UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

WASHINGTON D.C., 20460

OFFICE OF
CHEMICAL SAFETY AND
POLLUTION PREVENTION

PC Code : 059101
DP Barcode: 432921

April 14, 2016

MEMORANDUM

SUBJECT: Chlorpyrifos Refined Drinking Water Assessment for Registration Review

TO: Dana Friedman, Chemical Review Manager
Tom Myers, Team Leader
Kevin Costello, Branch Chief
Risk Management and Implementation Branch 2
Pesticide Re-Evaluation Division (7508P)

THROUGH: Dana Spatz, Chief
Environmental Risk Branch 3
Environmental Fate and Effects Division (7507P)

FROM: Rochelle F. H. Bohaty, Ph.D., Chemist
James Hetrick, Ph.D., Senior Science Advisor
Environmental Risk Branch 3
Environmental Fate and Effects Division (7507P)

This memorandum transmits the refined chlorpyrifos drinking water assessment for registration review as well as supporting documents and files.

Chlorpyrifos Drinking Water Assessment for Registration Review

Prepared by:	Rochelle F. H. Bohaty, Ph.D., Chemist James Hetrick, Ph.D., Senior Science Advisor Environmental Risk Branch 3 Environmental Fate and Effects Division (7507P)
Peer Reviewed by:	Nelson C. Thurman, Senior Science Advisor Environmental Fate and Effects Division Information and Support Branch Environmental Fate and Effects Division (7507P)
	William P. Eckel, Ph.D., Senior Science Advisor Environmental Risk Branch 6 Environmental Fate and Effects Division (7507P)
	Gabe Rothman, Environmental Scientist Environmental Risk Branch 5 Environmental Fate and Effects Division (7507P)

1. Executive Summary

This refined drinking water assessment serves to combine, update and complete the work presented in the 2011 and 2014 drinking water assessments for chlorpyrifos as part of the registration review process. This document provides exposure estimates for surface water that can be compared with a drinking water level of concern for chlorpyrifos or chlorpyrifos-oxon. The assessment considers a number of different refinement strategies in a two-step process to derive exposure estimates for chlorpyrifos and chlorpyrifos-oxon across the country. The first step considers potential exposure (*i.e.*, current maximum label rates) to chlorpyrifos and chlorpyrifos-oxon at a national level based on model estimates. The second step considers model estimates, as well as measured concentrations, at a more localized level (*e.g.*, regional, state or watershed scale) and more typical use scenarios.

While this drinking water assessment is more refined than the previous assessments, the results are consistent and suggest potential exposure to chlorpyrifos or chlorpyrifos-oxon in finished drinking based on currently labeled uses. This assessment demonstrates that actual exposure is sporadic, both temporally and spatially. This is supported by both model estimated concentrations as well as measured chlorpyrifos concentrations in surface water across the United States. The steps used in this assessment, as well as the associated results, are briefly discussed below and presented in further detail in the **Analysis** and **Results** sections of this document.

Drinking water treatment effects are vitally important to consider in determining which residues may be present in finished drinking water. Chlorpyrifos-oxon forms in the environment at relatively low concentrations via oxidation. However, during drinking water treatment with chlorine, chlorpyrifos readily converts to chlorpyrifos-oxon in high yields. The conversion of chlorpyrifos to chlorpyrifos-oxon is much lower with other disinfection processes. For example, chloramines are often used as an alternative to chlorine to disinfect drinking water. In the presence of chloramines, the reduction of chlorpyrifos ranges from 28 to 34 percent. To represent those facilities that use disinfectant processes other than free chlorine, 100 percent of the chlorpyrifos entering the facility is assumed to be unchanged in the finished drinking water. Alternatively, to represent those facilities that employ chlorine as a disinfectant, 100 percent of the chlorpyrifos entering the facility is assumed to convert to chlorpyrifos-oxon.

a. Step 1: Standard Assessment

Consistent with previous assessments, the national level assessment presented here indicates that chlorpyrifos and chlorpyrifos-oxon concentrations could be greater than 100 µg/L in drinking water based on model simulations completed for currently registered uses of chlorpyrifos at maximum labeled rates (**ATTACHMENT 1)**. The estimated drinking water concentrations (EDWCs) for two different use scenarios are provided in **Table 1**. It should be noted, that this national assessment focused on agricultural uses of chlorpyrifos, as these uses are expected to be the primary uses of chlorpyrifos and applications are expected to occur on a wide scale (*i.e.*, large footprint). Moreover, only liquid applications of chlorpyrifos were considered in the national scale assessment, as liquid applications are expected to be the most common application type and have the greatest potential for contaminating surface water due to drift and runoff/erosion.

Table 1. Surface Water Sourced Estimated Drinking Water Concentrations Resulting from the Use of Chlorpyrifos on a National Basis

Absolute Peak	1-in-10 Year Concentration (µg/L)			30 Year Annual Average
	Peak	21-day Average	Annual Average	
Michigan Tart Cherries				
172 (164)[b]	129 (123)	83.8 (80.0)	39.2 (37.4)	29.7 (28.3)
Georgia Bulb Onion				
8.5 (8.1)	6.2 (5.9)	3.1 (3.0)	1.2 (1.1)	0.8 (0.8)
Bracketed concentrations are for chlorpyrifos-oxon in treated drinking water assuming 100 percent conversion as a result of the use of chlorine. Results represent liquid applications.				

b. Step 2: Refined Assessment

i. Modeling

The regional level assessment presented here provides more spatially relevant chlorpyrifos and chlorpyrifos-oxon EDWCs for all chlorpyrifos uses including uses not previously considered as part of the national assessment such as wood treatments, mosquito adulticide, and wide area applications. This assessment also indicates that chlorpyrifos and chlorpyrifos-oxon concentrations are variable across the landscape, but could be greater than 100 µg/L in drinking water based on model simulations completed for currently registered uses of chlorpyrifos at maximum labeled rates. EDWCs for chlorpyrifos and chlorpyrifos-oxon are provided by HUC-02 region (see **Figure 1**) in **Table 2**. In general, higher concentrations of chlorpyrifos and chlorpyrifos-oxon are expected in areas with higher chlorpyrifos use and environmental conditions that make the site more vulnerable to runoff.

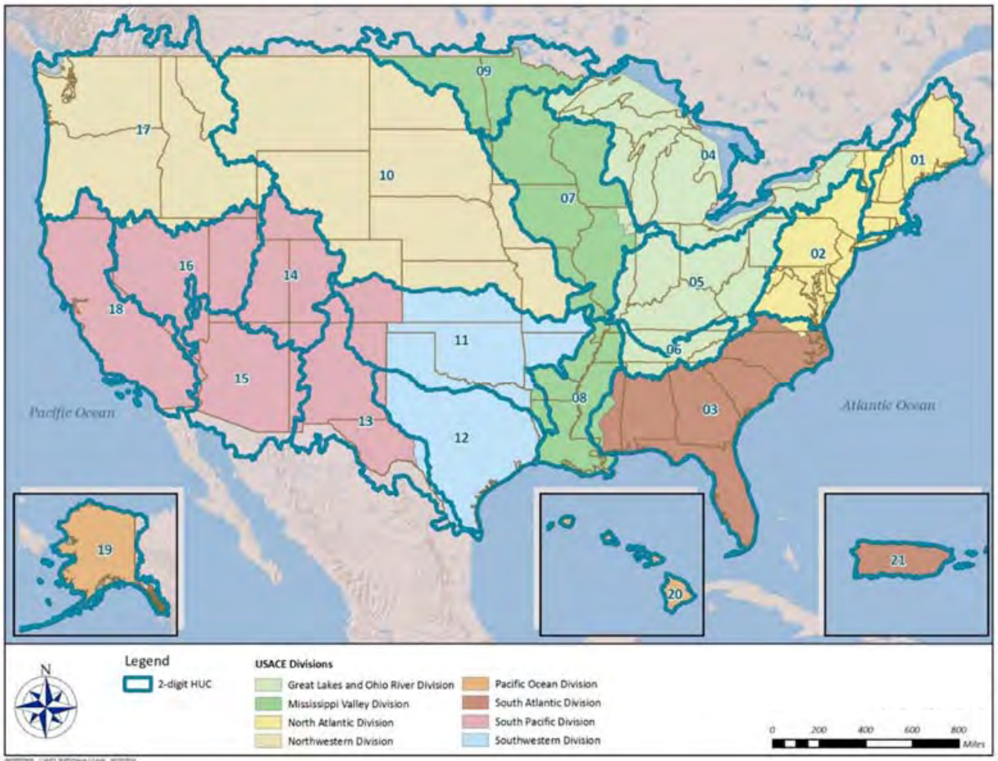


Figure 1. Hydrologic Unit Code (HUC)-02 Boundaries[1]

Table 2. Estimated Drinking Water Concentrations Resulting from the Use of Chlorpyrifos on a Regional Basis

HUC-02 Region	1-in-10 Year	
	1-day (24-hour) Average Concentration (µg/L)	21-day Average Concentration (µg/L)
HUC 1	0.996 - 606	0.547 - 344
HUC 2	0.859 - 858	0.545 - 426
HUC 3	0.983 - 681	0.533 - 389
HUC 4	0.837 - 669	0.579 - 406
HUC 5	0.817 - 614	0.498 - 374
HUC 6	1.13 - 676	0.622 - 315
HUC 7	1.16 - 694	0.76 - 414
HUC 8	1.16 - 677	0.762 - 321
HUC 9	0.894 - 750	0.543 - 461
HUC 10a	1.18 - 914	0.733 - 571
HUC 10b	0.601 - 464	0.378 - 299
HUC 11a	1.02 - 727	0.593 - 407
HUC 11b	0.984 - 949	0.535 - 513
HUC 12a	1.11 - 1120	0.583 - 495

[1] Image from http://www.corpsclimate.us/20141222news.cfm

HUC 12b	1.42 - 817	0.747 - 451
HUC 13	0.544 - 524	0.297 - 374
HUC 14	0.51 - 903	0.318 - 481
HUC 15a	0.748 - 812	0.49 - 410
HUC 15b	0.315 - 678	0.229 - 393
HUC 16a	0.373 - 515	0.259 - 315
HUC 16b	0.244 - 587	0.157 - 313
HUC 17a	1.55 - 593	1.04 - 347
HUC 17b	0.294 - 392	0.202 - 230
HUC 18a	1.15 - 660	0.767 - 398
HUC 18b	0.745 - 698	0.436 - 403
HUC 19a	0.585 - 250	0.366 - 160
HUC 19b	0.927 - 342	0.647 - 243
HUC 20a	2.83 - 1220	1.34 - 613
HUC 20b	1.82 - 779	1.13 - 408
HUC 21	1.91 - 573	1.05 - 331

Modeled daily chlorpyrifos (and corresponding chlorpyrifos-oxon) concentrations have sporadic peak concentrations without a predictable seasonal pattern. Examination of typical chlorpyrifos application rates suggest that chlorpyrifos may be applied at maximum single application rates but that the number of applications made per year is less than allowed on the labels.

A sensitivity analysis showed that even when alternative application dates or less conservative model input parameters (*e.g.*, aerobic soil metabolism half-life, sorption coefficient) are used, the EDWCs for chlorpyrifos and chlorpyrifos-oxon are not very different. Thus, deviation of standard model input parameter guidance to select less conservative model input parameters is not expected to change the risk assessment conclusions.

ii. Monitoring

Examination of monitoring data from 1992-2016 for a wide range of hydrologic types (rivers, streams, ditches, raw water, finished drinking water, etc.) confirm the potential for exposure to chlorpyrifos and chlorpyrifos-oxon via surface water used as source drinking water. Except for the Registrant Monitoring Program (MRID 44711601) conducted in California, none of the monitoring programs examined to date were specifically designed to target chlorpyrifos use. Therefore, concentrations of chlorpyrifos and chlorpyrifos-oxon measured in the various monitoring programs examined were likely biased low (*i.e.*, underestimate actual exposure). In general, measured concentrations of chlorpyrifos (and chlorpyrifos-oxon) varied greatly across the landscape. Higher concentrations are generally found in areas with higher chlorpyrifos use and environmental conditions that make the sampling site more vulnerable to pesticide runoff. These results are consistent with results derived from model simulations.

Several challenges were identified with assessing the potential exposure to chlorpyrifos and chlorpyrifos-oxon based on available monitoring data. These challenges include sample classification (*e.g.*, dissolved, filtered, total), low detection frequencies, different minimum reporting limits (MRLs), spatial distribution, and sample site vulnerability and water body type. Moreover, chemographs of daily chlorpyrifos concentrations have sporadic detections of low magnitude and short duration exposure periods. There is no predictable seasonal pattern to the detected chlorpyrifos concentrations. This situation is expected to increase the uncertainty in capturing peak and upper bound concentrations. Despite these challenges, careful consideration of the data permits useful characterization of the exposure to chlorpyrifos across the country.

The highest detection of chlorpyrifos was 14.7 µg/L in an unfiltered water sample and 5.61 µg/L in dissolved/filtered water samples. The vast majority of detected chlorpyrifos concentrations are below 1 µg/L. The most frequent concentrations of chlorpyrifos detected in terms of site-years (minimum of one sample per site per year) range from 0.01 to 1 µg/L (4945 site-years) and 0.001 to 0.01 µg/L (19879 site-years) for unfiltered water samples and filtered water samples, respectively. For chlorpyrifos, detection frequencies range from 0% of 166 total site-years in finished water samples to 57% of 273 site-years in water samples with particulates. For chlorpyrifos-oxon, the detection frequencies range from 0 site-years in finished water and 4.4% of site-years in unfiltered (total) samples. The state with the highest number of site-years of chlorpyrifos monitoring data for filtered and unfiltered samples is California with 6,496 site-years.

Also, because there are low sampling frequencies among the various monitoring programs, chlorpyrifos concentrations measured in these programs are expected to be biased low (*i.e.*, underestimate actual exposure). To account for this potential underestimation of exposure to chlorpyrifos in the available monitoring data, bias factors (BFs) were developed from several sites with daily measured chlorpyrifos concentrations. Although the sites used for BF development are limited to a few sites in California, Oregon, and Washington, the estimated BFs provide a measure on the potential extent of underestimation (*i.e.*, bias) in the monitoring data due to low sampling frequencies. For example, the mean BF for the 1-day average concentration for a 7 day sampling frequency is 8. For sampling frequencies greater than 7 days (*e.g.*, 14, 21, and 28 days) the BFs range from 15 to 38. Therefore, the use of a sampling BF is an option for predicting the extent of underestimation of the actual maximum 1-day concentration and maximum 21-day average concentration. BF can be used to derive upper bound exposure estimates based on the available monitoring data as shown in **Table 3**. In this example, a BF of 10 (*i.e.*, mean BF for 1-day average concentration for sampling frequencies between 7 and 28 days) is used to reasonably represent the bias calculated across the various monitoring programs examined. The resulting BF-corrected highest measured concentrations are consistent with model estimated concentrations for maximum agricultural label rates. The monitoring data are expected to represent typical (*i.e.*, actual) use practices and do not represent the upper bound on the potential exposure from use of chlorpyrifos at maximum label rates.

Table 3. Bias Factor Adjusted Measured Exposure Estimates of Chlorpyrifos in Surface Water

Highest Measured Concentration		**Most Frequently Detected Concentrations**	
unfiltered	**filtered**	**unfiltered**	**filtered**
147	56.1	0.1 - 10	0.01 - 0.1

It should be noted that chlorpyrifos and chlorpyrifos-oxon have not been measured in finished drinking water to date. There are several reasons why chlorpyrifos and chlorpyrifos-oxon may not have been detected in finished drinking water, including sample site location, sampling frequency, as well as drinking water treatment. There is insufficient data available to determine if the community water systems sampled for chlorpyrifos to date are located in watersheds vulnerable to chlorpyrifos contamination.

iii. Integration of Modeling and Monitoring Data Analyses

The integration of modeling and monitoring data for chlorpyrifos and chloropyrifos-oxon requires consideration of numerous factors including pesticide use, watershed properties, hydrology, monitoring site location, sampling frequency, and temporal and geographic extent of monitoring data, among others factors.

In order to compare the modeling results, which generally represent label maximum use rates being applied in vulnerable watersheds, to monitoring data that may represent actual use, model simulations were completed to represent two different water monitoring datasets – Washington State Department of Ecology and Agriculture Cooperative Surface Water Monitoring Program and Dow AgroSciences (MRID 44711601) Orestimba Creek. For both of these water monitoring programs, enough information was available, including chlorpyrifos use information, as well as the percent cropped area, to parameterize the model and post process the model output values to reasonably reflect actual use conditions. In these simulations, the modeled EDWCs were within an order of magnitude (considered a reasonable comparison within the environmental modeling field) of the measured concentrations. This suggests that the modeling results are not overly conservative and supports the use of the model to estimate chlorpyrifos and chlorpyrifos-oxon concentrations in drinking water.

The USGS watershed regression for pesticides (WARP) modeling output values are also presented in this assessment to characterize the magnitude of chlorpyrifos concentrations in streams and rivers according to USGS monitoring data and actual chlorpyrifos use data. The results, as expected, provide a range of estimated concentrations across the landscape that compare reasonably well with modeling results, when the model is parameterized to reflect typical use information.

Lastly, modeling and monitoring data were compared according to state and HUC-02 regions for the maximum 1-day chlorpyrifos concentrations in filtered water samples. This analysis provides spatial delineation of the model and monitoring data. Pesticide Water Calculator (PWC) and WARP model predicted chlorpyrifos concentrations showed non-significant positive correlation. Given the differences in modeling approaches, a positive correlation among the models indicates the models, as expected, generate higher chlorpyrifos concentrations with higher use rates. The use rate is a significant variable in both PWC and WARP modeling. As such, these modeling approaches provide insight into chlorpyrifos use relative to the available chlorpyrifos monitoring data, as well as support the use of model simulations to generate upper bound exposure based on potential use (*i.e.*, maximum label rates).

iv. Conclusions

As described above, there are a number of challenges (*e.g.*, highly censored monitoring data and drinking water treatment variations) in evaluating the potential exposure to chlorpyrifos and chlorpyrifos-oxon in drinking water. Our analysis shows that the concentrations of chlorpyrifos and chlorpyrifos-oxon in drinking water are expected to vary across the country with the highest potential for exposure in high use areas in vulnerable (*i.e.*, runoff prone) watersheds and is highly dependent on drinking water treatment processes.

Use of bias factor adjusted measured concentrations of chlorpyrifos (and corresponding chlorpyrifos-oxon) or the use of model estimated concentrations of chlorpyrifos and chlorpyrifos-oxon as an estimated upper bound exposure is expected to result in similar dietary risk assessment conclusions. However, to assess the potential exposure (maximum label rates) for individual chlorpyrifos uses, model estimated concentrations are recommended. Upper bound model exposure estimates for chlorpyrifos and chlorpyrifos-oxon are generally similar for the standard or refined assessment steps when the same chlorpyrifos use is compared. As such, either results from the national or regional level assessment may be used for dietary risk assessment depending on the spatial resolution required and the use being assessed.

2. Problem Formulation

a. Background

This highly refined drinking water assessment updates and completes the Agency's examination of exposure through drinking water for all registered uses of chlorpyrifos. Over the past 15 years there have been three significant investigations of potential chlorpyrifos exposure in drinking water. In the 2001 Interim Reregistration Eligibility Decision (IRED), OPP considered exposure to chlorpyrifos in drinking water[2,3] and recommended the quantitative use of monitoring data to estimate exposure in groundwater. At the time of the IRED, chlorpyrifos concentrations in groundwater (greater than 2000 µg/L) from termiticide uses were the primary focus of drinking water exposure. The model concentrations were orders of magnitude lower than the measured concentrations. The termiticide use was canceled after the IRED.

In 2011, a preliminary drinking water assessment derived estimated drinking water concentrations (EDWCs) for a number of agricultural uses of chlorpyrifos on a national basis, and examined available monitoring data as well.[4] That assessment recommended the use of surface water estimated EDWCs derived from modeling, and concluded that a range of agricultural uses could lead to high levels (peak concentrations greater than 100 µg/L) of chlorpyrifos in surface water that could potentially be used by community water systems to supply drinking water. The 2011 assessment also discussed the effects of drinking water treatment on chlorpyrifos. It concluded that once it reaches a drinking water treatment facility, chlorpyrifos can be readily converted to chlorpyrifos-oxon during disinfection processes, primarily through oxidative treatment methods such as chlorination. Therefore, chlorpyrifos and chlorpyrifos-oxon were considered residues of concern in the preliminary assessment to account for the variation of drinking water treatment methods used by community water systems around the country.

