12/2011	7:00	12.00	0.55	0.77	0.94	1.14	0.33	1.15	0.99	105.7
10	9/12/2011	7:00	9/12/2011	19:00	12.00	0.65	0.98	1.15	1.40	0.41	1.43	1.00	93.3
11	9/12/2011	19:00	9/13/2011	7:00	12.00	0.31	0.44	0.57	0.75	0.24	0.74	0.97	88.1

APPENDIX C

Integrated Horizontal Flux Method Concentration Calculations

IHF Method Concentration Parameters for Chlorpyrifos (Field Fortifications)

Period	Start		End		Duration (hours)	Period Averaged Concentrations (µg m^{-3})[1]					Regression Coefficients		
	Date	Time	Date	Time		15 cm	33 cm	55 cm	90 cm	150 cm	Slope	Intercept	R^2
2	9/9/2011	10:45	9/9/2011	13:00	2.25	31.419	25.804	22.213	17.929	12.935	-7.45	17.43	1.00
3	9/9/2011	13:00	9/9/2011	19:00	6.00	17.652	15.768	12.746	9.644	7.153	-4.47	9.81	0.95
4	9/9/2011	19:00	9/10/2011	1:00	6.00	10.750	10.308	7.459	5.673	2.699	-2.95	5.82	0.88
5	9/10/2011	1:00	9/10/2011	7:00	6.00	8.064	6.772	5.340	3.392	1.679	-2.56	3.52	0.96
6	9/10/2011	7:00	9/10/2011	19:00	12.00	5.255	4.828	3.714	3.011	2.073	-1.29	3.00	0.93
7	9/10/2011	19:00	9/11/2011	7:00	12.00	0.683	0.614	0.446	0.371	0.269	-0.18	0.36	0.94
8	9/11/2011	7:00	9/11/2011	19:00	12.00	1.173	1.010	0.793	0.679	0.425	-0.29	0.65	0.98
9	9/11/2011	19:00	9/12/2011	7:00	12.00	0.594	0.507	0.385	0.269	0.167	-0.18	0.27	0.97
10	9/12/2011	7:00	9/12/2011	19:00	12.00	0.608	0.498	0.371	0.323	0.196	-0.17	0.30	0.98
11	9/12/2011	19:00	9/13/2011	7:00	12.00	0.460	0.408	0.332	0.227	0.109	-0.13	0.24	0.93

1. As wind data were only provided up to 90 cm, only the concentration data up to 90 cm were used in generating the regression coefficients.

IHF Method Concentration Parameters for Chlorpyrifos (Stability Fortifications)

Period	Start		End		Duration (hours)	Period Averaged Concentrations (µg m^{-3}) [1]					Regression Coefficients		
	Date	Time	Date	Time		15 cm	33 cm	55 cm	90 cm	150 cm	Slope	Intercept	R^2
2	9/9/2011	10:45	9/9/2011	13:00	2.25	27.348	22.461	19.335	15.606	11.259	-6.49	15.17	1.00
3	9/9/2011	13:00	9/9/2011	19:00	6.00	15.365	13.725	11.095	8.395	6.227	-3.89	8.54	0.95
4	9/9/2011	19:00	9/10/2011	1:00	6.00	9.357	8.973	6.493	4.938	2.087	-2.56	5.06	0.88
5	9/10/2011	1:00	9/10/2011	7:00	6.00	7.019	5.895	4.648	2.623	1.299	-2.38	2.84	0.94
6	9/10/2011	7:00	9/10/2011	19:00	12.00	4.574	4.203	3.233	2.621	1.603	-1.13	2.61	0.93
7	9/10/2011	19:00	9/11/2011	7:00	12.00	0.528	0.475	0.395	0.329	0.238	-0.11	0.33	0.97
8	9/11/2011	7:00	9/11/2011	19:00	12.00	0.907	0.781	0.613	0.525	0.377	-0.22	0.50	0.98
9	9/11/2011	19:00	9/12/2011	7:00	12.00	0.459	0.392	0.341	0.238	0.148	-0.12	0.25	0.95
10	9/12/2011	7:00	9/12/2011	19:00	12.00	0.470	0.385	0.329	0.286	0.174	-0.10	0.27	1.00
11	9/12/2011	19:00	9/13/2011	7:00	12.00	0.407	0.361	0.294	0.201	0.097	-0.11	0.21	0.93

1. As wind data were only provided up to 90 cm, only the concentration data up to 90 cm were used in generating the regression coefficients.