The updated 2014 drinking water assessment took into account public comments received following release of the 2011 drinking water assessment. It also provided several additional analyses that focused on 1) clarifying labeled uses, 2) evaluating volatility and spray drift, 3) revising aquatic modeling input values following updated guidance documents, 4) comparing aquatic modeling and monitoring data, 5) summarizing the effects of drinking water treatment, 6) updating model simulations using current exposure tools, and 7) proposing a strategy to refine the assessment using the drinking water intake

---

[2] U.S. Environmental Protection Agency, Finalization of Interim Reregistration Eligibility Decisions (IREDs) and Interim Tolerance Reassessment and Risk Management Decisions (TREDs) for the Organophosphate Pesticides, and Completion of the Tolerance Reassessment and Reregistration Eligibility Process for the Organophosphate Pesticides, September 28, 2001

[3] Barrett, M, Nelson, H, Rabert, W., Spatz, D. Reregistration Eligibility Science Chapter for Chlorpyrifos Fate and Environmental Risk Assessment Chapter, June 2000

[4] Bohaty, R. Revised Chlorpyrifos Preliminary Registration Review Drinking Water Assessment, June 20, 2011, PC Code: 059101; DP Barcode: 368388, 389480

percent cropped area adjustment factors. The additional analyses did not change the overall exposure assessment conclusions previously reported in the 2011 DWA.

This drinking water assessment serves to combine, update and complete the work presented in the 2011 and 2014 drinking water assessments for chlorpyrifos as part of the registration review process. This document specifically focuses on the exposure estimates for surface water and does not consider a drinking water level of concern. The 2014 assessment presented an approach for deriving more regionally specific estimated drinking water exposure concentrations for chlorpyrifos and chlorpyrifos-oxon for two HUC-02 regions. This assessment updates those exposure assessments and provides estimates for the remaining (*i.e.*, 19) HUC-02 regions. Urban uses which had not previously been assessed primarily due to label ambiguities are provided herein as these ambiguities were not resolved by the registrant. This assessment also includes statistical analysis of all available monitoring data for chlorpyrifos and chlorpyrifos-oxon.

b. Use Characterization

Chlorpyrifos is an organophosphate used as an insecticide used on a wide variety of terrestrial food and feed crops, terrestrial non-food crops, greenhouse food/non-food, and non-agricultural indoor and outdoor sites. Based on an Office of Pesticide Programs Information Network (OPPIN) query (conducted February 2015) there are currently 31 active registrants of chlorpyrifos with 135 active product labels (86 Section 3s, 48 Special Local Needs, and 1 Section 18), which include formulated products (some with multiple active ingredients) and technical grade chlorpyrifos.

The Environmental Fate and Effects Division (EFED) in consultation with the Pesticide Re-evaluation Division (PRD), the Biological and Economic Analysis Division (BEAD), and the Health Effects Division (HED) developed a list of all chlorpyrifos registered uses (see Master Use Summary provided in **ATTACHMENT 1**). This summary reflects all currently registered labels and any agreed-upon changes to these labels from the registrants. While the current labels may not reflect all the agreed-upon changes, the registrants agreed to update the chlorpyrifos labels to be reflective of the attached Master Use Summary. In general, current single maximum chlorpyrifos application rates do not exceed 4 lb a.i./A nationwide; however, a single chlorpyrifos application of 6 lb a.i./A is permitted on citrus in a limited number of counties in California. Aerial applications are not permitted at rates higher than 2.0 lb a.i./A with the exception of treatment of Asian citrus psyllid (citrus use areas including California, Arizona, Texas, and Florida). In this situation, chlorpyrifos may be applied at a rate of up to 2.3 lb a.i./A by aerial equipment. The maximum annual rate of chlorpyrifos that may be applied to a crop site is 14.5 lb a.i./A for tart cherries.

Chlorpyrifos can be applied in a liquid, granular, or encapsulated form, or as a cattle ear tag or seed treatment. Aerial and ground application methods (including broadcast, soil incorporation, orchard airblast, and chemigation) are allowed. Registered labels for liquid applications (*i.e.*, flowable products) require 25-foot (ground boom and chemigation), 50-foot (orchard airblast), or 150-foot (aerial) no-spray buffer zones adjacent to waterbodies.

i. Agricultural Use Sites

Currently registered agricultural use sites include: agricultural farm premises (such as, barns, empty chicken houses, dairy areas, calving pens), poultry litter, cattle (impregnated collars/ear tags), alfalfa, orchards [including, almonds, apple, cherries, citrus, figs, filberts, non-bearing fruit and nuts (nursery), grapes, nectarine, peach, pear, pecan, plum/prune, seed orchard trees, and walnut], asparagus, beans, beets (grown for seed), sugar beets, carrots (grown for seed), clover (grown for seed), cole crops, corn (all), cotton, cranberry, cucumber, ginseng (medicinal), grass (forage/fodder/hay), legumes, mint, nursery stock, peanut, peas, pepper, pineapple, pumpkin, radish, rutabaga, sod farms, onions, sorghum, soybean, strawberry, sunflower, sweet potato, tobacco, triticale, turnip, wheat, and tree plantations [including, Christmas trees, nursery plantations (conifer and deciduous trees), reforestation programs, conifers, and hybrid cottonwood/poplar] (see **ATTACHMENT 1** for details).

ii. Non-agricultural Use Sites

Currently registered non-agricultural use sites include: commercial/institutional/industrial (indoor and outdoor – *e.g*., warehouses, food processing plants, ship holds, railroad cars), golf course turf, greenhouse, households (indoor), mosquito control (outdoor), nonagricultural buildings (outdoor – *e.g*., fences, construction foundations, dumps), ornamental plants, ornamental lawns, rights-of-way (including road medians), sewer manhole covers and walls, utilities (*e.g.*, power lines, railroad systems, telecommunication equipment), wide area general outdoor use (*e.g.*, for ants and other misc. pests), and wood protection treatment (for outdoor building products). (See **ATTACHMENT 1** for details).

iii. Usage Data

The spatial distribution of the 2012 agricultural usage data is presented in **Figure 2**. This map reveals intensive agricultural use of chlorpyrifos throughout the Midwest and the Atlantic states, as well as in parts of California, Oregon, Washington, and Idaho. The United State Geological Survey (USGS) pesticide agricultural usage data extrapolates pesticide usage from survey data to areas where pesticide usage information is not available. USGS intends these data to be used for broad-scale assessments such as at the national or regional level. Therefore, these data are presented for qualitative purposes only, in the form of maps, to provide a geographic footprint of a pesticide's use. These data are not suitable for sub-state quantitative analyses. In general, survey data tend to be more robust for pesticides that are applied on a regular basis (*i.e.*, herbicides) than for pesticides that are applied in response to pest pressures such as insecticides and fungicides.

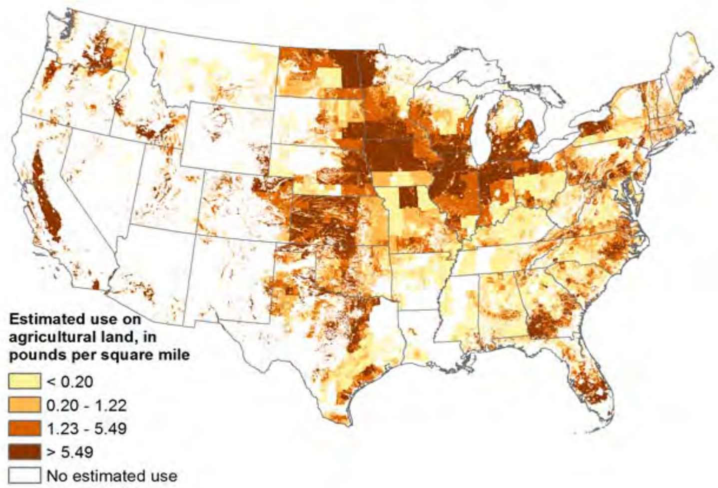


Figure 2. Spatial Distribution of Chlorpyrifos Agricultural Use (2012)[5]

Based on usage data provided by BEAD, approximately 7.2 million pounds of chlorpyrifos are used each year for agricultural purposes in the United States (based on yearly averages from 2004 to 2013). Approximately 21% and 19% of the total volume of chlorpyrifos used in the United States each year is applied to soybeans (1.5 million lbs) and corn (1.4 million lbs), respectively. However, on average only 5% of total soybean acreage and about 2.5% of total corn acreage is treated with chlorpyrifos each year. Other crops with relatively high usage of chlorpyrifos (at least 100,000 lbs/year) include alfalfa, almonds, apples, apricots, cotton, grapes, oranges, peanuts, pecans, sugar beets, walnuts and wheat. A large fraction, at least 40%, of the total acreage planted with apples, asparagus, broccoli, onions, and walnuts, is treated with chlorpyrifos. Considering agricultural uses, there has been a general trend of decreased usage per year from 1992 – 2012 as shown in **Figure 3**.

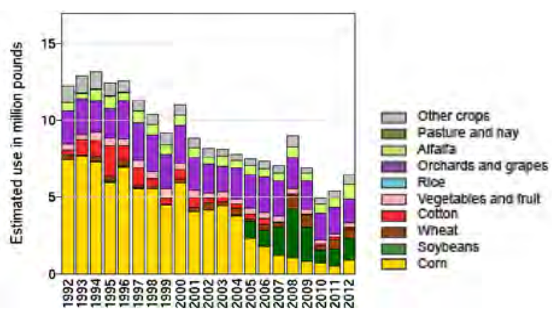


Figure 3. Chlorpyrifos Use by Year per Crop (1992 – 2012)[6]

No national-level chlorpyrifos usage data are available for registered non-crop use sites, including turf, golf courses, cattle ear tags, poultry farms, ultra-low volume (ULV) adult mosquito control, ornamental sites and indoor/outdoor pest control [*e.g.*, non-food areas of manufacturing, industrial, and food processing plants; warehouses; ship holds; railroad boxcars, domestic dwellings (*i.e.*, bait stations)]. Chlorpyrifos is also used as wood protection treatment for fence posts, utility poles, lumber and railroad

---

[5] http://water.usgs.gov/nawqa/pnsp/usage/maps/show_map.php?year=2012&map=CHLORPYRIFOS&hilo=L&disp=Chlorpyrifos

[6] http://water.usgs.gov/nawqa/pnsp/usage/maps/show_map.php?year=2012&map=CHLORPYRIFOS&hilo=L&disp=Chlorpyrifos

ties, *etc*.). In addition, chlorpyrifos may be used for general outdoor (*i.e.*, wide areas) treatment to control ants and other miscellaneous pests.

c. Exposure Characterization

i. Conceptual Exposure Model

Chlorpyrifos will initially enter the environment via direct application (*e.g.*, liquid spray and granular) to use sites (*e.g.*, soil, foliage, seed treatments, urban surfaces). It may move off-site via spray drift, volatilization (primarily following foliar applications), and runoff (generally by soil erosion rather than dissolution in runoff water). Degradation of chlorpyrifos begins with cleavage of the phosphorus ester bond to yield 3,5,6-trichloro-2-pyridinol (TCP) or oxidative desulfonation to form chlorpyrifos-oxon as shown in **Figure 4.** TCP may be converted to 3,5,6-trichloro-2-methoxypyridine (TMP) also shown in **Figure 4**. Environmental fate studies (except field volatility and air photolysis studies) submitted to EPA do not identify chlorpyrifos-oxon as a transformation product, yet organophosphates that contain a phosphothionate group (P=S), such as chlorpyrifos, are known to transform to the corresponding oxon analogue containing a phosphorus-oxygen double bond (P=O) instead. This transformation occurs via oxidative desulfonation and can occur through photolysis and aerobic metabolism, as well as other oxidative processes. Chlorpyrifos-oxon is considered less persistent than chlorpyrifos and may be present in air, soil, water, and sediment.

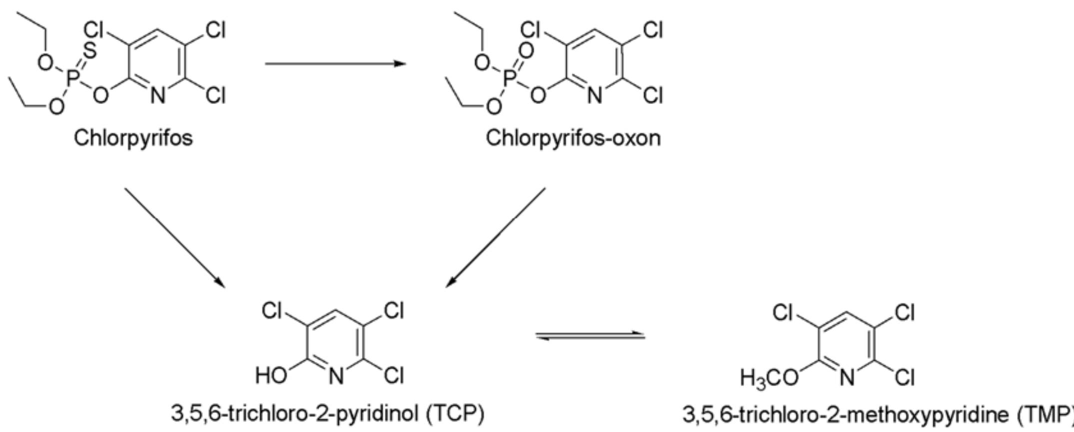


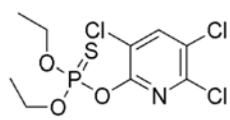
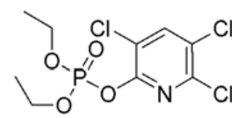
Figure 4. Environmental Transformation of Chlorpyrifos

ii. Residues of Concern

Chlorpyrifos and chlorpyrifos-oxon are considered residues of toxicological concern for dietary exposure including drinking water.[7] Physical chemical properties for chlorpyrifos and chlorpyrifos-oxon, are provided in **Table 4**. TCP and TMP are not considered residues of toxicological concern and, therefore, are not discussed in great detail in the remaining sections of this document.

[7] Email from Danette Drew (EPA/HED) to Rochelle Bohaty (EPA/EFED), September. 21, 2010.

Table 4. Physical/Chemical Properties of Chlorpyrifos and the Degradate of Concern, Chlorpyrifos-oxon

	Chlorpyrifos	Chlorpyrifos-oxon
IUPAC Name	*O,O*-diethyl o-(3,5,6-trichloro-2-pyridyl phosphorothioate	*O,O*-diethyl O-3,5,6-trichloropyridin-2-yl phosphate Diethyl 3,5,6-trichloro-2,6-pyridin-2-yl phosphate
Chemical Abstracts Service (CAS) Registry Number	2921-88-2	5598-15-2
Chemical Formula	$C_9H_{11}Cl_3NO_3PS$	$C_9H_{11}Cl_3NO_4P$
Smiles	S=P(OC1=NC(=C(C=C1Cl)Cl)Cl)(OCC)OCC	O=P(Oc1nc(c(cc1Cl)Cl)Cl)(OCC)OCC
Chemical Structure		
Molecular Mass (g/mol)	350.57	334.52
Vapor Pressure (Torr, 25°C)	1.87×10^{-5}	6.65×10^{-6}
Henry's Law Constant (atm - m^3/mol)	6.2×10^{-6}	5.5×10^{-9}
Solubility (20°C) (ppm)	1.4	26.0
Octanol-water partition coefficient (Log K_{ow})	4.7	2.89

iii. Environmental Fate

A detailed discussion of the fate and transport of chlorpyrifos and chlorpyrifos-oxon in the environment is provided below. Data summarized here include data submitted to the U.S. EPA and open literature data. The latter are included when the information was determined to add to the overall understanding of the environmental fate of chlorpyrifos and chlorpyrifos-oxon. Environmental fate parameters for chlorpyrifos and chlorpyrifos-oxon are provided in **Table 5** and **Table 6**, respectively. Each parameter is discussed in detail in the sections below. In summary, chlorpyrifos is expected to be persistent for several months in the environment with aerobic soil and aerobic aquatic metabolism being the primary routes of transformation. Major routes of dissipation include spray drift, volatilization and runoff via dissolved phase and eroded sediment.

Table 5. Summary of Environmental Fate and Transport Characteristics of Chlorpyrifos

Parameter	Test System Name or Characteristics	NAFTA Representative Half-life Values (fitting model)[a]	Study ID	Study Classification
Laboratory Data				
Hydrolysis half-life (days)	pH 5, 25°C	73	MRID 00155577	Acceptable
	pH 7, 25°C	72		
	pH 9, 25°C	16		
	pH 7, 25°C	81	MRID 40840901	Acceptable
Aqueous photolysis half-life (days)	pH 7	29.6	MRID 41747206	Acceptable

Parameter	Test System Name or Characteristics	NAFTA Representative Half-life Values (fitting model)[a]	Study ID	Study Classification
Soil photolysis half-life (days)	--	Stable	MRID 42495403	Supplemental
Air photolysis half-life (hours)	Indirect	2	MRID 48789701	Acceptable
	Direct	6		
Aerobic Soil Metabolism half-life (days)	Commerce Loam pH 7.4, 0.68% OC	19 (IORE)	Acc. 241547 MRID 00025619	Acceptable
	Barnes Loam, pH 7.1, 3.6% OC	36.7 (IORE)		
	Miami Silt Loam, pH 6.6, 1.12% OC	31.1 (IORE)		
	Catlin Silty Clay Loam, pH 6.1, 0.01% OC	33.4 (SFO)		
	Norfolk Loamy Sand, pH 6.6, 0.29% OC	156 (DFOP)		
	Stockton Clay pH 5.9, 1.01% OC	297 (IORE)		
	German Sandy Loam, pH 5.4, 1.01% OC	193 (IORE)		
	Sandy loam, pH 6.5, 0.8% OC	185 days (DFOP)	MRID 42144911	Acceptable
Aerobic Aquatic Metabolism half-life (days)	Water, pH 8.1 Sediment, pH 7.7 25 ˚C	30.4 days (SFO)	MRID 44083401	Supplemental
Anaerobic Soil Metabolism half-life (days)	Commerce, loam	78 (IORE)	MRID 00025619	Acceptable
	Stockton, clay	171 days (SFO) Values represent only anaerobic phase		
Anaerobic Aquatic Metabolism half-life (days)	Commerce pH 7.4	50.2 days (IORE)	MRID 00025619	Supplemental
	Stockton pH 5.9	125 days (SFO)		
Field Data				
Terrestrial Field Dissipation half-life (days)	Geneseo, Illinois Silt loam; pH 5.7, 3.1% OC	56	MRID 40395201	Supplemental
	Midland, Michigan Sandy clay loam; pH 7.7, 1.6% OC	33		
	Davis, California Loam; 0.91% OC pH 7.8	46		

a. SFO = Single First Order; IORE = Indeterminate order rate equation; DFOP = Double first-order in parallel; The value used to estimate a model input value is the calculated SFO DT_{50}, T_{IORE}, or the 2nd DT_{50} from the DFOP equation. The model chosen is consistent with that recommended using the, *Guidance for Evaluating and Calculating Degradation Kinetics in Environmental Media*, Health Canada, U.S. Environmental Protection

Parameter	Test System Name or Characteristics	NAFTA Representative Half-life Values (fitting model)[a]	Study ID	Study Classification
Agency, December 21, 2012. The same model used to estimate the value used to derive a model input, is used to describe the DT50 and DT_{90} results. An **acceptable** study is defined as a study that provides scientifically valid information that is fully documented and which clearly addresses the study objectives as outlined in the guidelines. A **supplemental** study provides scientifically valid information that address the study objectives as outlined in the guidelines, but deviates from guideline recommendations and/or is missing certain critical data necessary for a complete evaluation-verification.				