IHF Method Concentration Parameters for Total Residue (Field Fortifications)

Period	Start		End		Duration (hours)	Period Averaged Concentrations (µg m^{-3}) [1]					Regression Coefficients		
	Date	Time	Date	Time		15 cm	33 cm	55 cm	90 cm	150 cm	Slope	Intercept	R^2
2	9/9/2011	10:45	9/9/2011	13:00	2.25	42.035	34.523	29.718	23.987	17.305	-9.97	23.32	1.00
3	9/9/2011	13:00	9/9/2011	19:00	6.00	29.545	26.392	21.334	16.143	11.973	-7.48	16.42	0.95
4	9/9/2011	19:00	9/10/2011	1:00	6.00	12.349	11.841	8.568	6.517	3.020	-3.38	6.68	0.88
5	9/10/2011	1:00	9/10/2011	7:00	6.00	10.019	8.414	6.635	4.104	2.032	-3.23	4.29	0.95
6	9/10/2011	7:00	9/10/2011	19:00	12.00	12.041	11.064	8.510	6.900	4.361	-2.97	6.88	0.93
7	9/10/2011	19:00	9/11/2011	7:00	12.00	1.213	1.089	0.854	0.652	0.472	-0.32	0.66	0.95
8	9/11/2011	7:00	9/11/2011	19:00	12.00	1.958	1.686	1.323	1.133	0.703	-0.48	1.08	0.98
9	9/11/2011	19:00	9/12/2011	7:00	12.00	0.636	0.542	0.408	0.285	0.177	-0.20	0.28	0.96
10	9/12/2011	7:00	9/12/2011	19:00	12.00	1.754	1.437	1.060	0.923	0.560	-0.49	0.84	0.98
11	9/12/2011	19:00	9/13/2011	7:00	12.00	0.752	0.612	0.499	0.341	0.164	-0.22	0.34	0.98

1. As wind data were only provided up to 90 cm, only the concentration data up to 90 cm were used in generating the regression coefficients.

IHF Method Concentration Parameters for Total Residue (Stability Fortifications)

Period	Start		End		Duration (hours)	Period Averaged Concentrations (µg m^{-3}) [1]					Regression Coefficients		
	Date	Time	Date	Time		15 cm	33 cm	55 cm	90 cm	150 cm	Slope	Intercept	R^2
2	9/9/2011	10:45	9/9/2011	13:00	2.25	37.712	30.973	26.662	21.521	15.526	-8.95	20.92	1.00
3	9/9/2011	13:00	9/9/2011	19:00	6.00	26.507	23.678	19.141	14.483	10.742	-6.71	14.73	0.95
4	9/9/2011	19:00	9/10/2011	1:00	6.00	11.079	10.623	7.687	5.847	2.471	-3.04	5.99	0.88
5	9/10/2011	1:00	9/10/2011	7:00	6.00	8.989	7.549	5.952	3.359	1.663	-3.05	3.63	0.94
6	9/10/2011	7:00	9/10/2011	19:00	12.00	10.803	9.927	7.635	6.190	3.913	-2.66	6.17	0.93
7	9/10/2011	19:00	9/11/2011	7:00	12.00	0.992	0.891	0.699	0.617	0.447	-0.22	0.60	0.96
8	9/11/2011	7:00	9/11/2011	19:00	12.00	1.603	1.379	1.083	0.927	0.665	-0.39	0.89	0.98
9	9/11/2011	19:00	9/12/2011	7:00	12.00	0.520	0.444	0.386	0.269	0.167	-0.13	0.28	0.95
10	9/12/2011	7:00	9/12/2011	19:00	12.00	1.435	1.176	1.003	0.873	0.530	-0.32	0.83	1.00
11	9/12/2011	19:00	9/13/2011	7:00	12.00	0.615	0.579	0.472	0.323	0.155	-0.16	0.35	0.87

1. As wind data were only provided up to 90 cm, only the concentration data up to 90 cm were used in generating the regression coefficients.