Table 6. Summary of Environmental Fate and Transport Characteristics of Chlorpyrifos-oxon

Parameter	Test System Name or Characteristics	NAFTA Representative Half-life Values (fitting model)[a]	Study ID	Study Classification
Laboratory Data				
Hydrolysis half-life (days)	pH 4, 20°C	38	MRID 48355201	Supplemental
	pH 7, 20°C	5		
	pH 9, 20°C	2		
Air photolysis half-life (hours)	Indirect	11	MRID 48789701	Acceptable
	direct	6		
Aerobic Soil Metabolism half-life (days)	Missouri Silty clay loam soil (20°C, pH 5.9-6.2)	0.03 (IORE)	MRID 48931501	Supplemental
	Georgia Loamy sand soil (20°C, pH 5.3-5.6)	0.1 (IORE)		
	Texas Sandy clay loam soil (20°C, pH 7.6-7.9)	0.02 (SFO)		
	California Loam soil (20°C, pH 6.1-6.3)	0.06 (IORE)		

a. SFO = Single First Order; IORE = Indeterminate order rate equation; DFOP = Double first-order in parallel; The value used to estimate a model input value is the calculated SFO DT_{50}, T_{IORE}, or the 2[nd] DT_{50} from the DFOP equation. The model chosen is consistent with that recommended using the, *Guidance for Evaluating and Calculating Degradation Kinetics in Environmental Media*, Health Canada, U.S. Environmental Protection Agency, December 21, 2012. The same model used to estimate the value used to derive a model input, is used to describe the DT50 and DT_{90} results.

An **acceptable** study is defined as a study that provides scientifically valid information that is fully documented and which clearly addresses the study objectives as outlined in the guidelines.

A **supplemental** study provides scientifically valid information that address the study objectives as outlined in the guidelines, but deviates from guideline recommendations and/or is missing certain critical data necessary for a complete evaluation-verification.

Laboratory Studies

<u>*Hydrolysis*</u>

Chlorpyrifos hydrolysis is pH dependent; however, abiotic hydrolysis is not expected to play a significant role in chlorpyrifos dissipation in the environment. Chlorpyrifos is stable to hydrolysis under neutral (half-life values 72 to 81 days) to acid conditions. Under alkaline conditions (pH 9), laboratory studies show chlorpyrifos is susceptible to hydrolysis with a half-life of approximately two weeks. The major hydrolysis products, TCP and O-ethyl O-(3,5,6-trichloro-2-pyridinol) phosphorothioate, are stable to hydrolysis. Hydrolytic degradation of chlorpyrifos in sterilized, ambient water from four of the Chesapeake Bay tributaries demonstrated that pH alone cannot be used as a single parameter to predict hydrolysis of chlorpyrifos under environmental conditions.[8] Reported half-live values ranged from 24 days in the Patuxent River (pH 8.5) to 126 days in the Susquehanna River (pH 7.93). The other two tributaries had pH values of 7.66 and 7.99.

The hydrolysis half-life of chlorpyrifos-oxon (5 days at pH 7) is substantially shorter than that observed for chlorpyrifos. Chlorpyrifos-oxon hydrolyzes to form TCP, a major environmental degradation product reported for chlorpyrifos.

<u>*Photolysis*</u>

Soil Photolysis

Chlorpyrifos is stable to photolysis in soil, as the calculated half-life values for the dark control and the irradiated soil experiments were similar. However, transformation was observed suggesting that degradation processes are possible in soil as confirmed by aerobic soil metabolism studies. The major transformation product observed is TCP, which may photodegrade.

No data are available for the phototransformation of chlorpyrifos-oxon in soil.

Aquatic Photolysis

Chlorpyrifos is susceptible to photolysis in aqueous pH 7 buffered solution, with an estimated environmental half-life of approximately 30 days. No phototransformation products were observed to form at concentrations greater than 5% of the applied material. In another aquatic photolysis open literature study[9], chlorpyrifos was estimated to have a half-life of 13.3 minutes under the study conditions (125 W xenon lamp); however, the environmentally relevant half-life could not be derived. The only transformation product observed was chlorpyrifos-oxon; however, the maximum amount of chlorpyrifos-oxon did not exceed one percent at any point during the study. The degradation rate of chlorpyrifos-oxon was reported to be three times slower (half-life value of 42 minutes) than chlorpyrifos

[8] Liu, B., McConnell, L. L., and Torrents, A. (2001). Hydrolysis of chlorpyrifos in natural waters of the Chesapeake Bay. Chemosphere 44: 1315-1323.

[9] Bavcon Kralj, M., Franko, M., and Trebse, P. Photodegradation of Organophosphorus Insecticides - Investigations of Products and Their Toxicity Using Gas Chromatography-Mass Spectrometry and Ache-Thermal Lens Spectrometric Bioassay. Chemosphere. 2007, Feb; 67(1):99-107.

in a separate but similar study conducted by the same authors. Another open literature study confirms photodegradation of chlorpyrifos in aqueous systems.[10]

Based on the available data (*i.e.*, environmentally relevant half-life), photodegradation in aquatic environments is not expected to be a major route of chlorpyrifos dissipation primarily. The dissipation of chlorpyrifos in water is expected to depend on physical characteristics of the water (*e.g.*, sediment loading, depth, etc.) which have an effect on sunlight penetration as well as the rate of chlorpyrifos sediment partitioning.

Air Photolysis

Chlorpyrifos was reported to undergo indirect and direct photolysis [$t_{1/2}$ = 2 h (indirect) and 5 h (direct)].[11] The result obtained for indirect photolysis is consistent with the Estimation Program Interface (EPI) Suite[12] estimations. This study confirms the formation of chlorpyrifos-oxon via photolysis. Chlorpyrifos-oxon was reported to undergo indirect and direct photolysis [$t_{1/2}$ = 8 h (indirect) and 6 h (direct)]. The EPI Suite estimated indirect photolysis was similar to the calculated value. These data suggest the air photolytic may be a major route of transformation of chlorpyrifos and formation of chlorpyrifos-oxon.

Soil Metabolism

Aerobic

Chlorpyrifos degrades in soil under aerobic conditions (half-life values range from 19 to 297 days). This suggests that under some environmental conditions chlorpyrifos is very persistent. In general, chlorpyrifos transformation in soil is pH dependent – half-life values are shorter in higher pH soils – and suggest that hydrolysis is the primary transformation mechanism in soil. The major transformation product (>10%) observed in the aerobic soil metabolism studies is TCP. Another transformation product, TMP, was not observed at concentrations greater than 10%. Chlorpyrifos-oxon was not monitored for in this study. In general, transformation was observed to be biphasic. Aerobic soil metabolism data are summarized in **Table 2** while the kinetic analyses are presented in **ATTACHMENT 2**. Additional aerobic soil metabolism half-life values reported in the open literature are within the range of estimated half-life values derived from registrant submitted data for typical soil conditions.[13]

Laboratory data suggest that chlorpyrifos-oxon is non-persistent in soil under aerobic conditions. Half-life values were less than one day at 20 ˚C. The major transformation products observed were TCP, carbon dioxide, and 3,5-dichloro-l-methylpyridin-2(lH)-one. Another major transformation product ($C_5H_3Cl_2NO_4S$) was observed to form and a chemical structure was proposed; however, the structure was not confirmed. There were also increasing amounts of unextracted residues. The kinetic analyses for chlorpyrifos-oxon are also presented in **ATTACHMENT 2**.

---

[10] Kiss, Attila; Virag, Diana, Photostability and Photodegradation Pathways of Distinctive Pesticides. 2009; 38, (1): 157-163.

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

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

[13] Singh, Brajesh K., Walker, Allan, and Wright, Denis J. (2005). Cross-enhancement of accelerated biodegradation of organophosphorus compounds in soils: Dependence on structural similarity of compounds. Soil Biology and Biochemistry 37: 1675-1682.

Anaerobic

Chlorpyrifos was persistent in anaerobic (flooded-loam and clay) soils with estimated half-life values of 78 and 171 days. The major transformation product observed was TCP, which was persistent under anaerobic conditions. Small amounts of TMP were observed.

No data are available for chlorpyrifos-oxon under anaerobic soil conditions.

Aquatic Metabolism

Aerobic

The half-life estimated for chlorpyrifos in aerobic aquatic conditions is approximately one month. This study was conducted under slightly basic conditions (pH 8.1). Chlorpyrifos undergoes hydrolysis under basic conditions and, as a result, hydrolysis likely occurred at pH 8.1. The reported half-life value was not corrected for hydrolysis as no hydrolysis data were provided under the same conditions. Therefore, it is expected that some of the transformation of chlorpyrifos observed in this study is the result of hydrolysis in addition to metabolism. The major transformation product observed in this study was TCP. Chlorpyrifos-oxon was not monitored for in this study. The aquatic metabolism data suggest that chlorpyrifos partitions to soil/sediment while its degradation products are more likely to partition to water. Kinetic analysis for the aerobic aquatic metabolism study is presented in **ATTACHMENT 2**. An open literature study conducted with waters from four different sites in California suggest faster dissipation rates than one month. Half-life values ranged from 5.5 days to 15.2 days at 21 ˚C (MRID 49630501). The pH of these waters were also slightly high 7.98 to 8.86 (generally slightly higher in terms of environmentally relevant pHs). Sterilization of the waters prior to study initiation confirms that hydrolysis contributes to the transformation of chlorpyrifos in aquatic systems.

Another study that examined chlorpyrifos degradation in a nursery recycling pond sediment system (high organic matter content and high salinity) under aerobic aquatic conditions found chlorpyrifos half-life values ranged from 27 to 32 days at 22 ˚C for two different test systems.[14]

No aerobic aquatic metabolism data are available for chlorpyrifos-oxon.

Anaerobic

Anaerobic aquatic metabolism half-life values estimated for chlorpyrifos are 50 to 125 days. The major transformation product observed in this study was TCP.

Another study, previously sited in this document, examined chlorpyrifos degradation in a nursery recycling pond sediment system (high organic matter content and high salinity) under anaerobic aquatic conditions. The reported chlorpyrifos half-life values ranged from 41 to 53 days at 22 ˚C for two different test systems.[14]

No anaerobic aquatic metabolism data are available for chlorpyrifos-oxon.

---

[14] Lu Jianhang, Wu Laosheng, Newman Julie, Faber, B. e. n., Merhaut Donald J., and Gan Jianying (2006). Sorption and Degradation of Pesticides in Nursery Recycling Ponds. Journal of Environmental Quality [J. Environ. Qual.]. Vol. 35, no. 5, pp. 1795-1802. Sep 2006.

Sorption and Mobility

Batch equilibrium data (summarized in **Table 7**) for chlorpyrifos suggest that it is slightly mobile in soils and, therefore, is not expected to leach through the soil profiles. However, chlorpyrifos that is sorbed to soil may be transported off an application site. Soil binding was correlated with the organic carbon content of the soil, with k_{OC} values ranging from 4960 to 7300 mL/g_{oc}. An open literature batch equilibrium study reported a k_{OC} value of 5299 mL/g_{oc} for chlorpyrifos.[15] This study also suggests that soil management practices may impact chlorpyrifos sorption and mobility in the environment. Chlorpyrifos sorption was significantly reduced with increasing amounts of dissolved organic matter (DOM); therefore, DOM may enhance transport of chlorpyrifos in soil. Chlorpyrifos partitioning in a nursery recycling pond reported k_{OC} values of 1550 and 7430 mL/g_{oc} for chlorpyrifos in the two different test systems.[14] Sorption was reportedly correlated to both the organic matter content and sediment texture. Another open literature article also reports strong sorption of chlorpyrifos to soils and sediments that is correlated with the organic matter content.[16] In addition, desorption of chlorpyrifos was shown to be biphasic and that over time chlorpyrifos will slowly partition to the aqueous phase.

Table 7. Summary of Sorption/Mobility Parameters for Chlorpyrifos

Test System Name or Characteristics	K_d	K_{oc}	Study ID	Study Classification
Commerce loam	49.9	7300	Acc. 260794	Acceptable
Tracy sandy loam	95.6	5860		
Catlin silt loam	99.7	4960		
K_d = adsorption coefficient (mL/g) Koc = organic carbon normalized adsorption coefficient (mL/g)				

Chlorpyrifos-oxon is expected to be more mobile than chlorpyrifos in soil with K_{oc} values ranging from 146 to 270 mL/g_{oc} as shown in **Table 8**. Binding was observed to be slightly non-linear (1/n < 0.9).

Table 8. Summary of Sorption/Mobility Parameters for Chlorpyrifos-oxon

Test System Name or Characteristics	K_f (regressed)	K_{foc}	1/n	Study ID	Study Status
Tift Sand pH 4.8, 0.61% OC	1.3	270	0.85	MRID 48602601	Supplemental
Hagen Loamy sand pH 5.2, 1.1% OC	2.1	245	0.84		
Ebbinghof Loam pH 5.2, 1.5% OC	4.0	191	0.89		
Tehama Loam pH 5.7, 4.4% OC	4.2	301	0.89		
Chelmorton Silt loam pH 5.9, 2.9% OC	4.3	146	0.88		
%OC = percent organic carbon in the soil K_f = Freundlich adsorption coefficient (µg/g)/(µg/mL)$^{1/n}$ K_{Foc} = organic carbon normalized Freundlich adsorption coefficient (µg/g organic carbon)(µg/mL)$^{1/n}$ 1/n = Freundlich exponent					

[15] Li, Kun, Xing, Baoshan, and Torello, William A. (2005). Effect of organic fertilizers derived dissolved organic matter on pesticide sorption and leaching. Environmental Pollution 134: 187-194.

[16] Gebremariam, S. Y.; Beutel, M. W.; Flury, M.; Harsh, J. B., and Yonge, D. R. Nonsingular Adsorption/Desorption of Chlorpyrifos in Soils and Sediments: Experimental Results and Modeling. 2012; 46, (2): 869-875.

Field Studies

Terrestrial Field Dissipation

Field dissipation data indicate that chlorpyrifos is moderately persistent under field conditions. Calculated dissipation half-life values for chlorpyrifos were 33 to 56 days in three soils planted with field corn. Again, the half-life values appear to correlate with the soil pH. TCP was observed to form under field conditions. Additional field dissipation studies have been submitted to the Agency (MRIDs 40059001, 40356608, 40395201, 42874703, 42874704, 42924801, 42924802); however, these results are not discussed here due to the study design (*i.e.*, repeated applications to crops) making the interpretation of the studies difficult and does not add much value to the understand of the dissipation of chlorpyrifos in the environment. These studies are generally classified as supplemental but suggest that chlorpyrifos may persist under field conditions.

Aquatic Semi-Field Dissipation

The distribution of chlorpyrifos between sediment and water in an outdoor mesocosm study designed to simulate spray drift or partial overspray following spring and fall applications was examined by Bromilow et al.[17] In general, chlorpyrifos was uniformly distributed in the 30 cm of overlying water within 24 h and moved into the sediment within 30 days, but did not penetrate below 2.5 cm depth. Chlorpyrifos was observed to persist beyond 30 d with a dissipation half-life of 20 days (spring applications) discounting the substantial decrease in the mass balance on day 1. The mass balance of chlorpyrifos at 1 day was roughly 40 to 60 percent of the applied material depending on the study. This initial loss was attributed to processes such as volatilization. Following the fall application, an increase in chlorpyrifos concentration was observed following a freezing spell that may have resulted in chlorpyrifos being released from plant materials. Chlorpyrifos only slowly degraded over the remaining winter period.

Field Volatility

With a vapor pressure of 10^{-5} mmHg, chlorpyrifos is classified as semi-volatile and thus volatility could be expected to play a role in its dissipation. In fact, air (**Table 9**) and precipitation (**Table 10**) monitoring data highlight the potential for chlorpyrifos volatilization. Field volatility studies confirm volatility is a major route of dissipation for chlorpyrifos when applied to foliar surfaces. However, a soil volatility study (MRID 41829006) did not show volatilization from soil to be a significant dissipation pathway.

[17] Bromilow, R. H., De Carvalho, R. F., Evans, A. A., and Nicholls, P. H. (2006). Behavior of Pesticides in Sediment/Water Systems in Outdoor Mesocosms. J. Environ. Sci. Health Part B 41: 1-16.

Table 9. Air Monitoring Data Summary for Chlorpyrifos and Chlorpyrifos-oxon[a,b]

Study	Year of Study	Type of Study	Sampler/Site Location	Maximum Air Concentration (ng/m³)	Maximum Air Concentration (ng/m³)
				Chlorpyrifos	Chlorpyrifos-oxon
Washington DOH	2008	Ambient	North Central District	21	5
		General–near field		607	108
		Perimeter Site		1145	61
		Ambient	Yakima Valley	30	10
		General–near field		243	21
		Perimeter Site		1002	124
Lompoc County, CA (CARB)	2003	Ambient	Central	8.3	2.9
			Northwest	8.4	1.9
			Southwest	6.8	1.9
			West	17	0.5
Tulare, CA (CARB)	1996	Ambient	Air Resource Board	39	60
			Jefferson Elementary School	432	173
			Kaweah School	412	230
			Sunnyside Union Elementary School	815	90
		Application Site	University of CA, Lindcove Field Station	168	174
			North	27,700	No data
			East	14,700	
			South	25,400	
Cowiche, WA (PANNA)	2006	Ambient	Unspecified	462	No data
Tieton, WA (PANNA)	2005	Ambient	Unspecified	475	No data
Lindsay, CA (PANNA)	2004	Ambient	Blue House	137	No data
Lindsay, CA (PANNA)	2004	Ambient	Green House	718	No data
Lindsay, CA (PANNA)	2004	Ambient	Orange House	1,340	No data
Lindsay, CA (PANNA)	2004	Ambient	Purple House	177	No data
Lindsay, CA (PANNA)	2004	Ambient	Red House	90	No data
Lindsay, CA (PANNA)	2005	Ambient	Blue House	421	No data

Study	Year of Study	Type of Study	Sampler/Site Location	Maximum Air Concentration (ng/m^3)	Maximum Air Concentration (ng/m^3)
				Chlorpyrifos	Chlorpyrifos-oxon
Lindsay, CA (PANNA)	2005	Ambient	Green House	1,119	No data
Lindsay, CA (PANNA)	2005	Ambient	Orange House	561	No data
Lindsay, CA (PANNA)	2005	Ambient	Purple House	515	No data
Alaska	2003-2005	Ambient	--	1.6	Combined as total chlorpyrifos

a. Fenske, R., Yost, M., Galvin, K., Tchong, Negrete, M., Palmendez, P., Fitzpatrick, C. 2009. Organophosphorus Pesticides Air Monitoring Project, Department of Environmental and Occupational Health Sciences University of Washington School of Public Health

b. Chlorpyrifos data are taken from USEPA, Chlorpyrifos: Preliminary Human Health Risk Assessment for Registration Review, June 30, 2011, D388070

Department of Health (DOH); California Air Resource Board (CARB); Pesticide Action Network North America (PANNA)

Table 10. Precipitation Monitoring Data Summary for Chlorpyrifos and Chlorpyrifos-oxon

Study	Year of Study	Type of Study	Sampler/Site Location	Maximum Concentration (µg/L)	Maximum Air Concentration (µg/L)
				Chlorpyrifos	Chlorpyrifos-oxon
San Joaquin River Basin[a]	2001	Ambient	Barnhardt Road near Turlock	0.052	No data
			Wastewater Treatment Plant Rooftop at Modesto	0.086	
			Cadoni Road lift Station at Modesto	0.071	
			MID Lateral 4 near Modesto	0.034	
			MID rooftop at Modesto	0.063	
			Albers Road near Turlock	0.148	
Alaska	2003-2005	Ambient	snow		Combined as total chlorpyrifos

a. Zamora, Celia.; Kratzer, Charles R.; Majewski, Michael S.; Knifong, Donna L., “Diazinon and Chlorpyrifos Loads in Precipitation and Urban and Agricultural Storm Runoff during January and February 2001 in the San Joaquin River Basin, California”(2003) USGS

Chlorpyrifos and chlorpyrifos-oxon have both been detected in air monitoring studies (including fog[18,19,20]) while only chlorpyrifos was detected in precipitation studies[21,22,23]. In addition, chlorpyrifos has been detected in dust samples collected from homes in agricultural areas.[20] These data confirm the potential for atmospheric transport; however, the mechanism (*i.e.*, spray drift, volatilization, particle transport or combination) could not be determined. Nevertheless, longer range atmospheric transport and redeposition of various pesticides, including chlorpyrifos, has been recorded.[24,25,26,27,28] Chlorpyrifos has been observed in snow collected at remote alpine sites.[29,30]

Volatilization of chlorpyrifos and/or chlorpyrifos-oxon from treated crops is a pathway of dissipation in the environment that may result in exposure to the vapor phase or the redeposition of chlorpyrifos and chlorpyrifos-oxon downwind of a treated field. In fact, volatilization of chlorpyrifos followed by oxidation in air is likely the major route of chlorpyrifos-oxon formation in the environment. Two studies were conducted at rates lower than the current maximum single broadcast application. While the absolute amount of chlorpyrifos observed to volatilize off the treated field in the potato study is higher than the alfalfa study, the volatilization profiles[31] are similar in both studies. Field volatility studies conducted on alfalfa and potato fields showed approximately 28 - 71 percent of the applied chlorpyrifos volatilized off

---

[18] Glotfelty, D. E.; Seiber, J. N., and Liljedahl, L. A. Pesticides in Fog. 1987; 325, 602-605.
[19] Glotfelty, D. E.; Majewski, M. S.; Selber, J. N. Distribution of Several Organophosphorus Insecticides and Their Oxygen Analogues in a Foggy Atmosphere. *Environ. Sci. Technol.*, **1990**, *24 (3)*, 353-357.
[20] Harnly, M. E.; Bradman, A.; Nishioka, M.; McKone, T. E.; Smith, D.; McLaughlin, R.; Kavanagh-Baird, G.; Castorina, R., and Eskenazi, B. Pesticides in Dust from Homes in an Agricultural Area. 2009; 43, (23): 8767-8774.
[21] Mast, M Alisa; Alvarez, David a, and Zaugg, Steven D. Deposition and Accumulation of Airborne Organic Contaminants in Yosemite National Park, California. 2012 Mar; 31, (3): 524-533.
[22] Zamora, Celia.; Kratzer, Charles R.; Majewski, Michael S.; Knifong, Donna L., "Diazinon and Chlorpyrifos Loads in Precipitation and Urban and Agricultural Storm Runoff during January and February 2001 in the San Joaquin River Basin, California"(2003) USGS
[23] Vogel, J. R.; Majewski, M. S., and Capel, P. D. Pesticides in Rain in Four Agricultural Watersheds in the United States. 2008; 37, 1101-1115.
[24] Fellers, G.M, L.L. McConnell, D. Pratt, S. Datta. 2004. Pesticides in Mountain Yellow-Legged Frogs (Rana Mucosa) from the Sierra Nevada Mountains of California, USA. Environ. Tox. Chem. 23 (9):2170-2177.
[25] Sparling, D.W., Fellers, G.M., McConnell, L.L., 2001. Pesticides and amphibian population declines in California USA. Environ. Tox. Chem. 20: 1591-1595.
[26] LeNoir, J.S., L.L. McConnell, G.M. Fellers, T.M. Cahill, J.N. Seiber. 1999. Summertime Transport of Current-use pesticides from California's Central Valley to the Sierra Nevada Mountain Range, USA. Environmental Toxicology & Chemistry 18(12): 2715-2722.
[27] Muir, D. C. G., Teixeira, C., Wania, F., 2004. Emperical and Modeling Evidence of Regional Atmospheric Transport of Current-Use Pesticides, Environ. Tox. Chem. 23 (10):2421-2432.
[28] Primbs, T., Wilson, G., Schmedding, D., Higginbotham, C., and Simonich, S. M. Influence of Asian and Western United States Agricultural Areas and Fires on the Atmospheric Transport of Pesticides in the Western United States. Environ Sci Technol. 2008, Sept. 1; 42(17): 6519-25.
[29] Hoferkamp, Lisa; Hermanson, Mark H; Muir, Derek Cg, and Hoferkamp, Lisa. Current Use Pesticides in Arctic Media; 2000-2007. 2010 Jul 1; 408, (15): 2985-2994.
[30] Hageman, K. J.; Hafner, W. D.; Campbell, D. H.; Jaffe, D. A.; Landers, D. H., and Simonich, S. L. M. Variability in Pesticide Deposition and Source Contributions to Snowpack in Western US National Parks. 2010; 44, (12): 4452-4458.
[31] A flux profile is the emissions from a treated field over a defined period of time (*i.e.*, an hourly time series of flux estimates during a period of measurement following application).

treated fields, respectively (MRIDs 48883201[32] and 48998801[33]). Field volatility studies (summarized below) indicate that chlorpyrifos-oxon concentrations are approximately 3% of the total residue observed to come off the treated field. However, one air monitoring study measured higher concentrations of chlorpyrifos-oxon than chlorpyrifos (ratio of 5.6:3.9; chlorpyrifos-oxon: chlorpyrifos).[19]

Study 1: Alfalfa

Dow AgroSciences (DAS) submitted a field volatility study that measured both vapor phase chlorpyrifos and chlorpyrifos-oxon in air samples following a foliar application of a low VOC formulation[34,35,36] of chlorpyrifos to alfalfa. Approximately 30% of the applied chlorpyrifos was emitted from the treated field in the first 24 hours (28% considering chlorpyrifos only; 30% considering chlorpyrifos and chlorpyrifos-oxon combined). The volatilization profile for chlorpyrifos is similar to those generally observed for fumigants (un-tarped applications) in that there is a peak emission shortly after application during the warmer part of the day. The study measured chlorpyrifos for a period of 72 hours following application.

Study 2: Potato

A field volatility study published in the open literature was conducted with a foliar application of a non-low VOC formulation of chlorpyrifos applied to potatoes.[37,38] This study measured parent chlorpyrifos, but did not measure concentrations of chlorpyrifos-oxon. Approximately 71% of the applied chlorpyrifos

---

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

[33] Leistra, M; Smelt, J. H.; Weststrate, J. H.; Van Den Berg, F; Aalderink, R. Environ. Sci. Technol. **2006**, *40*, 96-102.

[34] California's Department of Pesticide Regulation (Cal DPR) defines a low VOC pesticide formulation when the total emission potential (see **footnote 53**) is 25% or less (see **footnote 54**). The emission rate corresponds to total VOC emissions and not specially one component of the formulation (*i.e.*, the active ingredient). EPA does not currently define low VOC pesticide formulations.

[35] Emission potential is based on Thermogravimetric Analysis; Oros, D., Spurlock, F. California Department of Pesticide Regulation, ESTIMATING PESTICIDE PRODUCT VOLATILE ORGANIC COMPOUND OZONE REACTIVITY. PART 1: Speciating TGA-Based Volatile Organic Compound Emissions Using Confidential Statements Of Formula, January 27, 2011 http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/analysis_memos/2286_segawa.pdf

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

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

[38] Since the raw data for this study could not be obtained, the flux rates could not be independently verified by EPA and, thus, evaluation of experimental details and associated data quality review of this study is not as rigorous as that associated with the alfalfa study. The results from this study are presented in this assessment to provide another line of evidence of the potential volatility of chlorpyrifos, as demonstrated in the registrant submitted study, and to help describe the potential variability in chlorpyrifos flux rates due to different study conditions (*e.g.*, crop canopy, formulation, and weather).

was estimated to volatilize from the treated field within 24 hours following application, assuming continuous volatilization.[39]

iv. Drinking Water Treatment Effects

Because drinking water for a large percentage of the population is derived from community water systems that treat raw water[40] prior to consumption, the impact of water treatment on pesticide removal and transformation are considered, when possible, in estimating drinking water exposure.[41,42,43] There is a wide range of drinking water treatment processes utilized by community drinking water systems across the country, including disinfection, coagulation/flocculation, sedimentation, and filtration.[44] The effect of various processes has been investigated for a number of pesticides[45] including chlorpyrifos. The results from one study are shown in **Table 11** and suggest that the removal of chlorpyrifos is highly dependent on the treatment method employed by an individual community drinking water treatment facility.[46]

---

[39] Sampling did not occur at night; therefore, in order to develop a 24 hour flux profile. EPA developed a flux rate for the missing sampling periods by averaging the flux rate prior to and after the time period when sample collection did not occur.
[40] United States Environmental Protection Agency. 1989. Technologies for Upgrading Existing or Designing New Drinking Water Treatment Facilities. EPA/625/4-89/023.
[41] Assessment of pesticide concentrations in drinking water and water treatment effects on pesticide removal and transformation, FIFRA Scientific Advisory Panel Meeting September 26-29, 2000
[42] *Progress Report on Estimating Pesticide Concentrations in Drinking Water and Assessing Water Treatment Effects on Pesticide Removal and Transformation: A Consultation.* FIFRA Scientific Advisory Panel Meeting, Sept 29, 2000; SAP Report No. 2001-02. February 12, 2011.
[43] U.S. Environmental Protection Agency, Office of Pesticide Programs. The Incorporation of Water Treatment Effects on Pesticide Removal and Transformations in Food Quality Protection Act (FQPA) Drinking Water Assessment, October 25, 2001
[44] U.S. Environmental Protection Agency, 2006 Community Water System Survey.
[45] *Progress Report on Estimating Pesticide Concentrations in Drinking Water and Assessing Water Treatment Effects on Pesticide Removal and Transformation: A Consultation.* FIFRA Scientific Advisory Panel Meeting, Sept 29, 2000; SAP Report No. 2001-02 February 12, 2011.
[46] Chamberlain, E. Shi, H., Wang, T., Ma, Y., Fulmer, A., Adams. C. J Agric. Food Chem. *2012*, 60, 354-363

Table 11. Chlorpyrifos Reduction Under Typical Drinking Water Treatment Conditions; Drinking Water Treatment Processes Utilized by Community Water System Based on Population Served

Treatment Method[1]	***FC***		***MCA***		***ClO_2***		***MnO_4-***		***UV***		***H_2O_2***		***O_3***		***Softening***
	pH 6.6	***pH 8.6***	***pH 6.6***	***pH 8.6***	***pH 6.6***	***pH 8.6***	***pH 6.6***	***pH 8.6***	***pH 6.6***	***pH 8.6***	***pH 6.6***	***pH 8.6***	***pH 6.6***	***pH 8.6***	***pH 12***
Percent Reduction[2]	90.3	85.7	8.7	9.2	34.3	27.5	15.3	5.2	14.5	1.9	7.6	3.1	60.9	30.3	100.0
System Population Category	***Percentage of Plants Performing Each Treatment Practice for Surface Water***[3]														
100 or less	98.4		0		0		1.6		3.1		-	-	0		0
101-500	79		1.2		0		9.2		1.7		-	-	*1.4*		2.5
501-3,300	97.4		2.2		0		7.8		2.2		-	-	1.5		3.4
3,301-10,000	80.8		13.7		11		24.7		1.4		-	-	*1.4*		19.2
10,001-50,000	80.5		14.8		8.7		32.9		1.3		-	-	1.2		16.9
50,001-100,000	75.1		17.1		18.5		26.8		2.6		-	-	11.8		5.2
100,001-500,000	78.9		32.4		14		26.3		4.7		-	-	15.8		11.8
Over-500,000	78.0		35.6		2.5		21.2		1.7		-	-	14.4		21.2

1. Experimental time was representative of typical drinking water treatment condition
2. Chamberlain, E. Shi, H., Wang, T., Ma, Y., Fulmer, A., Adams. C. J Agric. Food Chem. **2012** *60*, 354-363
3. U.S. EPA Office of Water 2006 Community Water System Survey, **May 2009** (survey data)

Chlorine (FC); Chlorine dioxide (ClO_2); Chloramines (MCA); Lime/soda ash softener (assumed to be similar to hydrolysis at pH 12); Ultraviolet light (UV); Ozone (O_3); Potassium permanganate *(*MnO_4-)

In the presence of free chlorine, the most common disinfection process utilized by community water systems (see **Table 11**), chlorpyrifos reduction is high (>90%). Chlorination results in the formation of chlorpyrifos-oxon in high quantities.[47] The transformation of chlorpyrifos to chlorpyrifos-oxon in the presence of chlorine proceeds via rapid oxidation by the oxychlorine species. This transformation yields almost 100% oxon.

Reduction of chlorpyrifos in the presence of monochloramines, often used as an alternative to chlorine as a means to avoid transformation bi-products, is low (<10%). Use of monochloramines is more commonly used by community water systems severing larger (>100,001) populations. Of those community water systems serving populations greater than 100,001 individuals only 32 to 35 percent use monochloramines. This is consistent with other publications.[48,49]

Alternatively, water softening (alkaline pH >10) will significantly increase the rate of chlorpyrifos (hydrolysis half-life of approximately 10 days at pH 9.7; hydrolysis half-life of approximately 1.5 days at pH 10.4)[50] and chlorpyrifos-oxon (hydrolysis half-life of approximately 1.2 days at pH 10) [51] hydrolysis. The presence of TCP is more likely under such conditions.

Once formed as a disinfection by-product, chlorpyrifos-oxon is expected to be relatively stable to drinking water distribution conditions and times (few hours to a few days). Chlorpyrifos-oxon was shown to be relatively stable ($t_{1/2}$ = 12 days) under typical water purification conditions (pH 8).[52] The observed half-life of chlorpyrifos-oxon is 12 days at pH 8. Empirical data suggest more than 80% of chlorpyrifos is present as the oxon at 5 days post drinking water treatment and less than 20% is present as TCP. A comparison of the amount of chlorpyrifos, chlorpyrifos-oxon and TCP following drinking water treatment is presented as a function of time in **Figure 5**. The oxidation rate for chlorpyrifos is significantly higher than the rates of hydrolysis; therefore, all chlorpyrifos is expected to be oxidized to chlorpyrifos-oxon.

Very limited data on physical removal processes such as coagulation/flocculation, sedimentation, and filtration are available for chlorpyrifos or chlorpyrifos-oxon is available. However, such processes, with the exception of granular activated carbon[53], have been shown to be ineffective for select organic pesticides.[43] Based on the physical-chemical properties of chlorpyrifos and chlorpyrifos-oxon, granular activated carbon likely reduces the amount of both chemicals to some extent. One study shows addition of powder activated-carbon reduces the amount of chlorpyrifos by ninety percent. [49] However, data are not available on the exact removal efficiency for chlorpyrifos-oxon treated with granular activated carbon or powder activated carbon. Generally, carbon sources are added early in the treatment process. It should be noted that granular activated carbon is not a common treatment practice for all treatment

---

[47] Tierney, D. P.; Christensen, B. R.; Culpepper, V. C. Chlorine Degradation of Six Organophosphate Insecticides and Four Oxons in Drinking Water Matrix. *Submitted by Syngenta Crop Protection, Inc.* **2001**.
[48] Duirk, S. W. Desetto, L. M., Davis, G. M., Lindell, C., Cornelison, C. T. Water Research 2010, 44, 761-768
[49] Ormad, M. P., Miguel, N., Matesanz, J. M., Ovelleiro, J. L., Chemosphere, 2008, 71 97-106
[50] Macalady, D. L.; Wolfe, N. L.. New Perspective of the Hydrolytic Degradation of the Organophosphorothioate Insecticide Chlorpyrifos. *J. Agric. Food Chem*. **1983**, *31*, 1139-1147
[51] Duirk, S. E.; Collette, T. W.; Degradation of Chlorpyrifos in Aqueous Chlorine Solutions: Pathways, Kinetics, and Modeling. *Environ. Sci. Technol.*, 2006, *40(2)*, 546-550.
[52] pH 8 and residual chlorine concentration of 1 ppm.
[53] U.S. Environmental Protection Agency. 1998. Small System Compliance Technology List for the Non-Microbial Contaminants Regulated Before 1996. EPA 815-R-98-002.

facilities. Additionally, powdered activated carbon, which is used for taste and odor control, is not used year round.

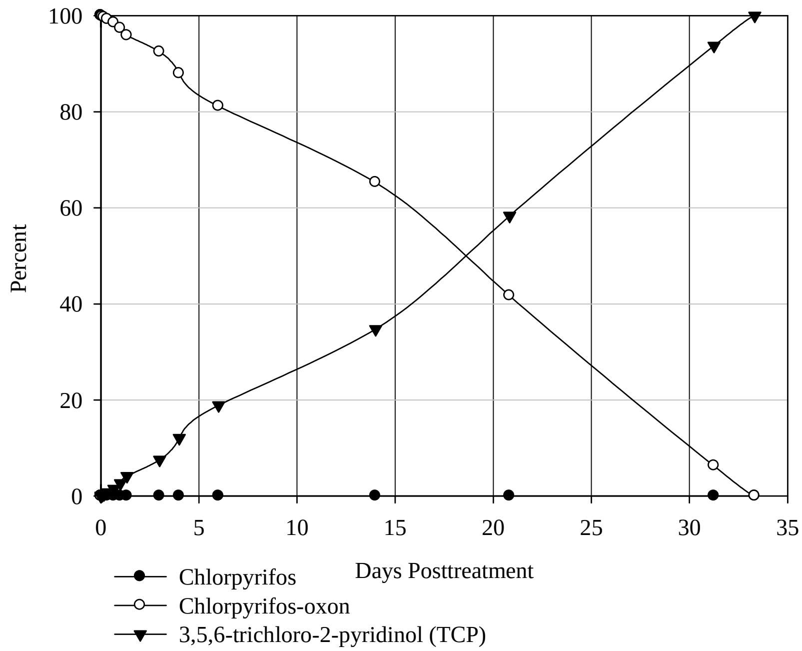


Figure 5. Comparative Analysis of Chlorpyrifos and Its Transformation Products Following Drinking Water Treatment[51]

Limited monitoring data are available for chlorpyrifos and chlorpyrifos-oxon following drinking water treatment. Available sources include the USEPA/USGS Pilot Reservoir Monitoring Program and the USDA Pesticide Data Program. Chlorpyrifos and chlorpyrifos-oxon were not detected in finished water in either of these programs; however, when raw and finished water samples were collected, the correlation between samples could not be made for chlorpyrifos. In this study, the finished water was collected prior to raw water collection. As such, the samples to no reflect the same potential pesticide loading. Thus, the impact of treatment could not be conclusively determined. Nevertheless, USEPA/USGS Pilot Reservoir Monitoring Program for other organophosphates (*e.g.,* malathion) suggests that in the presence of chlorine treatment processes, oxon formation occurs.

In summary, given the wide range of removal and transformation efficiencies of chlorpyrifos under the various drinking water treatment processes, it is assumed that it is possible, depending on the community water system and associated treatment processes, that source water containing chlorpyrifos may result in exposure to chlorpyrifos and chlorpyrifos-oxon in varying amounts.

Therefore, in order to address the multitude of water treatment possibilities, a bounding approach is used in this assessment. That is, to represent those facilities that use disinfectant processes other than free chlorine, 100 percent of the chlorpyrifos entering the facility was assumed to be unchanged in the finished drinking water. Alternatively, to represent those facilities that employ chlorine as a disinfectant, 100 percent of the chlorpyrifos entering the facility was assumed to convert to chlorpyrifos-oxon. The treatment methods and data for the associated population served data are provided in **Table 11**. In general, chlorine is used by treatment facilities that serve small populations, while treatment facilities serving larger populations, although still predominantly utilizing chlorine, tend to use alternative disinfection processes such as monochloramine more often than facilities serving smaller populations. An exception is New York City, which serves a population of nine million and uses chlorine to disinfect drinking water. Chlorpyrifos and chlorpyrifos-oxon are not expected to degrade during distribution, as distribution times typically range from a few hours to a few days. As such, these chemicals are considered residues of exposure concern in drinking water.

3. Analysis

This drinking water assessment serves to combine, update and complete the work presented in the 2011 and 2014 drinking water assessments for chlorpyrifos as part of the registration review process. As such, some of the information is repeated for consistency and clarity. This document specifically focuses on the exposure estimates for chlorpyrifos and chlorpyrifos-oxon in drinking water and does not consider any particular drinking water level of concern.