APPENDIX D

Aerodynamic Flux Method Temperature and Wind Speed Calculations

AD Method Temperature Parameters for Chlorpyrifos and Total Residues

Period	Start		End		Duration (hours)	Period Averaged Temperature ºC				Regression Coefficients			Temperature ºC	
	Date	Time	Date	Time		15 cm	33 cm	55 cm	90 cm	Slope	Intercept	R^2	90 cm	33 cm
2	9/9/2011	10:45	9/9/2011	13:00	2.25	29.7	29.4	29.4	29.0	-0.33	30.60	0.88	29.1	29.5
3	9/9/2011	13:00	9/9/2011	19:00	6.00	31.3	31.5	31.6	31.7	0.25	30.59	0.97	31.7	31.5
4	9/9/2011	19:00	9/10/2011	1:00	6.00	22.4	22.7	23.0	23.4	0.57	20.79	0.97	23.4	22.8
5	9/10/2011	1:00	9/10/2011	7:00	6.00	17.0	17.3	17.6	18.1	0.64	15.13	0.96	18.0	17.4
6	9/10/2011	7:00	9/10/2011	19:00	12.00	29.8	29.8	29.8	29.8	0.01	29.75	0.14	29.8	29.8
7	9/10/2011	19:00	9/11/2011	7:00	12.00	20.6	20.7	20.8	21.0	0.18	20.11	0.97	20.9	20.8
8	9/11/2011	7:00	9/11/2011	19:00	12.00	22.8	22.7	22.7	22.7	-0.06	22.94	0.81	22.7	22.7
9	9/11/2011	19:00	9/12/2011	7:00	12.00	17.7	17.8	17.9	18.1	0.26	16.93	0.98	18.1	17.8
10	9/12/2011	7:00	9/12/2011	19:00	12.00	25.8	25.6	25.6	25.4	-0.20	26.34	0.92	25.4	25.6
11	9/12/2011	19:00	9/13/2011	7:00	12.00	17.4	17.7	17.9	18.2	0.45	16.18	0.99	18.2	17.7

AD Method Wind Speed Parameters for Chlorpyrifos and Total Residues

Period	Start		End		Duration (hours)	Period Averaged Wind Speed m/s				Regression Coefficients			Wind Speed m/s	
	Date	Time	Date	Time		15 cm	33 cm	55 cm	90 cm	Slope	Intercept	R^2	90 cm	33 cm
2	9/9/2011	10:45	9/9/2011	13:00	2.25	0.44	0.56	0.63	0.74	0.16	-0.01	0.99	0.73	0.56
3	9/9/2011	13:00	9/9/2011	19:00	6.00	0.79	1.11	1.23	1.59	0.42	-0.37	0.96	1.52	1.10
4	9/9/2011	19:00	9/10/2011	1:00	6.00	0.31	0.44	0.57	0.74	0.23	-0.35	0.96	0.71	0.474
5	9/10/2011	1:00	9/10/2011	7:00	6.00	0.23	0.36	0.48	0.62	0.22	-0.38	0.98	0.60	0.38
6	9/10/2011	7:00	9/10/2011	19:00	12.00	0.55	0.76	0.94	1.14	0.33	-0.36	0.99	1.12	0.79
7	9/10/2011	19:00	9/11/2011	7:00	12.00	0.92	1.18	1.40	1.69	0.43	-0.27	0.98	1.649	1.222
8	9/11/2011	7:00	9/11/2011	19:00	12.00	0.60	0.83	0.97	1.17	0.31	-0.24	0.99	1.15	0.84
9	9/11/2011	19:00	9/12/2011	7:00	12.00	0.55	0.77	0.94	1.14	0.33	-0.35	0.99	1.12	0.79
10	9/12/2011	7:00	9/12/2011	19:00	12.00	0.65	0.98	1.15	1.40	0.41	-0.47	1.00	1.384	0.972
11	9/12/2011	19:00	9/13/2011	7:00	12.00	0.31	0.44	0.57	0.75	0.24	-0.35	0.97	0.71	0.47

APPENDIX E

Aerodynamic Flux Method Concentration Calculations

AD Method Concentration Parameters for Chlorpyrifos (Field Fortifications)

Period	Start		End		Duration (hours)	Period Averaged Concentrations (µg m^{-3})[1]					Regression Coefficients			Chlor. µg/m³	
	Date	Time	Date	Time		15 cm	33 cm	55 cm	90 cm	150 cm	Slope	Intercept	R^2	90 cm	33 cm
2	9/9/2011	10:45	9/9/2011	13:00	2.25	31.419	25.804	22.213	17.929	12.935	-7.45	51.76	1.00	18.21	25.69
3	9/9/2011	13:00	9/9/2011	19:00	6.00	17.652	15.768	12.746	9.644	7.153	-4.47	30.39	0.95	10.28	14.76
4	9/9/2011	19:00	9/10/2011	1:00	6.00	10.750	10.308	7.459	5.673	2.699	-2.95	19.38	0.88	6.13	9.08
5	9/10/2011	1:00	9/10/2011	7:00	6.00	8.064	6.772	5.340	3.392	1.679	-2.56	15.31	0.96	3.79	6.36
6	9/10/2011	7:00	9/10/2011	19:00	12.00	5.255	4.828	3.714	3.011	2.073	-1.29	8.96	0.93	3.14	4.44
7	9/10/2011	19:00	9/11/2011	7:00	12.00	0.683	0.614	0.446	0.371	0.269	-0.18	1.20	0.94	0.38	0.56
8	9/11/2011	7:00	9/11/2011	19:00	12.00	1.173	1.010	0.793	0.679	0.425	-0.29	1.97	0.98	0.68	0.97
9	9/11/2011	19:00	9/12/2011	7:00	12.00	0.594	0.507	0.385	0.269	0.167	-0.18	1.11	0.97	0.29	0.47
10	9/12/2011	7:00	9/12/2011	19:00	12.00	0.608	0.498	0.371	0.323	0.196	-0.17	1.06	0.98	0.31	0.48
11	9/12/2011	19:00	9/13/2011	7:00	12.00	0.460	0.408	0.332	0.227	0.109	-0.13	0.82	0.93	0.25	0.38

1. As wind and temperature data were only provided up to 90 cm, only the concentration data up to 90 cm were used in generating the regression coefficients.

AD Method Concentration Parameters for Chlorpyrifos (Storage Stability Fortifications)

Period	Start		End		Duration (hours)	Period Averaged Concentrations (µg m^{-3})[1]					Regression Coefficients			Chlor. µg/m³	
	Date	Time	Date	Time		15 cm	33 cm	55 cm	90 cm	150 cm	Slope	Intercept	R^2	90 cm	33 cm
2	9/9/2011	10:45	9/9/2011	13:00	2.25	27.348	22.461	19.335	15.606	11.259	-6.49	45.05	1.00	15.86	22.36
3	9/9/2011	13:00	9/9/2011	19:00	6.00	15.365	13.725	11.095	8.395	6.227	-3.89	26.45	0.95	8.95	12.85
4	9/9/2011	19:00	9/10/2011	1:00	6.00	9.357	8.973	6.493	4.938	2.087	-2.56	16.87	0.88	5.33	7.91
5	9/10/2011	1:00	9/10/2011	7:00	6.00	7.019	5.895	4.648	2.623	1.299	-2.38	13.82	0.94	3.09	5.48
6	9/10/2011	7:00	9/10/2011	19:00	12.00	4.574	4.203	3.233	2.621	1.603	-1.13	7.80	0.93	2.73	3.86
7	9/10/2011	19:00	9/11/2011	7:00	12.00	0.528	0.475	0.395	0.329	0.238	-0.11	0.85	0.97	0.34	0.45
8	9/11/2011	7:00	9/11/2011	19:00	12.00	0.907	0.781	0.613	0.525	0.377	-0.22	1.52	0.98	0.52	0.75
9	9/11/2011	19:00	9/12/2011	7:00	12.00	0.459	0.392	0.341	0.238	0.148	-0.12	0.79	0.95	0.26	0.38
10	9/12/2011	7:00	9/12/2011	19:00	12.00	0.470	0.385	0.329	0.286	0.174	-0.10	0.75	1.00	0.28	0.39
11	9/12/2011	19:00	9/13/2011	7:00	12.00	0.407	0.361	0.294	0.201	0.097	-0.11	0.73	0.93	0.22	0.34

1. As wind and temperature data were only provided up to 90 cm, only the concentration data up to 90 cm were used in generating the regression coefficients.

AD Method Concentration Parameters for Total Residues (Field Fortifications)