Previous assessments for currently registered uses of chlorpyrifos report higher EDWCs for surface water than groundwater based on both model estimates and evaluation of available monitoring data. Therefore, the focus of this assessment is drinking water exposure to chlorpyrifos and chlorpyrifos-oxon via surface water. A detailed discussion of the methods and assessment strategies used in this assessment are described in the sections below. These methods and strategies are well-established and have undergone FIFRA Scientific Advisory Panel (SAP) review and follow currently approved guidance, unless otherwise noted.

a. Model Simulations

i. Models

Pesticide in Water Calculator

The Pesticide Root Zone Model (PRZM5) (Young and Fry, 2014)[54] and the Variable Volume Water Model (VVWM) (Young, 2014)[55] are used to estimate pesticide movement and transformation on an agricultural field and in the receiving surface water body (*i.e.*, index reservoir), respectively. These models are linked with a user interface, the Pesticide in Water Calculator (PWC), previously called the Surface Water Concentration Calculator (SWCC). The PRZM5 and VVWM documentation, installation files, and source code are available at the USEPA Water Models website.[56]

PRZM5 simulates pesticide sorption to soil, in-field decay, erosion, and runoff from an agricultural field or drainage area following pesticide application(s). The VVWM estimates water and sediment concentrations in an adjacent surface water body (*i.e.*, index reservoir) receiving the pesticide loading by runoff, erosion, and spray drift from the field. The index reservoir has dimensions and characteristics

---

[54] Young, D.F. and Fry, M.M., 2014. A Model for Predicting Pesticide in Runoff, Erosion, and Leachate: User Manual, U.S. Environmental Protection Agency, Washington, DC. USEPA/OPP 734F14002.
[55] Young, D. F., 2014. The Variable Volume Water Model, U.S. Environmental Protection Agency, Washington, DC. USEPA/OPP 734F14003.
[56] Available: http://www2.epa.gov/pesticide-science-and-assessing-pesticide-risks/models-pesticide-risk-assessment

based on those of Shipman City Lake — a small, vulnerable midwestern reservoir located in an agricultural setting that was formerly used for source drinking water.[57]

There is a large suite of existing agricultural [and wide area use (*e.g.*, right of way)] scenarios available (123 total) for use in PRZM5/VVWM (PWC) simulations, spanning a range of agricultural and non-agricultural pesticide use sites.[58] These are referred to as PRZM scenarios through the remainder of this document. These scenarios represent specific soil, crop, weather, and hydrological factors. The locations of the existing scenarios are presented in **Figure 6**. These scenarios are known to span a range of vulnerabilities, but are all expected to result in high end exposure estimates. In generally, there are several scenarios representing the same location, as such, there are several scenarios overlapped in **Figure 6**.

[57] See "Development and Use of the Index Reservoir in Drinking Water Exposure Assessments" at http://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/development-and-use-index-reservoir-drinking-water

[58] Available: http://www2.epa.gov/pesticide-science-and-assessing-pesticide-risks/models-pesticide-risk-assessment#aquatic

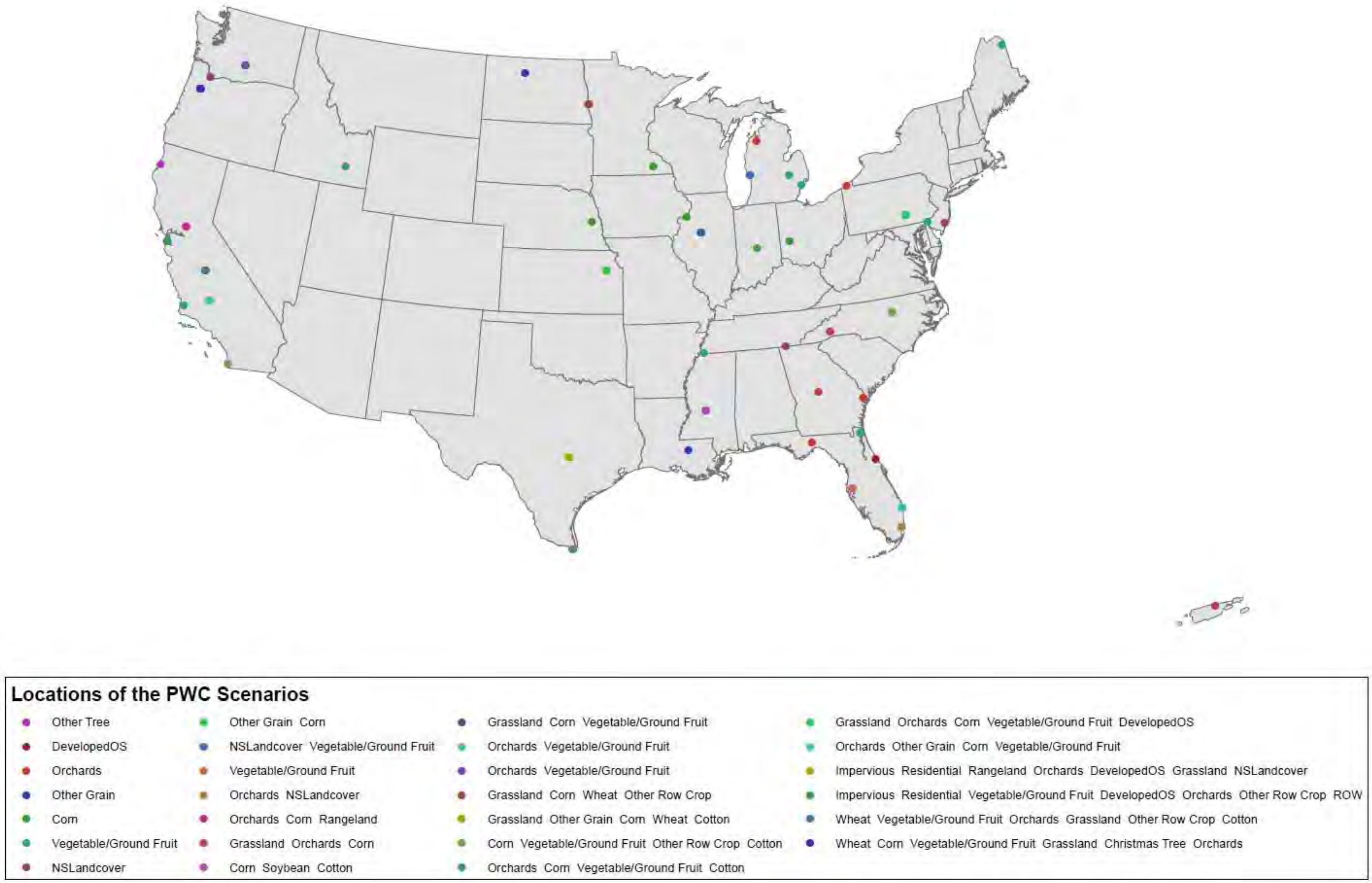


Figure 6. Location of Existing Aquatic Exposure Modeling Scenarios

For each PWC model simulation, an approximately 30-year time series of estimated exposure concentrations representing is developed. From these data, the estimated 1-in-10 year return frequency concentrations are calculated for several exposure durations including peak (instantaneous), 1-day, 4-day, 21-day, 60-day, 90-day, annual and simulation average concentrations. For this assessment, the one-day (24-hour) average concentration (acute exposure) or 21-day time-averaged concentrations (for steady state exposure) are summarized and reported for simplicity; however, all the data are available for the PWC model simulations. The 1-day and 21-day are expected to reasonable represent the exposure durations of concern for chlorpyrifos and chlorpyrifos-oxon.

Pesticide Flooded Application Model

Pesticide Flooded Application Model (PFAM, version 1.09) is a model developed specifically for regulatory applications to estimate exposure for pesticides used in flooded agriculture such as rice paddies and cranberry bogs. The model considers the environmental fate properties of pesticides and allows for the specifications of common management practices that are associated with flooded agriculture, such as scheduled water releases and refills. Unlike the Tier 1 rice model that assumes application to water and instantaneous partitioning between the water and sediment phases, PFAM allows for the simulation of pesticide applications to a dry patty/bog and degradation in soil before water is introduced to the patty/bog.

PFAM is used in this assessment to estimate chlorpyrifos concentrations in flood water releases from a cranberry bog. The concentrations are representative of the water releases from the bog and are not mixed with any additional water (*i.e.*, receiving water body). As a result, the estimated concentrations presented may be greater than those expected in adjacent water bodies due to additional degradation and dilution. While PFAM can simulate concentrations in a receiving water body, a validated conceptual model for a receiving water body has not yet been developed. Therefore, this feature is not included here. Differences in the concentration of the pesticide in the flood water compared to an adjacent water body depend on 1) the length of time the pesticide is in the flooded field, 2) the distance the water travels between the flooded field and the receiving water body, 3) the amount of dilution in the receiving water body, and 4) whether the flood water is mixed with additional water that also contains the pesticide.

ii. Approach

This assessment takes a two-step approach to assess the potential exposure to chlorpyrifos and chlorpyrifos-oxon in drinking water based on currently labeled uses of chlorpyrifos. The first step considers potential exposure to chlorpyrifos and chlorpyrifos-oxon at a national level, while the second step considers exposure estimates, as well as measured concentrations, at a more localized level (*e.g.*, regional, state or watershed scale). This assessment considers a number of different refinement strategies, as well as provides a sensitivity analysis to further characterize the potential exposure estimates. This is considered a highly refined drinking water assessment.

National Level Assessment

A national level drinking water assessment was completed in 2011 and updated in 2014 for the registration review of chlorpyrifos, with focus on the agricultural uses within the 48 contiguous United States. Consistent with these previous assessments, a range of agricultural (liquid applications) uses along with golf course turf were screened based on maximum labeled rates and minimum re-treatment intervals included in the master use summary document (**ATTACHMENT 1**).

Standard PRZM scenarios were utilized in this analysis as well as in previous analyses. When a standard PRZM scenario is not available for a given use scenario, an existing surrogate scenario, including associated meteorological data that is representative of the use pattern, is utilized. Best professional judgement is utilized in selecting appropriate surrogate scenarios. This typically entails making the determination that the crop is agronomically similar to the existing scenario, grown in similar geography, and with a runoff curve number (an empirical parameter used to predict direct runoff) of similar magnitude. For example, the California almond scenario can be used to model chlorpyrifos applications to other tree nuts.

Based on the results of this screen, a bounding approach was utilized to illustrate a range of EDWCs by examining two maximum label rate application scenarios in greater detail. Chlorpyrifos use on tart cherries has the highest annual application rate (14.5 pounds per acre per year with a maximum single application rate of 4.0 pounds per acre) of all the chlorpyrifos uses captured in the master use summary table (**ATTACHMENT 1**). Bulb onion production in Georgia was identified as a lower bound scenario, as the maximum single and yearly application rate is 1 pound per acre. For these two scenarios, standard PRZM scenarios (MICherries and GAOnion) were used in model simulations. BEAD assisted in parameterizing the application scenario to better reflect actual use practices (*i.e.*, application dates and methods) while still considering the potential exposure from the maximum labeled rate.

This national assessment (as well as previous assessments) did not consider non-agricultural use sites, with the exception of golf course turf, nor did it consider granular or micro-encapsulated formulations. This was done because agricultural uses of chlorpyrifos are expected to be the largest in terms of pounds on the ground as well as the footprint in terms of total acres treated. As such, chlorpyrifos use in agricultural sites and on golf-course is expected to result in the highest potential exposure to chlorpyrifos and chlorpyrifos-oxon in drinking water.

Regional Level Assessment

As a refinement, exposure on a HUC-02 regional (**Figure 7**)[59] basis was completed because the potential exposure to chlorpyrifos and chlorpyrifos-oxon is expected to vary across the landscape. The primary factor, aside from geographical restrictions and application scenarios (rates, retreatment intervals, methods), contributing to the variability in exposure estimates is the runoff potential, which is a combination of soil conditions, weather, and agronomic practices. This assessment builds upon the regional level drinking water case study presented in the 2014 assessment (*i.e.*, HUC-02 Region 3: South Atlantic-Gulf and HUC-02 Region 17: Pacific Northwest) for all HUC-02 regions (**Figure 7**). The results for the additional 19 HUC-02 regions are provided in this assessment.

[59] Hydrologic units are part of a hierarchical system for classifying and mapping drainage areas in the United States. The largest units (regions) are designated by two digits, and hence are often called 2-digit HUCs. Subdivisions of regions are designated with additional digits. There are 2,264 8-digit HUCs in the United States.
Seaber P.R., Kapino, F. P., Knapp, G. L., 1997 Hydrological Unit Maps. W. S. P. United States Geological Survey. March 2007. Available at http://pubs.usgs.gov/wsp/wsp2294/ (Accessed March 5, 2016)

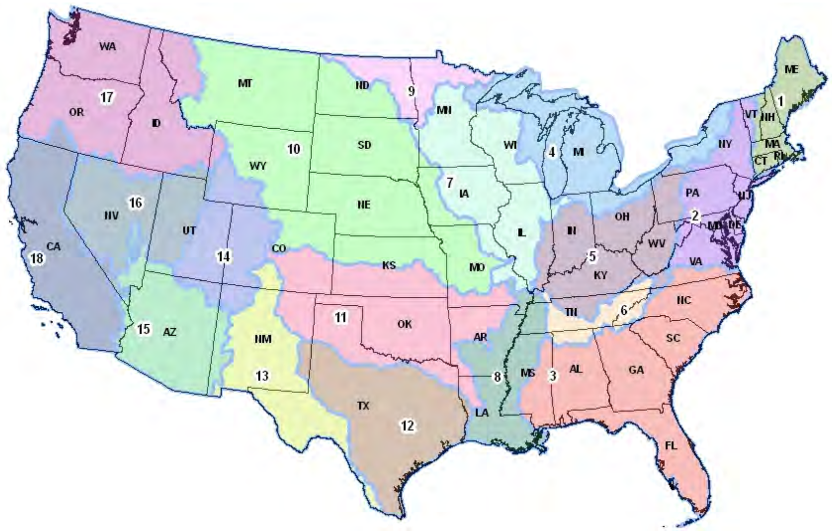


Figure 7. Spatial Distribution of HUC-02 Regions and U.S. State Boundaries

However, instead of running all available standard PRZM scenarios in a given region as was done in the regional case study presented in the 2014 assessment, representative surrogate scenarios were identified or developed based on soil and weather conditions for a given use site or group of use sites. This approach expands the availability of scenarios in a simplified and consistent process and also facilitates the scenario selection process. While soil conditions, weather, and agronomic practices still vary on a regional basis (see spatial distribution of HUC-02 regions in **Figure 7**), this approach assumes variability is less on a regional basis than on a national one, as well as assumes that a runoff curve number (or combination of curve numbers) can be selected based on known vulnerability to represent different soil types with similar runoff potentials. Use of these scenarios is not expected to result in EDWCs that are much different than those previously reported (*i.e.*, 2011 or 2014 assessments), but the EDWCs will be more spatially refined (*i.e.*, HUC-02 region).

Regional Surrogate Scenario Approach

The standard PRZM scenarios were binned based on location and crop into HUC-02 region-crop group combinations. The scenario with the highest runoff curve number was identified per HUC-02 region-crop group (*e.g.*, vegetable, orchard; see Association to Agricultural and Nonagricultural Data Layers section below) combination, as it represents the highest runoff potential. This was done recognizing that the selected scenario represents vulnerable locations within the HUC-02 region. For those HUC-02 region-crop group combinations where input scenarios are not available, a surrogate scenario (with the highest runoff potential) from a neighboring HUC-02 region was selected. For nonagricultural uses of chlorpyrifos, including adult mosquito control, developed lands, right-of-way (ROW), and wide area use, the CArightofwayRLF_V2 scenario was used. For impervious and residential uses, the CAImperviousRLF and CAresidentialRLF scenarios were used, respectively. This is the same approach that was employed for the Biological Evaluation of Chlorpyrifos[60] and is not different than what has been done for chlorpyrifos or other chemicals in the past. A scenario matrix with the assigned standard PRZM scenarios to each HUC-02 region and crop group combination is provided in **Table 12** and **Table 13**. The scenarios listed in these tables were coupled with regionally specific meteorological data as described below.

[60] http://www.epa.gov/endangered-species/biological-evaluation-chapters-chlorpyrifos

Table 12. PRZM Surrogate Scenarios Used for Exposure Modeling in Regional Assessment

HUC 2	Corn	Soybean	Cotton	Developed, Open Space/ Golf	Grassland	Pasture/ Hay/Rangeland/ Other Crops
01	MIbeansSTD	MIbeansSTD		PATurfSTD	ILalfalfaNMC	See grassland
02	PAcornSTD	PAcornSTD	NCcottonSTD	PATurfSTD	PAturfSTD	See grassland
03	NCcornWOP	NCcornWOP	MSCottonSTD	FLTurfSTD	NCalfalfaOP	See grassland
04	MIbeansSTD	MIbeansSTD		PATurfSTD	PAturfSTD	See grassland
05	OHCornSTD	OHCornSTD	MSCottonSTD	PATurfSTD	ILalfalfaNMC	See grassland
06	NCcornWOP	NCcornWOP	MSCottonSTD	FLTurfSTD	NCalfalfaOP	See grassland
07	ILcornSTD	ILcornSTD	MSCottonSTD	PATurfSTD	ILalfalfaNMC	See grassland
08	MSCornSTD	MSCornSTD	MSCottonSTD	FLTurfSTD	TXalfalfaOP	See grassland
09	NDCornOP	NDCornOP		PATurfSTD	MNalfalfaOP	See grassland
10	KScorn	KScorn	STXcottonNMC	PATurfSTD	ILalfalfaNMC	See grassland
11	NECornSTD	NECornSTD	STXcottonNMC	FLTurfSTD	TXalfalfaOP	See grassland
12	STXcornNMC	STXcornNMC	STXcottonNMC	FLTurfSTD	TXalfalfaOP	See grassland
13	TXcornOP	TXcornOP	STXcottonNMC	CATurfRLF	TXalfalfaOP	See grassland
14	TXcornOP	TXcornOP	STXcottonNMC	CATurfRLF	TXalfalfaOP	See grassland
15	TXcornOP	TXcornOP	CAcotton_WirrigSTD	CATurfRLF	TXalfalfaOP	See grassland
16	TXcornOP	TXcornOP		CATurfRLF	TXalfalfaOP	See grassland
17	ORswcornOP	ORswcornOP		CATurfRLF	ORwheatOP	See grassland
18	CAcornOP	CAcornOP	CAcotton_WirrigSTD	CATurfRLF	CArangelandhayRLF_V2	See grassland
19				CATurfRLF	ORwheatOP	See grassland
20	FLcorn	NCcornWOP		CATurfRLF	FLTurf	See grassland
21	FLcorn			FLTurfSTD		

Table 13. PRZM Surrogate Scenarios Used for Exposure Modeling (continued)

HUC 2	Non-specified land cover	Orchards/ Vineyards	Other Trees Christmas Tree[a]	Other Grain	Other Row Crop	Wheat	Vegetables/ Ground Fruit
01	MInurserySTD	NYgrapesSTD	NYgrapesSTD	PAalfalfaOP	MEpotatoSTD	PAalfalfaOP	MEpotatoSTD
02	NJnurserySTD_V2	PAapplesSTD_V2	PAapplesSTD_V2	PAalfalfaOP	NJmelonSTD	PAalfalfaOP	PAvegetableNMC
03	FLnurserySTD_V2	FLcitusSTD	FLcitusSTD	FLsugarcaneSTD	NCpeanutSTD	NCalfalfaOP	FLpotatoNMC
04	MInurserySTD	NYgrapesSTD	MIcherriesSTD	ILalfalfaNMC	MImelonsSTD	NDwheatSTD	MImelonsSTD
05	NJnurserySTD_V2	PAapplesSTD_V2	PAapplesSTD_V2	KSsorghumSTD	NCpeanutSTD	KSsorghumSTD	MIbeansSTD
06	TNnurserySTD_v2	NCappleSTD	NCappleSTD	NCalfalfaOP	NCcornWOP	NCalfalfaOP	FLpotatoNMC
07	TNnurserySTD_v2	FLcitusSTD	FLcitusSTD	ILalfalfaNMC	ILcornSTD	ILalfalfaNMC	ILbeansNMC
08	FLnurserySTD_V2	FLcitusSTD	FLcitusSTD	LAsurgarcaneSTD	MOmelonSTD	ILalfalfaNMC	MOmelonSTD
09	MInurserySTD	NYgrapesSTD	MIcherriesSTD	NDcanolaSTD	Mnsugarbeet	NDwheatSTD	MNsugarbeatSTD
10	TNnurserySTD_v2	ORFilbert	FLcitusSTD	KSsorghumSTD	KScorn	NDwheatSTD	MNsugarbeatSTD
11	TNnurserySTD_v2	OrchardBSS	FLcitusSTD	TXwheatOP	NECornSTD	TXwheatOP	STXmelonNMC
12	NurseryBSS_V2	OrchardBSS	OrchardBSS	TXwheatOP	STXcornNMC	TXwheatOP	STXmelonNMC
13	NurseryBSS_V2	OrchardBSS	OrchardBSS	TXwheatOP	STXcornNMC	TXwheatOP	STXmelonNMC
14	TNnurserySTD_v2	OrchardBSS	OrchardBSS	TXwheatOP	STXcornNMC	TXwheatOP	STXmelonNMC
15	NurseryBSS_V2	CAcitrus_WirrigSTD	CAcitrus_WirrigSTD	TXwheatOP	STXcornNMC	TXwheatOP	CALettuce w/irrigation
16	CAnurserySTDV	CAcitrus_WirrigSTD	CAcitrus_WirrigSTD	TXwheatOP	STXcornNMC	TXwheatOP	CALettuce w/irrigation
17	ORnursery	ORappleSTD	ORxmastresSTD	ORwheatOP	ORhopsSTD	ORwheatOP	ORsnbeanSTD
18	CAnurserySTDV	CAalmond_WirrigSTD	CAalmond_WirrigSTD	CAWheatRLF_V2	CArowcropRLF_V2	CAWheatRLF_V2	CAlettuceSTD
19	ORnursery	ORappleSTD	ORxmastresSTD	ORwheatOP		ORwheatOP	ORsnbeanSTD
20	FLnurserySTD_V2	FLcitrusSTD	FLcitrusSTD	FLsugarcaneSTD	FLpotatoNMC		FLtomatoSTD
21	FLnurserySTD_V2	PRCoffee	PRCoffee				FLtomatoSTD

a. Christmas tree scenario only developed for HUC-02 regions 1-19.