Period	Start		End		Duration (hours)	Period Averaged Concentrations (µg m^{-3}) [1]					Regression Coefficients			Total Res µg/m³	
	Date	Time	Date	Time		15 cm	33 cm	55 cm	90 cm	150 cm	Slope	Intercept	R^2	90 cm	33 cm
2	9/9/2011	10:45	9/9/2011	13:00	2.25	42.035	34.523	29.718	23.987	17.305	-9.97	69.24	1.00	24.37	34.37
3	9/9/2011	13:00	9/9/2011	19:00	6.00	29.545	26.392	21.334	16.143	11.973	-7.48	50.87	0.95	17.21	24.71
4	9/9/2011	19:00	9/10/2011	1:00	6.00	12.349	11.841	8.568	6.517	3.020	-3.38	22.26	0.88	7.04	10.43
5	9/10/2011	1:00	9/10/2011	7:00	6.00	10.019	8.414	6.635	4.104	2.032	-3.23	19.19	0.95	4.63	7.88
6	9/10/2011	7:00	9/10/2011	19:00	12.00	12.041	11.064	8.510	6.900	4.361	-2.97	20.53	0.93	7.19	10.17
7	9/10/2011	19:00	9/11/2011	7:00	12.00	1.213	1.089	0.854	0.652	0.472	-0.32	2.12	0.95	0.69	1.01
8	9/11/2011	7:00	9/11/2011	19:00	12.00	1.958	1.686	1.323	1.133	0.703	-0.48	3.28	0.98	1.13	1.61
9	9/11/2011	19:00	9/12/2011	7:00	12.00	0.636	0.542	0.408	0.285	0.177	-0.20	1.19	0.96	0.31	0.50
10	9/12/2011	7:00	9/12/2011	19:00	12.00	1.754	1.437	1.060	0.923	0.560	-0.49	3.08	0.98	0.89	1.38
11	9/12/2011	19:00	9/13/2011	7:00	12.00	0.752	0.612	0.499	0.341	0.164	-0.22	1.38	0.98	0.37	0.59

1. As wind and temperature data were only provided up to 90 cm, only the concentration data up to 90 cm were used in generating the regression coefficients.

AD Method Concentration Parameters for Total Residues (Storage Stability Fortifications)

Period	Start		End		Duration (hours)	Period Averaged Concentrations (µg m^{-3}) [1]					Regression Coefficients			Total Res µg/m³	
	Date	Time	Date	Time		15 cm	33 cm	55 cm	90 cm	150 cm	Slope	Intercept	R^2	90 cm	33 cm
2	9/9/2011	10:45	9/9/2011	13:00	2.25	37.712	30.973	26.662	21.521	15.526	-8.95	62.12	1.00	21.86	30.84
3	9/9/2011	13:00	9/9/2011	19:00	6.00	26.507	23.678	19.141	14.483	10.742	-6.71	45.64	0.95	15.44	22.17
4	9/9/2011	19:00	9/10/2011	1:00	6.00	11.079	10.623	7.687	5.847	2.471	-3.04	19.97	0.88	6.31	9.36
5	9/10/2011	1:00	9/10/2011	7:00	6.00	8.989	7.549	5.952	3.359	1.663	-3.05	17.69	0.94	3.95	7.02
6	9/10/2011	7:00	9/10/2011	19:00	12.00	10.803	9.927	7.635	6.190	3.913	-2.66	18.42	0.93	6.45	9.12
7	9/10/2011	19:00	9/11/2011	7:00	12.00	0.992	0.891	0.699	0.617	0.447	-0.22	1.61	0.96	0.62	0.84
8	9/11/2011	7:00	9/11/2011	19:00	12.00	1.603	1.379	1.083	0.927	0.665	-0.39	2.68	0.98	0.93	1.32
9	9/11/2011	19:00	9/12/2011	7:00	12.00	0.520	0.444	0.386	0.269	0.167	-0.13	0.90	0.95	0.29	0.43
10	9/12/2011	7:00	9/12/2011	19:00	12.00	1.435	1.176	1.003	0.873	0.530	-0.32	2.29	1.00	0.86	1.18
11	9/12/2011	19:00	9/13/2011	7:00	12.00	0.615	0.579	0.472	0.323	0.155	-0.16	1.08	0.87	0.37	0.53

1. As wind and temperature data were only provided up to 90 cm, only the concentration data up to 90 cm were used in generating the regression coefficients.