Currently, each PRZM scenario is linked to a specific weather station from the National Oceanic and Atmospheric Administration (NOAA) National Climatic Data Center's (NCDC) Solar and Meteorological Surface Observation Network (SAMSON). The SAMSON dataset[61] provides daily rainfall, pan evaporation, solar radiation, temperature, and wind speed for 242 National Weather Service (NWS) locations, spanning the years 1961 to 1990. Because the runoff curve number is fairly generic (USDA, 1986 Tables 2.2a, b and c[62]), holding all chemical inputs the same, a scenario modeled with another weather station can provide a reasonable estimate of exposure relative to the original scenario, by accounting for variations in rainfall and evaporation (*i.e.* rainfall totals, timing and intensity).

A representative SAMSON weather station was therefore associated with each PRZM scenario based on the highest 30-year rainfall level (**Table 14**) to create a representative scenario. In order to identify the representative station for use with the scenarios, the 242 meteorological stations were grouped by HUC-02 and the cumulative 30-year precipitation value was estimated. The meteorological station with the median cumulative precipitation value for a HUC-02 region was selected as the representative weather station except where there was a large difference in the precipitation values (*i.e.*, the maximum cumulative 30-year precipitation value for a HUC-02 is three times greater than the minimum value). Examination of using alternative weather stations (*e.g.*, station with highest precipitation) indicted that the data of application had more of an impact on the estimated concentrations than the cumulative rainfall. As such, the median value was determined to be sufficient for modeling purposes and it does not lead to the perception of compounding conservative assumptions in model simulations. For HUC-02 regions where a large rainfall difference occurs, the median precipitation value was used as a demarcation between a high-precipitation and low-precipitation group. The median station for both the high-precipitation and the low-precipitation groups are identified as representative weather stations and two sets of modeling was conducted for each of these HUC-02 regions. For HUC-02 regions 15, 16 and 20, a large disparity exists between the highest precipitation station and remaining stations in the HUC-02. For these HUC-02 regions, the highest precipitation weather station is selected along with the weather station with the median cumulative 30-year precipitation value for the remaining stations. Locations of the selected representative meteorological data are provided in **Figure 8**.

Table 14. Representative Weather Stations by HUC-02 Region[a]

HUC2	Value	WBAN	Precip (cm)	Precip Range (cm)	HUC2	Value	WBAN	Precip (cm)	Precip Range (cm)
1	Median	14740 Hartford, CT	3367	2774 – 3641	13	Median	23044 El Paso, TX	673	581 – 578
2	Median	13733 Lynchburg, VA	3120	2759 – 3629	14	Median	24027 Rock Springs, WY	760	661 – 856
3	Median	13874 Atlanta, GA	3870	3019 – 5009	15	Median (1)	03103 Flagstaff, AZ	585	315 – 915
4	Median	14839 Milwaukee, WI	2514	1890 – 3183	15	Highest (2)	23183 Phoenix, AZ	1740	1740

[61] NOAA National Climatic Data Center, 1993. Solar and Meteorological Surface Observation Network (SAMSON) 1961-1990, Version 1.0, Sep 1993. Available: http://www2.epa.gov/exposure-assessment-models/meteorological-data

[62] USDA, 1986. Urban Hydrology for Small Watersheds, TR-55. United States Department of Agriculture, Technical Release 55. Natural Resources Conservation Service. Available: http://www.cpesc.org/reference/tr55.pdf

HUC2	Value	WBAN	Precip (cm)	Precip Range (cm)	HUC2	Value	WBAN	Precip (cm)	Precip Range (cm)
5	Median	93814 Cincinnati, OH	3151	2650 – 3607	16	Median (1)	24127 Salt Lake City, UT	628	475 – 877
6	Median	13891 Knoxville, TN	3594	3083 – 4362	16	Highest (2)	24128 Winnemucca, NV	1238	1238
7	Median	14933 Des Moines, IA	2525	2091 – 2979	17	Median (1)	24156 Pocatello, ID	928	608 – 1438
8	Median	13964 Fort Smith, AR	4641	3992 – 4746	17	Median (2)	24221 Eugene, OR	3762	1438 – 6291
9	Median	14914 Fargo, ND	1487	1342 – 1859	18	Median (1)	23232 Tuscon, AZ	756	296 – 909
10	Median (1)	14935 Grand Island, NE	1107	838 – 1390	18	Median (2)	23188 San Diego, CA	1338	909 – 2862
10	Median (2)	24029 Sheridan, WY	1902	1390 – 3282	19	Median (1)	26415 Big Delta, AK	913	347-1215
11	Median (1)	13963 Little Rock, AR	1491	710 – 2220	19	Median (2)	26528 Talkeetna, AK	2224	1215-11525
11	Median (2)	23047 Amarillo, TX	3121	2220 – 3875	20	Median (1)	22521 Honolulu, HI	1682	1598 – 3287
12	Median (1)	03927 Grapevine, TX	1861	1141 – 2397	20	Highest (2)	21504 Hilo, HI	9891	9891
12	Median (2)	13897 Nashville, TN	2569	2397 – 4359	21	Median	11641 San Juan, PR	3974	3974

a. WBAN - Weather Bureau Army Navy. The number in parenthesis indicates the median station for the low-precipitation group (1) and the median or highest station for the high-precipitation group (2).

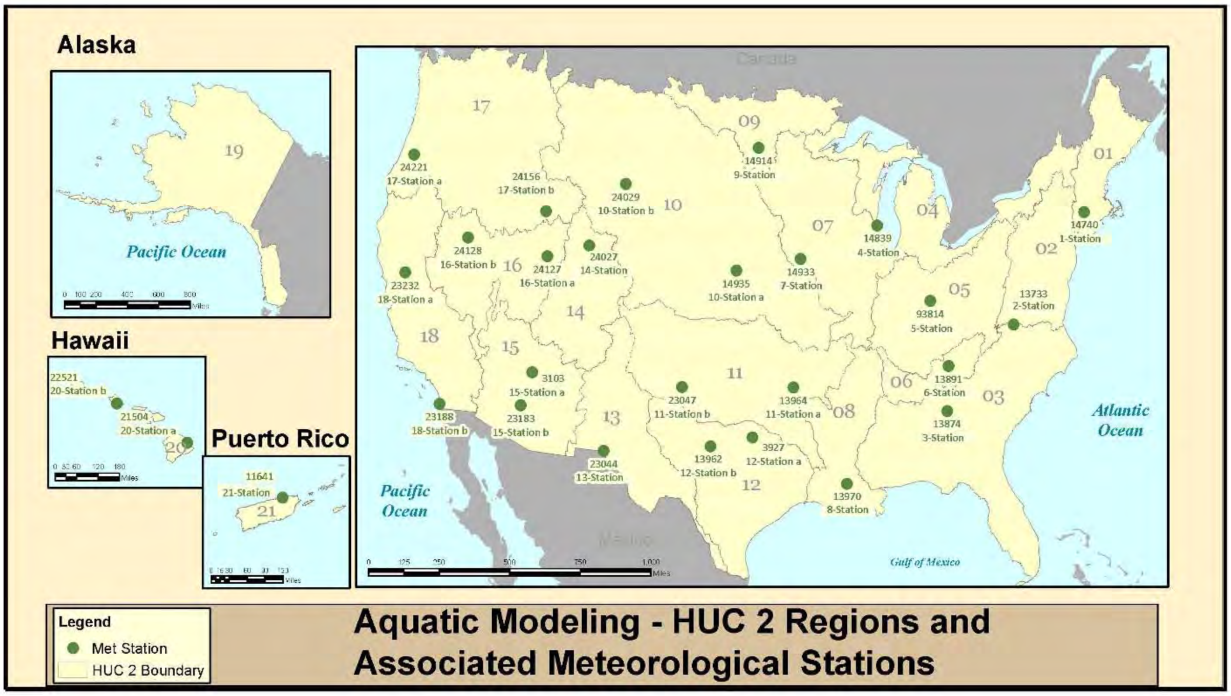


Figure 8. Representative Weather Stations by HUC-02 Region

Representative or surrogate PRZM scenarios were selected for each labeled chlorpyrifos use site based on crop/use site grouping and HUC-02 region. The approach provides a logical, consistent and data driven means for selecting representative scenarios for model simulations and accounts for local rainfall, soil, runoff and erosion.

Association to Agricultural and Nonagricultural Data Layers

The crop/use site group is based on the USDA National Agricultural Statistics Service (NASS) Cropland Data Layer (CDL)[63], which offers annual, geospatially referenced crop-specific land cover information from satellite imagery. Using Geographical Information System (GIS) software, the HUC-02 regions are overlaid with the USDA CDL to identify the cropped areas (in acres) within each HUC-02 region. Five CDL years (2010-2014) were temporally aggregated, and the 111 crop categories native to CDL were grouped into 11 general classes: corn, cotton, soybean, wheat, pasture/hay, other crops (*e.g.*, clover, fallow field, sod/grass for seed), orchards and vineyards, other trees (*e.g.*, managed forests), other grains (*e.g.*, barley, buckwheat, canola, rye, sugarcane), other row crops (*e.g.*, peanuts, sugarbeet, sunflower, tobacco), and vegetables and ground fruit.

The NASS Agricultural Census data was used to confirm growing regions for each crop group. If any crops were identified in the Agricultural Census that were not otherwise identified within a HUC-02 region based on the CDL data, an input scenario was assigned for the corresponding HUC-02 region-crop group combination. The results of this analysis are presented in (as shown in **Table 4.1** of **ATTACHMENT 4**). Cotton, orchards and vineyards, and other trees are the only crop groups identified with no acreage

[63] Han, W., Yang, Z., Di, L., Yue, P., 2014. A geospatial Web service approach for creating on-demand Cropland Data Layer thematic maps. Transactions of the ASABE, 57(1), 239-247.
Available: http://www.nass.usda.gov/Research_and_Science/Cropland/SARS1a.php

within certain HUC-02s. Based on this analysis, the HUC-02 region-crop group combinations that have no acreage are excluded from the scenario selection process (shown as blacked out cells). Even if a small acreage is noted for a HUC-02 region-crop group combination, it was considered as a potential use site and modeled.

Unless a use pattern is restricted to a particular geographic area (*e.g.*, ginseng use is only allowed in Michigan and Wisconsin), the National Agricultural Statistics Census of Agriculture 2012 (NASS) data along with cropland data were used to determine which chlorpyrifos uses would be modeled for each represented HUC-02 region. If the NASS data indicated any amount of acres of a crop grown (even if small acreage) in a specific HUC-02 region, it is assumed that the crop is grown in that HUC-02 region and chlorpyrifos may be used on that crop. If there are no reported NASS cropped acres grown in a particular HUC-02 region, it is assumed that the use does not occur in the HUC.

Twelve nonagricultural chlorpyrifos uses sites were identified for modeling, including adult mosquito control, developed commercial areas, developed open space (*e.g.*, recreational areas), golf, impervious, unspecified land cover (*e.g.*, nurseries), rangeland, right-of-way, wide area use, and Christmas tree orchards. A crop use-HUC-02 region matrix for chlorpyrifos is provided in **ATTACHMENT 4 (Table 4.2** and **Table 4.3)**.

iii. Model Input Parameters

Chemical Specific Physical-Chemical Properties

Summaries of the environmental fate input parameters used in the PWC and PFAM modeling of chlorpyrifos are presented in **Table 15**. Input parameters were selected in accordance with the following EPA guidance documents:

- Guidance for *Selecting Input Parameters in Modeling the Environmental Fate and Transport of Pesticides*, Version 2.1[64] (USEPA, 2009),
- *Guidance for Evaluating and Calculating Degradation Kinetics in Environmental Media*[65] (NAFTA, 2012; USEPA, 2012c), and
- *Guidance on Modeling Offsite Deposition of Pesticides Via Spray Drift for Ecological and Drinking Water Assessment*[66] (USEPA, 2013)

Table 15. Input Values Used for Tier II Surface Water Modeling Using the PWC and PFAM

Parameter (units)	Value	Source	Comments
Organic-carbon Normalized Soil-water Partitioning Coefficient (K_{OC} (L/kg-$_{OC}$))	6040	Acc. # 260794	The mean K_{oc} value (K_{oc} values = 7300, 5860 and 4960 mL/g) is used for modeling.
Water Column Metabolism Half-life or Aerobic Aquatic Metabolism Half-life (days) 25 °C	91.2	MRID 44083401	Only one half-life value is available, so this value (30.4 days) is multiplied by 3 to get 91.5 days. This half-life values was not corrected for hydrolysis. Recall the hydrolysis half-life of chlorpyrifos at pH 7 ranged from 72-81 days. Since hydrolysis is likely to be the driver for transformation of chlorpyrifos in aquatic systems use of aerobic aquatic

[64] http://www.epa.gov/oppefed1/models/water/input_parameter_guidance.htm (accessed April 11, 2014)
[65] http://www.epa.gov/oppfead1/international/naftatwg/guidance/degradation-kin.pdf (accessed April 11, 2014)
[66] http://www.regulations.gov/#!docketDetail;D=EPA-HQ-OPP-2013-0676 (accessed April 11, 2014)

Parameter (units)	Value	Source	Comments
			metabolism half-life of 91.5 days will not result in substantial different model estimated concertation than if hydrolysis were assumed to be the sole contributor to transformation in aquatic systems.
Benthic Metabolism Half-life or Anaerobic Aquatic Metabolism Half-life (days)25^{o}C	202.7	MRID 00025619	The 90th percentile confidence bound on the mean chlorpyrifos half-life value determined following the NAFTA kinetics guidance is 87.6 + [(3.078 x 52.9)/√2)] = 202.7 days.
Aqueous Photolysis Half-life at pH 7 (days) and 40° Latitude, 25^{o}C	29.6	MRID 41747206	
Hydrolysis Half-life (days)	0	MRIDs 00155577 (Acc. # 260794) and 40840901	Since the aerobic aquatic metabolism half-life value was not corrected for hydrolysis, it is possible that hydrolysis would be double-counted in the model simulation. Therefore, hydrolysis is set to 0 (stable) here as it is already accounted for in the aerobic aquatic metabolism study and input parameter.
Soil Half-life or Aerobic Soil Metabolism Half-life (days) and Reference Temperature	170.6, 25 ˚C	Acc. # 241547 and MRID 42144911	Half-life values of 19, 36.7, 31.1, 33.4, 156, 297, 193, and 185 days are obtained from empirical data following the NAFTA kinetics guidance. The 90th percentile confidence bound on the mean chlorpyrifos half-life value is 118.9 + [(1.415 x 103.3)/√8)] = 170.6 days.
Molecular Weight (g/mol)	350.57	product chemistry	
Vapor Pressure (Torr) at 25 ^{o}C	1.87 x 10^{-5} torr	product chemistry BC 2062713	
Solubility in Water at 25 ˚C (mg/L)	1.4	MRID 41829006	The water solubility of chlorpyrifos is reported to be between 0.5-2.0 mg/L for temperatures between 20 - 25 °C. Based on data submitted to EPA, 1.4 mg/L was used in modeling.
Foliar Half-life (days)	35	Default value	
Application Efficiency	0.99 (ground; air-blast)) 0.95 (aerial)	Default Values	
Application Drift	See **Table 17**	AgDRIFT modeling based on label restrictions	Labels contain aquatic buffer distances of 25, 50 and 150 ft. for ground, airblast and aerial applications.

While volatility has been observed to be a major route of dissipation of chlorpyrifos in the environment, the extent of deposition following volatilization and the area of deposit off a treated field is unknown. Furthermore, field volatility data for chlorpyrifos are limited. Only two studies are available, as described in the **Environmental Fate** and **Field Volatility** subsection section on page 24, the estimated rates of volatilization vary under different environmental conditions and with different foliar surfaces. As a conservative approach, all of the applied chlorpyrifos is assumed to be available for runoff, spray drift, and erosion in model simulation. As a result, the reported EDWCs may be higher than chlorpyrifos concentrations found in the environment because volatilization is not accounted for in model simulations. Volatility is the likely reason chlorpyrifos is detected in remote regions or in precipitation collected from locations far from potential applications sites. In addition, in some cases chlorpyrifos monitoring is conducted in irrigation canals that discharge to streams and rivers where chlorpyrifos was not observed in the irrigation water, yet samples of river water showed levels of chlorpyrifos. This may be the result of volatilization followed by redeposition.

When data are available on the foliar decay of a pesticide, as opposed to foliar dissipation, it may be used in surface water simulations. There are limited data available on the fate of chlorpyrifos on foliar surfaces, with most of the available data from foliar dissipation (*i.e.*, disappearance via routes such as transformation, runoff, and volatilization) studies that do not measure foliar decay (transformation). Due to the absence of foliar decay data for chlorpyrifos, a value of 35 days is used for surface water modeling to be consistent with the default value typically used in terrestrial modeling efforts.

Although limited environmental fate data are available for chlorpyrifos-oxon, model runs for chlorpyrifos-oxon are not included in this assessment as little data are available on the formation (rate or percent) of chlorpyrifos-oxon from chlorpyrifos in the environment. In fact, the only studies available do not show formation of chlorpyrifos by routes other than photolysis in the environment. To address potential exposure to chlorpyrifos-oxon, its formation during drinking water treatment is described in the *Water Treatment Effects* section of this document. Exposure to chlorpyrifos-oxon following drinking water treatment with chlorine is expected to be much higher than any exposure through formation of chlorpyrifos-oxon in the environment.

Use Scenarios

All chlorpyrifos uses included on the master use summary (**ATTACHMENT 1**) were modeled at maximum labeled rates and minimum retreatment intervals on a HUC-02 regional basis. Alternative use scenarios were also simulated including 1 lb. a.i./A per year for each crop/use site group for each HUC-02 region, as well as one adult mosquito control application per year. A 1 lb. a.i./A per year application was selected because typical use information (**ATTACHMENT 3**) for chlorpyrifos indicates that single applications at maximum rate are likely to occur; however, the number of applications over the course of a year are generally less than what is allowed on the label. When considering one application, the resulting EDWCs are linearly related to the application rate. Therefore, results for 1 lb. a.i./A per year can be adjusted to higher single application rates. For example, to determine the EDWCs associated with a single 4 lb. a.i./A per year application, the EDWCs for the 1 lb. a.i,/A per year would be multiplied by 4. Consideration of multiple applications would need to be done on a case-by-cases and is considered outside the scope of this assessment since there are an infinite number of alternative use scenarios for chlorpyrifos that could be supported by the registrant.

Chlorpyrifos-specific modeling scenarios were used for modeling each use, including the selection of scenarios (as described previously) and agronomic practices (*e.g.*, applications methods, dates). All chlorpyrifos uses including nonagricultural use sites were binned by HUC-02 region based on known crop acres as described in the *Association of Chlorpyrifos Use Sites to Agricultural and Nonagricultural Data Layers* section of this document. The results of this process are provided in **ATTACHMENT 4 (Table 4.2** and **Table 4.3)** and were used to facilitate the selection of a reasonable surrogate PRZM scenario for model simulations. **ATTACHMENT 5** includes all modeled chlorpyrifos scenarios by use site along with any relevant notes. All model input files are provided in **ATTACHMENT 6**. The general conditions outlined in the sections below were taken into account in the development of these scenarios.

Application Method

During application of pesticides, methods of application as well as product formulation used by an applicator can impact the off-site transport of the active ingredient. Label directions (such as spray drift buffers, droplet size restrictions, application equipment and agronomic practices such as soil incorporation) as well as product formulation (*e.g.*, granular or seed treatment) are considered as part of the development of the use scenario modeled.

There are many different types of chlorpyrifos applications included in the master use summary (**ATTACHMENT 1**) including those that occur in both agricultural and non-agricultural settings. Application equipment include aircraft, tractors, and irrigation systems as well as backpack and handheld sprayers. Chlorpyrifos applications may occur at different times throughout the year including multiple application to the same crop occurring at different crop stages. When multiple types of applications are allowed on a crop within one calendar year, such as pre-plant or soil incorporation applications along with foliar applications, all applications are simulated considering the appropriate application timing (*e.g.*, dormant, foliar, and post-harvest applications to a crop). For additional information see **ATTACHMENT 5**.

There are several types of chlorpyrifos formulations; however, for modeling purposes these formulations are subdivided into liquid [emulsifiable concentrate (EC), water dispersible granular (WDG), wettable powder (WP), or ready to use (RTU)] or dry (granular and seed treatment) applications. Microencapsulated formulations are also modeled as a liquid formulation. This assumes that all the chlorpyrifos contained within the microcapsule is released into a liquid solution prior to application. However, it should be noted that microencapsulation likely slows the release of chlorpyrifos into the environment. The approach taken in this assessment provides a conservative peak concentration; however, may result in an underestimation of longer term exposure as some chlorpyrifos may remain in the microcapsule and not be susceptible to hydrolysis, microbial degradation or volatilization, the primary dissipation routes for chlorpyrifos in the environment. Nevertheless, it is unclear how encapsulation (either in the form of a microcapsule or granular formulation) impacts the rate of dissipation of chlorpyrifos in the environment, which leads to uncertainty in the exposure estimates derived for these formulations. A sensitivity analysis (discussed below) helps characterize this by examining different rates of dissipation for chlorpyrifos in the environment.

For seeds treated with chlorpyrifos, all of the chlorpyrifos applied to the seeds is assumed to be available for runoff and erosion, since no seed leaching data are available for chlorpyrifos. This approach provides a conservative peak concentration; however, it may over estimate actual exposure as some chlorpyrifos may remain on the seed coat.

Application Timing

In selecting application dates for aquatic modeling, EPA considers a number of factors including label directions, timing of pest pressure, meteorological conditions, and pre-harvest restriction intervals. Agronomic information is consulted to determine the timing of pest pressure and seasons for different crops. General sources of information include crop profiles (http://www.ipmcenters.org/cropprofiles/), agricultural extension bulletins, and/or available state-specific use information. A general discussion of the considerations is provided below, while the selected application dates for each scenario are provided in **ATTACHMENT 5**.

Chlorpyrifos may be applied during different seasons of the year and the directions for use indicate the timing of application, such as, at plant, dormant season, foliar, *etc.* For most chlorpyrifos uses, application dates are chosen based on these timings, the crop emergence and harvest timings specified in the PRZM scenario, and precipitation data for the meteorological station for the PWC. At-plant applications are specified as occurring seven days before crop emergence. While not all crops emerge 7 days after planting, 7 days is assumed given that any difference in potential exposure based on slight variations in the application date is compensated for by using a 30-year weather simulation. Foliar applications are assumed to occur when the crop is on the field (*i.e.*, between emergence and harvest) in the PWC scenario. When choosing an application date within a time window (*i.e*., dormant season or foliar application), the first or fifteenth of the month with the highest amount of precipitation (for the meteorological station for the PWC scenario) for that time window is chosen. Once the first day of application is selected, minimum retreatment intervals are assumed to determine when subsequent applications would occur. If multiple types of applications are allowed on one crop within one year, such as pre-plant or soil incorporation along with a foliar application(s), the retreatment interval is selected to reflect the specified timings. All application scenarios considered the pre-harvest intervals required on the labels; therefore, applications are not specified to occur during the pre-harvest interval.

Meteorological information is also considered, as pesticide loading to surface water is directly affected by precipitation events. The wettest month (*e.g.*, the month with the highest cumulative precipitation) is identified and a systematic date (*e.g.*, the first of the month and the middle of the month as mentioned above) is considered in an effort to maintain the probability of the distribution of environmental exposure concentrations generated. In some cases, the wettest month is the same month that emergence occurs.

Weather information is considered as part of the application date selection process, as pesticide loading to surface water is affected by precipitation events. The wettest month (*e.g.*, the month with the highest daily average precipitation) is identified and a random date (*e.g.*, the first of the month, the middle of the month) is considered in an effort to maintain the probability of the distribution of environmental exposure concentrations generated. In some cases, the wettest month is the same month that emergence occurs. A listing of the months in decreasing average daily precipitation is provided in **Table 16**.

Table 16. Weather Analysis to Determine Wettest Months for Each HUC-02 Region

HUC2	Wettest Month Rank						
	1st	2nd	3rd	4th	5^{th}	6th	7th
1	11	5	4	9	12	6	8
2	7	5	10	8	6	3	2
3	3	2	7	1	4	12	5
4	4	8	9	7	6	5	3
5	5	3	7	6	4	11	8
6	3	7	12	2	1	5	6
7	6	8	7	5	9	4	10
8	7	2	8	4	12	9	1

HUC2	Wettest Month Rank						
	1st	2nd	3rd	4th	5th	6th	7th
9	6	7	5	8	9	4	10
10a	6	5	9	7	8	4	3
10b	5	6	4	9	10	3	7
11a	5	11	4	3	10	6	9
11b	6	8	7	5	9	10	4
12a	5	4	10	9	6	3	2
12b	9	5	6	8	10	7	4
13	9	8	7	10	6	12	2
14	5	4	9	6	7	3	8
15a	7	8	3	12	2	9	1
15b	12	8	9	3	7	2	11
16a	4	3	5	10	12	2	11
16b	11	6	12	4	5	3	1
17a	12	11	1	2	3	10	4
17b	5	3	4	11	12	6	1
18a	1	2	11	3	12	4	10
18b	1	3	2	12	11	4	10
20a	4	11	3	12	2	5	1
20b	12	1	11	2	10	3	4
21	11	5	10	9	8	12	7

PRZM5/VVWM assumes applications occur on fixed dates, specified by the user as absolute dates (*e.g.*, February 12th) or dates relative to crop emergence. Usage data obtained from California's Pesticide Use Reporting system and other pesticide use surveys show that for large watersheds not all farmers apply a pesticide on the same date, every day for 30 years. Applications in a larger watershed would be spread out over a period of time, based on pest pressure, relative planting date, precipitation events, and availability of the applicator. To account for this process, spreading out an application event over a fixed number of days was explored and is further discussed in the sensitivity analysis section. Retreatment intervals may also affect the days over which applications can be made.

Spray Drift Exposure

AgDRIFT v 2.1.1 (Spray Drift Task Force, 2011)[67] is used to evaluate the deposition fractions for aerial, ground, and orchard applications based on label specifications. Drift fractions were calculated for each application method, corresponding buffer distance, and droplet size distribution and are presented in **Table 17**. Spray drift estimates reflect the most recent offsite deposition guidance[68,69] and consider the

[67] Available: http://www2.epa.gov/pesticide-science-and-assessing-pesticide-risks/models-pesticide-risk-assessment

[68] U.S. Environmental Protection Agency, Brady, D. Guidance on Modeling Offsite Deposition of Pesticides via Spray Drift for Ecological and Drinking Water Assessments, December 20, 2013.

[69] U.S. Environmental Protection Agency, White, K., Khan, F., Peck, C., Corbin, M. Guidance on Modeling Offsite Deposition of Pesticides via Spray Drift for Ecological and Drinking Water Assessments, December 19, 2013.

currently labeled buffer restrictions [25 ft. (ground), 50 ft. (air-blast), and 150 ft. (aerial)] for aquatic water bodies included on all agricultural chlorpyrifos labels. These fractions are used in PRZM5/VVWM model simulations to capture the fraction of pesticide applied that reaches the water body by spray drift.

Table 17. Chlorpyrifos Spray Drift Estimates for Liquid Formulations for Use in PRZM5/VVWM Model Simulations

Spray Drift Fraction (unitless) Application Method and Buffer		
Ground	**Air-blast**	**Aerial**
25 ft	**50 ft**	**150 ft**
0.008	0.009	0.039

No spray drift is assumed for granular formulations and chlorpyrifos-treated seeds.

Adult mosquito control applications for chlorpyrifos are unique in that the pesticide is applied as an ultra-low volume (ULV) spray designed to target the flying adult mosquito and to remain airborne. The spray droplets must be small enough to be produced in sufficient numbers for probability of contact and large enough to impact or impinge readily on the surface of adult mosquitos.[70] As a result, the purpose of adult mosquito control applications is for the pesticide to reside in the air, causing the pesticide to drift. In addition, adult mosquito control applications of chlorpyrifos do not require a spray drift buffer.

Spray drift for adult mosquito control applications (*e.g.*, aerial ultra-low volume applications at release heights of > 75 ft) are evaluated using the AGDISP version 8.26 model. The input parameters provided in **Table 18** are used to model estimated drinking water concentrations for chlorpyrifos.

Table 18. Input Parameters for Modeling ULV Adult Mosquito Control Applications in AGDISP

Parameter	Value
Product	MOSQUITOMIST TWO U.L.V. (Reg. No. 8329-18)
Aircraft type	Air Tractor AT-401
Aircraft speed (mph)	120
Percent active ingredient	24.6
Pounds active ingredient per gallon of product	1.98
Application rate (lbs ai/A)	0.01
Minimum release height (ft)	75
Minimum wind speed (mph)	1
Temperature (°F) / Relative humidity (%)	65 / 50
Canopy	None
Surface roughness length (ft)	0.0246
Stability	Overcast
Number of nozzles	1, oriented along center of craft
Volume, diameter, 50th percentile DV_{50} (µm)	60
Volume, diameter, 90th percentile DV_{90} (µm)	115
Spray volume (gal/A)	0.005 (0.01 lbs ai/A ÷ 1.98 lbs ai/gallon product)
Active fraction	0.246

[70] Mount, G.A. 1970. Optimum droplet size for adult mosquito control with space sprays or aerosols of insecticides. Mosquito News, 30, 70–75.

Parameter	Value
Nonvolatile fraction	1.0
Specific gravity, carrier and active+additive	0.96 (1.98 lbs ai/gallon product ÷ 0.246 lbs ai/lb product ÷ 8.34 lbs water/gallon water)
Number of swaths	1
Swath width (ft)	112
Swath displacement (ft)	0
Swath offset	0 swath

Typical aerial ULV adulticide applications employ a 500-1500 ft swath width.[71] An initial swath width of 500 ft was selected in order to generate conservative application efficiencies (*e.g.*, a measure of how much active material lands on the spray block) and spray drift fractions to nearby waterbodies. When running the AGDISP model, point deposition fractions (*e.g.*, the fraction of the amount applied that deposits at a specific location) much greater than 1 (approximately 3-4) were estimated when a 500 ft swath was used. Believing this to be an error, swath widths were adjusted to 112 ft for chlorpyrifos, in order to generate a maximum deposition fraction close to 1 and then the deposition versus distance calculations were adjusted for a 500 ft swath. Deposition fractions starting from the edge of the treatment block (*e.g.*, the area immediately below the application swath) are generated by using linear interpolation between the adjusted values. For instance, for chlorpyrifos the deposition fraction at the edge of the treatment block (0 ft) is estimated using linear interpolation between the deposition value at -0.8656 ft (0.02397) and the deposition value at 5.696 ft (0.02297) (slope of -0.00015 and intercept of 0.023834). The deposition values are then averaged over the width of the 500 ft swath to estimate an application efficiency and averaged over the width of the waterbody bins to estimate aquatic deposition values. The resulting application efficiency is 0.21 and spray drift fraction of 0.015.

Chlorpyrifos can also be applied via ground application. Labeled specifications for drop size distributions for ground applications require a DV_{50} of 30 µm and DV_{90} of 50 µm. The labels also indicate an effective swath width for ground applications of 300 ft. EPA has yet to approve the use of the ground modeling algorithm, available in the AGDISP model, for use in assessing ground applications of pesticides. Therefore modeling of ground applied adult mosquito control was not conducted. However, in 2013, EPA (DP Barcode 407817)[72] conducted a comparison of ground and aerial applications of adult mosquito control using open literature information and other modeling and concluded that the maximum deposition was similar between the two methods of application. Based on this analysis, aerial deposition fractions are considered to be the same as those expected for ground applications.

Some labels do not have the aquatic buffers requirement. In general, these types of applications occur using handheld or backpack spray equipment. Data are not available on the spray drift that result from these types of applications; however, these application methods are not expected to result in substantial drift, therefore, no spray drift is assumed for these application methods.

---

[71] Florida Coordinating Council on Mosquito Control. 2009. Florida Mosquito Control 2009. http://mosquito.ifas.ufl.edu/Documents/Florida_Mosquito_Control_White_Paper.pdf

[72] USEPA. 2013. Spray Drift Analysis for the Etofenprox Label Amendment (Petition No. 1E7925). DP Barcode 407817. March 28, 2013.

Special Agricultural Considerations

Multiple Crop-cycles Per Year

Some labels permit applications on crops that may be planted in rotation or may have multiple crop seasons (*e.g.*, various vegetables) per year that could result in multiple applications on the same field. While crop rotations are highly likely for some chlorpyrifos use sites, including corn-wheat and wheat-sunflower, such rotations were not modeled, but the potential higher exposure is noted. Other crops commonly rotated include vegetable crops grown in four regions. PRZM scenarios are readily available for vegetables (California, Florida, Texas, and Michigan). Planting of the same crop on the same plot of land is less likely than crop rotation, but does occur sometimes. As a conservative approach, when maximum label application rates are specified on a crop cycle basis, it is assumed that multiple crops per year could be planted on the same plot of land. It should be noted that modifications to the PWC-scenarios (*i.e.*, the curve number) are not made to reflect the change in cropping pattern (*i.e.*, various crop stages or various crops) as the impact on the estimated environmental concentrations are minimal (well within an order of magnitude depending on the crop) based on a sensitivity analysis that examined the impact of adjusting the crop coverage within the PWC-scenarios.

Cranberry Modeling for Surface Water

To estimate the potential exposure to chlorpyrifos and chlorpyrifos-oxon in drinking water following use on cranberry, the PWC and PFAM were used. Exposure due to movement of residues in water released from bogs is evaluated using PFAM. The PWC is used to estimate exposure to chlorpyrifos residues from runoff and spray drift from dry harvested cranberries. Together the results from the PFAM and the PWC were used to represent the various agronomic practices utilized for growing cranberry in a weight of evidence approach for evaluating the potential exposure associated with the use of chlorpyrifos on cranberries.

For cranberries, the PFAM model was used to simulate a 12-inch flood on October 1, followed by draining the bog on October 4th. The modeled flood date was selected as a plausible date of harvest based on a 60 preharvest interval. A winter flood was also simulated on December 1, followed by draining the bog on March 16. The maximum aerial coverage for berry crops used in the OR berries PRZM scenario for the PWC was used in PFAM. Five different meteorological data files were used to capture the potential exposure to chlorpyrifos in the major cranberry growing regions of the country. **Table 19** summarizes the PFAM inputs used to model chlorpyrifos applications. Release of water into a receiving water body is not simulated because a conceptual model for this is not currently available.

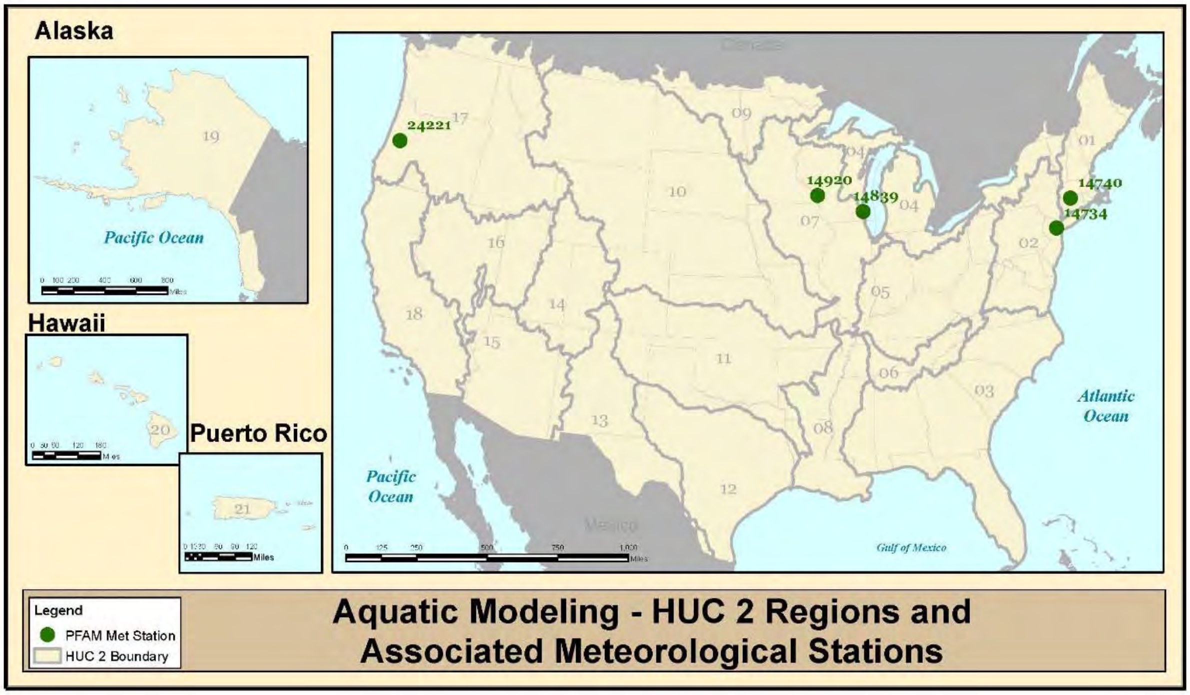


Figure 9. Location of Meteorological Stations Used for PFAM Modeling

Table 19. PFAM Specific Input Values Used for Tier II Surface Water Modeling

Input Parameter	Value	Source	Comment
Chemical Tab, see Table 3.7			
Applications Tab			
Application rate	1.5 lb a.i./A 1.68 kg a.i./ha	Chlorpyrifos Use Summary Table (**ATTACHMENT 1**)	
Number of Applications	2	---	---
Application Dates (MM/DD)	07/01 7/11	---	10 day minimum retreatment interval
Slow Release 1/day	0	--	Not applicable
Drift Application	0	--	Drift to an adjacent water body or mixing cell was not modeled.
Flood Tab			
Number of Flood Events	4	--	Harvest occurs between September and November. Field is flooded just prior to harvest. Field may also be flooded over the winter from December through March 15 (Cape Cod Cranberry Growers Association, 2001). The winter flood height was assumed to be similar to the harvest flood height. In some areas, there is also a late water flood to control spring frost where the bog is flooded in late April for one month. This was not simulated.
Date of Event 1 (Month-Day)	10-01	--	
Turn Over (1/day)	0	Assumed	
Days After (Month-day)	**Fill Level, Min Level (m)**	**Weir (m)**	
0 (Oct-1)	0.305	0.458	
3 (Oct-4)	0	0	
61 (Dec-1)	0.305	0.458	
105 (March-15)	0	0	

Crop Tab		
Zero Height Reference	05/01	Information from Maine Cooperative Extension (Armstrong, 2015)
Days from Zero Height to Full Height	120 (08/29)	Assumed
Days from Zero Height to Removal	153 (10/1)	Assumed
Maximum Fractional Areal Coverage	0.2	Value from OR berries PE scenario
Physical Tab		
Meteorological files	W14740 Hartford, CT W14734 Newark, NJ W14839 Milwaukee, WI W14920 La Crosse, WI W24221 Eugene, OR	Weather stations from cranberry growing areas
Latitude	42.3	Latitudes are CT 41.6, 40.0 NJ, 44.5 in WI, and 44.0 in Oregon. These are close enough that a default latitude was chosen.
Area of Application (m^2)	526,090	Represents 10x the area of the Index Reservoir
Weir Leakage (m/d)	0	PFAM default
Benthic Leakage (m/d)	0	PFAM default
Water-sediment mass transfer coefficient (m/s)	$1x10^{-8}$	PFAM default
Reference depth (m)	0.458	Set to same depth as weir height.
Benthic depth (m)	0.05	PFAM default
Benthic porosity	0.50	PFAM default
Dry bulk density (g/cm^3)	1.35	PFAM default
F_{OC} Water Column on SS	0.04	PFAM default
F_{OC} benthic	0.01	PFAM default
Suspended Sediment (mg/L)	30	PFAM default
Water column DOC (mg/L)	5.0	PFAM default
Chlorophyll CHL (mg/L)	0.005	PFAM default
Dfac	1.19	PFAM default
Q10	2	PFAM default

To account for the potential exposure to chlorpyrifos as a result of a runoff event that occurs prior to or after a flooding event (*i.e.*, not directly associated with an intentional flooding event) in a cranberry bog, as well as to represent cranberries grown in a more traditional field setting, PWC is used to estimate chlorpyrifos concentrations in the index reservoir. While the typical surface runoff simulated in the PWC does not apply to cranberries grown in bogs, residues related to runoff from cranberries will occur and the PWC is the tool available to capture exposure due to transport in runoff and spray drift. Additionally, some cranberries are dry harvested and may not be grown in a depressed area or in these hydrologically unique areas. Therefore, the PWC simulations for cranberry may also be used to estimate chlorpyrifos applications to cranberries that are dry harvested.