APPENDIX F

Total Residue Estimation

Period	Sampler	Sampler Flowrate (L/min)	Chlorpyrifos (µg)	Oxon (µg)	Ratio of Total Oxon to Total Chlorpyrifos	Revised Oxon (µg)	Total Residue Adjusted for FF (µg)	Total Residue Adjusted for FF (µg/m^3)	Total Residue Adjusted for SS (µg)	Total Residue Adjusted for SS (µg/m^3)
2	A1 (15 cm)	1.076	3.630	0.082	0.031581	0.115	5.925	42.03	5.316	37.71
	B1 (33 cm)	1.047	2.901	0.082		0.092	4.735	34.52	4.248	30.97
	C1 (55 cm)	1.029	2.473	0.083		0.078	4.037	29.72	3.621	26.66
	D1 (90 cm)	1.081	2.097	0.086		0.066	3.423	23.99	3.071	21.52
	E1 (150 cm)	1.043	1.470	0.064		0.046	2.399	17.31	2.153	15.53
3	A2 (15 cm)	1.011	5.266	0.21	0.060431	0.318	10.753	29.55	9.648	26.51
	B2 (33 cm)	1.022	4.766	0.169		0.288	9.732	26.39	8.731	23.68
	C2 (55 cm)	1.018	3.827	0.256		0.231	7.815	21.33	7.011	19.14
	D2 (90 cm)	1.026	2.928	0.274		0.177	5.979	16.14	5.364	14.48
	E2 (150 cm)	1.047	2.210	0.239		0.134	4.513	11.97	4.049	10.74
4	A3 (15 cm)	1.014	3.206	0.015	0.015332	0.049	4.493	12.35	4.031	11.08
	B3 (33 cm)	0.993	3.012	0.032		0.046	4.221	11.84	3.787	10.62
	C3 (55 cm)	0.980	2.157	0.035		0.033	3.023	8.57	2.712	7.69
	D3 (90 cm)	0.980	1.636	0.048		0.025	2.293	6.52	2.057	5.85
	E3 (150 cm)	1.027	0.751	0.035		0.012	1.117	3.02	0.914	2.47
5	A4 (15 cm)	0.992	2.367	0.051	0.023382	0.055	3.588	10.02	3.219	8.99
	B4 (33 cm)	1.008	2.020	0.047		0.047	3.062	8.41	2.747	7.55
	C4 (55 cm)	1.004	1.582	0.042		0.037	2.398	6.63	2.151	5.95
	D4 (90 cm)	1.005	0.926	0.022		0.022	1.489	4.10	1.219	3.36
	E4 (150 cm)	1.011	0.461	0.01		0.011	0.741	2.03	0.607	1.66
6	A5 (15 cm)	1.015	3.146	0.258	0.113496	0.357	8.795	12.04	7.891	10.80
	B5 (33 cm)	1.007	2.864	0.273		0.325	8.007	11.06	7.184	9.93
	C5 (55 cm)	1.018	2.230	0.252		0.253	6.235	8.51	5.593	7.64
	D5 (90 cm)	1.016	1.802	0.247		0.205	5.038	6.90	4.520	6.19
	E5 (150 cm)	1.016	1.139	0.239		0.129	3.184	4.36	2.857	3.91
7	A6 (15 cm)	1.018	0.378	0.024	0.073153	0.028	0.891	1.21	0.729	0.99
	B6 (33 cm)	1.023	0.341	0.023		0.025	0.804	1.09	0.658	0.89
	C6 (55 cm)	1.022	0.267	0.021		0.020	0.630	0.85	0.515	0.70
	D6 (90 cm)	1.015	0.221	0.018		0.016	0.478	0.65	0.453	0.62
	E6 (150 cm)	1.017	0.160	0.014		0.012	0.346	0.47	0.328	0.45

Period	Sampler	Sampler Flowrate (L/min)	Chlorpyrifos (µg)	Oxon (µg)	Ratio of Total Oxon to Total Chlorpyrifos	Revised Oxon (µg)	Total Residue Adjusted for FF (µg)	Total Residue Adjusted for FF (µg/m^3)	Total Residue Adjusted for SS (µg)	Total Residue Adjusted for SS (µg/m^3)
8	A7 (15 cm)	1.026	0.652	0.021	0.063848	0.042	1.446	1.96	1.183	1.60
	B7 (33 cm)	1.055	0.577	0.026		0.037	1.280	1.69	1.047	1.38
	C7 (55 cm)	1.039	0.446	0.037		0.028	0.989	1.32	0.809	1.08
	D7 (90 cm)	1.047	0.385	0.027		0.025	0.854	1.13	0.699	0.93
	E7 (150 cm)	1.039	0.258	0.037		0.016	0.525	0.70	0.497	0.67
9	A8 (15 cm)	1.025	0.330	0.001	0.011029	0.004	0.469	0.64	0.384	0.52
	B8 (33 cm)	1.017	0.279	0.000		0.003	0.397	0.54	0.325	0.44
	C8 (55 cm)	1.019	0.229	0.003		0.003	0.299	0.41	0.283	0.39
	D8 (90 cm)	0.975	0.153	0.004		0.002	0.200	0.28	0.189	0.27
	E8 (150 cm)	0.997	0.097	0.004		0.001	0.127	0.18	0.120	0.17
10	A9 (15 cm)	1.072	0.353	0.040	0.170997	0.060	1.353	1.75	1.107	1.43
	B9 (33 cm)	1.048	0.283	0.040		0.048	1.085	1.44	0.888	1.18
	C9 (55 cm)	1.070	0.232	0.048		0.040	0.816	1.06	0.773	1.00
	D9 (90 cm)	1.086	0.205	0.037		0.035	0.721	0.92	0.683	0.87
	E9 (150 cm)	1.048	0.120	0.039		0.021	0.422	0.56	0.400	0.53
11	A10 (15 cm)	1.005	0.270	0.011	0.050336	0.014	0.544	0.75	0.445	0.62
	B10 (33 cm)	1.001	0.238	0.011		0.012	0.440	0.61	0.417	0.58
	C10 (55 cm)	0.987	0.191	0.010		0.010	0.353	0.50	0.334	0.47
	D10 (90 cm)	0.990	0.131	0.007		0.007	0.242	0.34	0.229	0.32
	E10 (150 cm)	1.005	0.064	0.006		0.003	0.118	0.16	0.112	0.15

APPENDIX G

Stability of Chlorpyrifos and Chlorpyrifos-oxon on Sorbent Tubes

The study authors reported that in a recent air monitoring study (Fenske et al., 2009) where chlorpyrifos-oxon was analyzed in air samples, it was found that oxon could form on the air sampler sorbent resin. Fenske et al. examined the rate of conversion as a function of the starting chlorpyrifos concentration and sampler flow rate. However, by correcting for this conversion artifact, Fenske et al. could still not account for all of the oxon found and thus concluded that it had formed in the environment.

To further examine these issues, the study authors spiked separate sets of sorbent tubes at 50, 500, and 2000 ng chlorpyrifos, oxon and 3,5-6 tricloropyridinol (TCP) per tube. Sets were aged in a laboratory hood (ambient conditions, approximately 70°F)) for 6 and 12 hours, with half aged with airflow at 1 L/min and the other half with no flow (each sample was run in triplicate). Duplicate spiked controls (non-aged) were also included. Tubes spiked with parent chlorpyrifos were analyzed for chlorpyrifos, chlorpyrifos-oxon and TCP. Tubes spiked with oxon were analyzed for oxon and TCP, and tubes spiked with TCP were analyzed for TCP only. As a result, TCP analyses were determined to be necessary during the course of analytical method validation, as chlorpyrifos-oxon was found to significantly convert to TCP on the sorbent material.

Based on the sorbent tube analyses, study authors estimated correction factors of 1.1, 3.4 and 6.8% for 2, 6 and 12 hour sampling periods, respectively. These correction factors were then applied to the analytical results for parent and oxon. For example, a measured chlorpyrifos concentration from a 12-hour sample period would be increased by a factor of 1.068 (6.8%) and the corresponding oxon reduced by same molar amount. Final oxon values were expressed as the sum of oxon and TCP values (with TCP in oxon molar equivalents).

The raw data are presented below (**Table G-1**). This raw data was used to develop a regression equation to estimate the correction factors (see **Figure G-1**).

Table G-1. Storage Stability Data Used to Develop Correction Factors

Sample Name	Measure chlorpyrifos (µg/tube)	Measure oxon (µg/tube)	Total oxon, chlorpyrifos equivalents[1]	% oxon in CPF equivalents
No flow				
L-c-sp1-50-nf-1	0.040	0	0	0
L-c-sp1-50-nf-2	0.046	0	0	0
L-c-sp1-50-nf-3	0.044	0	0	0
L-c-sp1-500-nf-1	0.432	0	0	0
L-c-sp1-500-nf-2	0.467	0	0	0
L-c-sp1-500-nf-3	0.449	0	0	0
L-c-sp1-2000-nf-1	1.833	0	0	0
L-c-sp1-2000-nf-2	1.910	0	0	0
L-c-sp1-2000-nf-3	1.757	0	0	0
L-c-sp2-50-nf-1	0.046	0	0	0
L-c-sp2-50-nf-2	0.047	0	0	0
L-c-sp2-50-nf-3	0.043	0	0	0
L-c-sp2-500-nf-1	0.436	0	0	0
L-c-sp2-500-nf-2	0.539	0	0	0
L-c-sp2-500-nf-3	0.482	0	0	0
L-c-sp2-2000-nf-1	1.890	0	0	0
L-c-sp2-2000-nf-2	1.940	0	0	0
L-c-sp2-2000-nf-3	1.894	0	0	0
6-hour flow period				
L-c-sp1-50-1	0.040	0	0	0
L-c-sp1-50-2	0.043	0	0	0
L-c-sp1-50-3	0.046	0	0	0
L-c-sp1-500-1	0.463	0	0	0
L-c-sp1-500-2	0.458	0	0	0
L-c-sp1-500-3	0.449	0	0	0
L-c-sp1-2000-1	1.818	0.039	0.041	2.25
L-c-sp1-2000-2	1.824	0.043	0.045	2.46
L-c-sp1-2000-3	1.781	0.044	0.046	2.58
12-hour flow period				
L-c-sp2-50-1	0.048	0	0	0
L-c-sp2-50-2	0.048	0	0	0
L-c-sp2-50-3	0.049	0	0	0
L-c-sp2-500-1	0.408	0.017	0.041	9.97
L-c-sp2-500-2	0.513	0.020	0.048	9.33
L-c-sp2-500-3	0.485	0.024	0.056	11.58
L-c-sp2-2000-1	1.760	0.071	0.074	4.21
L-c-sp2-2000-2	1.936	0.061	0.064	3.28
L-c-sp2-2000-3	1.845	0.065	0.068	3.71

1. Total oxon (chlorpyrifos equivalents) = total oxon * (350.59/334.52).

Using the percent oxon (in CPF equivalents) values above as a function of aging time, the plot and regression shown below was produced. Although there is some difference in stability at the 12-hr aging period between spiking levels, there was not sufficient data to form a complete relationship with measured concentration (oxon was only

detected at the highest spiking level at 6 hours), the data were combined to form the regression shown. Using the regression, the % correction factors were 1.1, 3.4 and 6.8% for 2, 6 and 12 hour sampling periods, respectively.

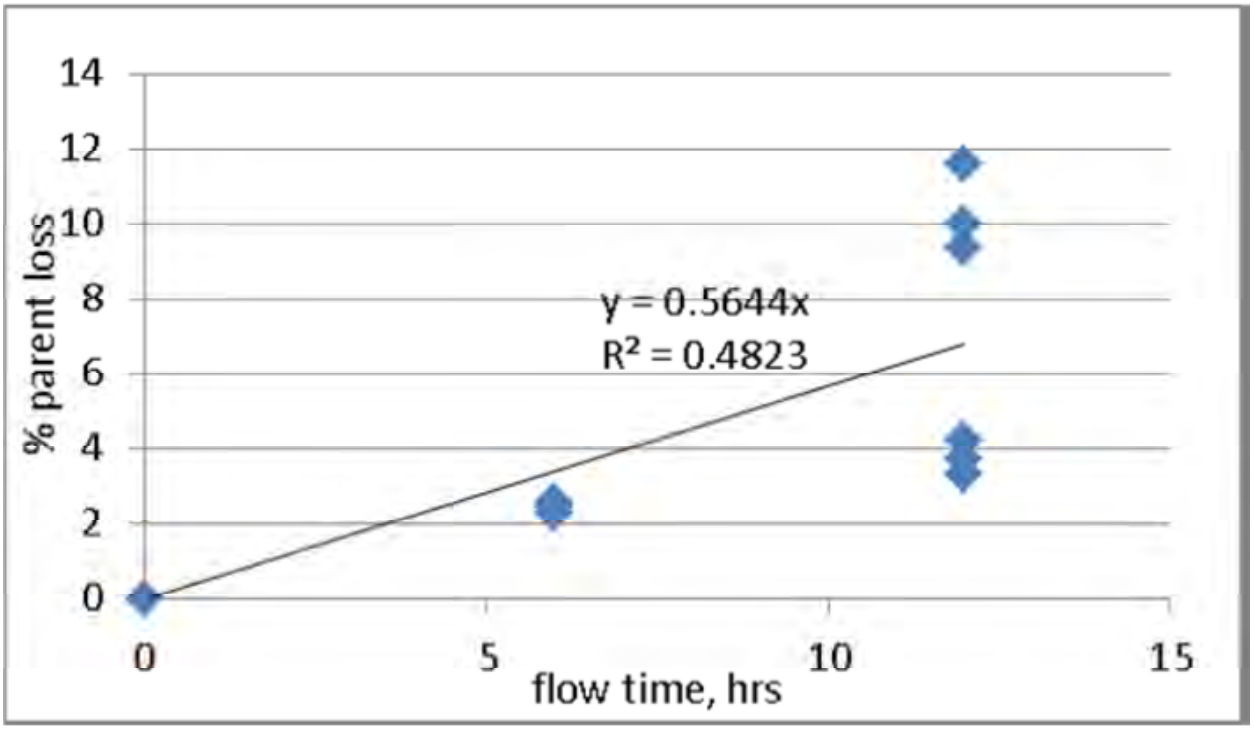

Figure G-1. Regression Analysis for Correction Factors