Non-Agricultural Uses and Considerations

As described in the master use summary document (**ATTACHMENT 1**) there are a number of non-agricultural use sites for chlorpyrifos; however, these are primarily (with the exception of bait stations and adult mosquito control) non-residential developed use sites such as commercial, institutional, industrial premises and equipment, nonagricultural outdoor building structures, as well as general area use. Examination of the application methods permitted on current labels for these uses indicates that backpack and hand wand spray equipment are the primary methods of application. An exception is wide areas use, which is modeled as a broadcast application like agricultural uses and is not further discussed in this section.

In addition, examination of the target pests (*e.g.*, ants and flies) and type of applications (*e.g.*, drench, crack and crevice, and perimeter) listed on the non-agricultural chlorpyrifos labels suggest that these applications are not expected to occur on a large scale (*i.e.*, field or watershed). Therefore, these uses are not expected to result in the magnitude of exposure that may result from traditional broadcast applications of chlorpyrifos to multiple acres of agricultural crops. Moreover, these types of applications are less likely to occur on the same day throughout an entire watershed. As such, these urban uses of chlorpyrifos do not fit the standard modeling paradigm employed by EPA to assess pesticide exposure (*i.e.*, where pesticides are uniformly applied over large areas at specific intervals during a growing season).

Urban Exposure Model

Several community drinking water intakes and the associated watersheds are known to occur in urban environments. Exposure estimates are derived using an urban exposure conceptual model (based on EPA's residential exposure conceptual model). An urban exposure conceptual model similar to the residential exposure model previously employed by EPA to assess exposure to pesticides in residential settings is used to assess exposure to chlorpyrifos from urban use sites. Use of this conceptual model is more realistic than assuming the entire watershed is treated with chlorpyrifos for these type of uses. The assumption is that the houses in the residential exposure model scenario represent commercial, non-agriculture buildings or areas (footprint) that would not be treated directly with chlorpyrifos, but that chlorpyrifos applications may be applied around the structure (**Figure 3.2**).

Exposure estimates for each non-agricultural use are derived individually. In some cases, an aggregation of multiple scenarios (developed and impervious) was done in a summation approach. An explanation of the assumptions for building perimeter, utilities, fences, and trash bins for model simulation is provided below. It is possible that multiple urban chlorpyrifos uses and/or applications may occur within an urban watershed. It should be noted that the contribution of other chlorpyrifos uses such as run-off and erosion from ornamentals that may also occur in urban environments are not considered. These applications, could result in treatment over a larger area such as a park or nursery. Therefore, such uses are considered separately and are expected to provide a higher exposure estimate on a broader scale than the uses aggregated as part of this urban exposure model.

The urban exposure conceptual model (**Figure 10**) consists entirely of quarter acre (10,890 ft^2; 104.36 ft x 104.369 ft) lots. Each lot contains one 1000 square feet commercial or non-agricultural building. The building is assumed to be square with sides of 31.6 feet with a 15 feet x 25 feet driveway. In addition, adjacent to the driveway is a trash storage area that is assumed to be equal in size to the driveway. On the opposite side of the lot is a utility easement of 10 feet wide that runs the entire length of the property. A 6 feet tall wood fence (including a gate in front of the trash storage area and drive way) that runs the perimeter of the lot is also assumed. This urban scenario, however, does not consider the streets that may fall between the commercial lots. The contribution or adjusted percent area treated (APAT) of each of the corresponding chlorpyrifos uses is described below.

Calculation of the APAT for outdoor commercial applications of chlorpyrifos is based on a 10 feet (Reg. No. 84575-5) perimeter band (soil broadcast; pervious surface) treatment adjacent to a building along with a 3 feet high foundation treatment (Reg. No. 84575-5) as shown below:

<u>Perimeter</u>

$$((31.6 \text{ ft} \times 2 \text{ sides}) + ((31.6 \text{ ft+ } 20 \text{ ft}) \times 2 \text{ sides}) - 30 \text{ ft driveway and trash storage area}) \times 10 \text{ ft} = 1364 \text{ ft}^2$$

$1364\ ft^2/10{,}890\ ft^2 = 0.13*1.1$ lb a.i./A = 0.14 lb a.i./A (developed scenario)

<u>Foundation</u>

$$(31.6\text{ft} \times 4 \text{ sides} - 30 \text{ ft driveway and trash storage area}) \times 3 \text{ ft} = 289 \text{ ft}^2 \text{ (developed scenario)}$$

$$(30 \text{ ft driveway and trash storage area}) \times 3 \text{ ft} = 90 \text{ ft}^2 \text{ (impervious scenario)}$$

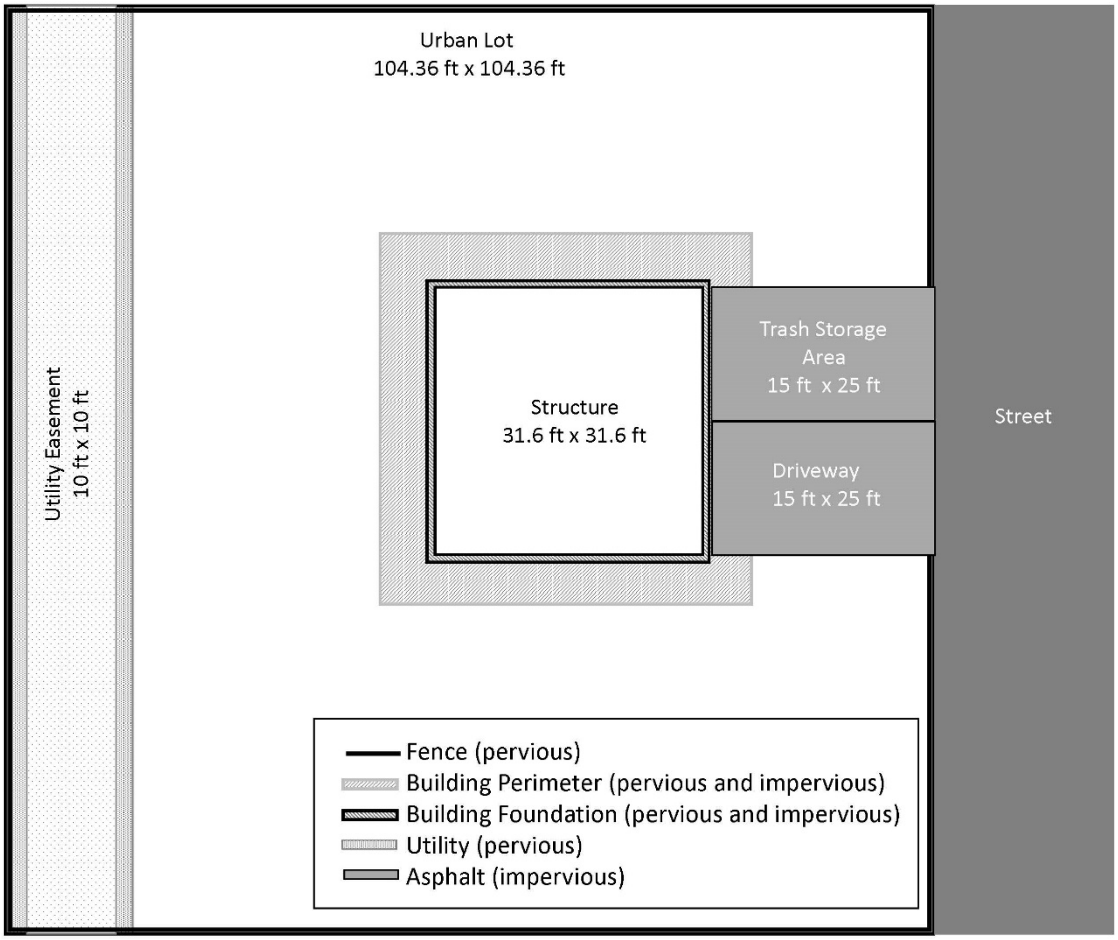


Figure 10. Urban Lot Conceptual Model

The total area that may be treated with perimeter treatment of chlorpyrifos and drain through a perimeter and foundation area is 1653 square feet (1364 ft^2 + 289 ft^2) and 90 square feet, respectively, assuming that 100% of the chlorpyrifos applied to both horizontal (soil) and vertical surfaces (walls/foundation) are available to run off the treated area. The perimeter treatment was assessed by adjusting the application rate by the APAT while the foundation application was assessed using a post processing strategy to combine contributions result from application to developed and impervious areas. APATs are summarized in **Table 20** by use site and urban scenario [impervious or pervious (right-of-way)].

Table 20. Adjusted Percent Area Treated For Urban Chlorpyrifos Uses

Use Site	Impervious	Developed	Maximum Application Rate (lb a.i./A)
Perimeter		0.13	1.1
Foundation/Wall	0.01	0.03	1.0
Trash Storage	0.03		4.9
Utility		0.13	1.0
Fence	1	1	16.65 lb a.i./ 10,000 ft^2 wood

The contribution of a targeted chlorpyrifos spray application to trash storage area in an urban setting is derived using the calculation below (impervious surface) and the APAT is provided in **Table 20**. No over spray to adjacent areas is assumed. The application rate was adjusted to reflect the APAT.

$$(15 \text{ ft trash storage}) \times 25 \text{ ft} = 375 \text{ ft}^2 \text{ (impervious scenario)}$$

A chlorpyrifos application to a 10 feet utility pad or easement the length (104.36 ft) of the property with a 2 ft spray buffer on either side of the easement (Reg. No. 13283-14) is estimated based on the equation below and the APAT also provided in **Table 3.4**:

$$(104.36 \text{ ft} \times (10 \text{ ft} + 4 \text{ ft})) = 1461 \text{ ft}^2 \text{ (developed scenario)}$$

Chlorpyrifos may also be applied as a wood protectant (16.65 lb a.i./10,000 ft^2 wood). A 6 foot wood fence is assumed to be located on the perimeter of the property with a wood gate that extends over the driveway and trash area. No wood leaching data are available for chlorpyrifos. Therefore, all the applied chlorpyrifos is assumed to be available to leach out of the wood or runoff the treated wood to adjacent surfaces, the equations below are used to determine the potential contribution of this chlorpyrifos use to the overall exposure to chlorpyrifos in an urban environment. This is done by adjusting the application rate for wood to area based on the described scenario and assuming APAT of one hundred percent. No overspray is assumed.

$$(104.36 \text{ ft} \times 4 \text{ slides}) - 30 \text{ ft}) \text{ x } 6 \text{ ft}) = 2{,}325 \text{ ft}^2 \text{ wood (developed scenario)}$$
$$(30 \text{ ft x } 6 \text{ ft}) = 180 \text{ ft}^2 \text{wood (impervious scenario)}$$

2,325 ft^2 wood x 16.65 lb a.i./ 10,000 ft^2 wood = 3.9 lb a.i./ lot or 15.5 lb a.i./A (developed)
180 ft^2 wood x 16.65 lb a.i./ 10,000 ft^2 wood= 0.30 lb a.i./ lot or 1.2 lb a.i./A (impervious)

iv. Post-processing or Output Adjustments

Percent Use Area Adjustment Factors

Watersheds large enough to support a drinking water facility are generally not comprised of only one land cover type, nor planted completely with a single crop. In order to account for variability in land cover, the USEPA uses percent cropped area (PCA) adjustment factors to reflect the percentage of a watershed that is covered by a particular land cover type and/or crop. Modeled concentrations of pesticides in surface waters are multiplied by a PCA factor to account for the areal fraction of a watershed that may be treated with a particular pesticide based on the pesticide uses and the land cover types (*i.e.*, crops) associated with those uses. In 2014, PCA factors were released for community water system (CWS) across the United States based on watersheds delineated for surface-source drinking water intakes (DWI). The new PCAs are an improvement over previously calculated PCAs in terms of relevance to human health risk assessment because the PCAs were derived for known drinking water sources as opposed to Hydrologic Unit Code 8 (HUC-08) regions.

In summary, 6,550 CWS DWI locations were available. Of the 6,550 locations, 74% (4,840) had unique, delineated watersheds. Of these, all but two (4,838) were located in the continental United States. A breakdown of the surface water source types for the 1,710 CWS DWI without validated watersheds is provided in **Table 21**. For the subset of 666 quality assured DWI locations in the continental U.S. quality assured watersheds, HUC-12 regions were taken as watershed surrogates. Maximum PCAs for the quality assured watersheds and HUC-12 surrogates in the continental U.S. (listed by HUC-02 water resource region). The national maximum value(s) in each case are shaded in the tables. When using PCAs to modify surface water modeling results, all of the potential pesticide use sites must be considered together, and used to select an appropriate PCA.

Table 21. Breakdown of Surface Water Source Types for the 1,710 Community Water System Drinking Water Intakes without a Validated Watershed

Surface Water Source Type	Count
NO WATERSHED FEASIBLE: Outside the cont. 48, abandoned, or Groundwater/Surface water	
Alaska	115
Hawaii	3
Abandoned/Inactive/Destroyed	71
Identified as Well in name (but not classified)	5
Identified as Mixed SW & GW in name	1
TOTAL	**195**
WATERSHED NOT APPROPRIATE: Groundwater influence, quarry, sea water, Great Lakes	
mine or quarry (14)	49
water bank (CA) (15)	1
infiltration gallery (4)	50
spring (7)	164
well under SW influence (CA) (19)	77
Great Lake (8)	138
sea water (16)	11
TOTAL	**490**
WATERSHED DELINEATION APPROPRIATE, BUT NOT VALIDATED - USE SURROGATE FOR PCA	
river/stream (1)	166
lake/pond (2)	94
reservoir (3)	396
lock & dam (6)	4
upstream reservoir (9)	5
low-head dam (10)	1
TOTAL	**666**
NEED FURTHER INFORMATION ON DRINKING WATER SOURCE TO DETERMINE FURTHER NEED	
aqueduct (11)	13
CA aqueduct (20)	42
canal (5)	210
terminal reservoir for canal (13)	43
Storage reservoir in distribution system (12)	35
unknown (0)	16
TOTAL	**359**

While the field size and the index reservoir (the receiving water body) used in the PWC simulations may provide reasonable upper bound EDWCs on a national scale, the watershed sizes and the receiving water bodies represented by the CWS DWI dataset vary substantially from very large to very small (**Figure 10**). The index reservoir represents a vulnerable drinking water scenario in the Midwest (*i.e.*, Shipman City Lake in Shipman, Illinois) and represents the drainage area/normal capacity of a drinking water reservoir in other parts of the United States.[73] In addition, as the water body size changes, the relative watershed size is also expected to change. Therefore, the mass coming from the treated watershed relative to the water body volume may stay relatively constant for vulnerable scenarios. Nevertheless, the assumption that the entire watershed is treated with chlorpyrifos on the same day at the same rate is likely conservative for larger watersheds (27,887 square mile; 95th centile). However, as the watershed size decreases, it is more likely that an entire watershed could be treated with chlorpyrifos on the same day, especially when considering some of the small watersheds (1 square mile; 8th centile). The index reservoir is approximately 0.67 square miles (approximately 5th centile). As such, there are 236 community water systems with delineated watersheds that are smaller than that represented by the index reservoir.

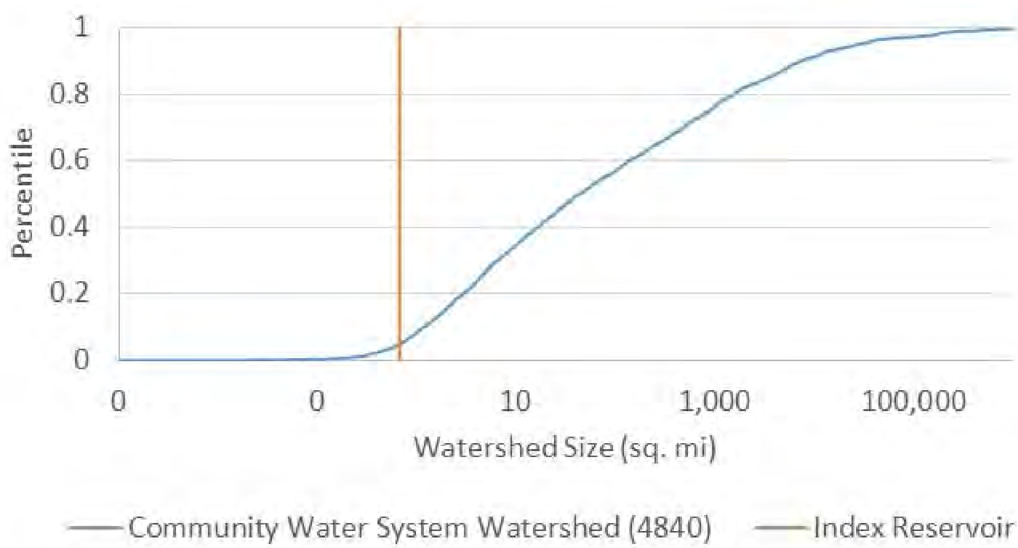


Figure 10. Drinking Water Intake Watershed Size Distribution

The population-served data found in the Safe Drinking Water Information System Federal Version (SDWISFED)[74] was also examined. The method of reporting appears to be different for different community water systems, as some systems use round/whole numbers while other systems appear to report the exact number of people served. Some even report a population served as zero. Nevertheless, comparison of population-served data found in SDWISFED for the highest all-agricultural PCA compare well to what is listed on the websites for the various systems. This gives some level of confidence in the population data supplied in SDWISFED, although a thorough quality assurance/quality control analysis

[73] U.S. Environmental Protection Agency. Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) Scientific Advisory Panel: Proposed Methods for Basin-scale Estimation of Pesticide Concentrations in Flowing Water and Reservoirs for Tolerance Reassessment; Linear Low Dose Extrapolation for Cancer Risk Decisions; DDVP Risk Issues; FQPA 10 Safety Factor Status Report; and Chlorothalonil: Mechanism for the Formation of Renal and Forestomach Tumors, **July 29-30, 1998**.

[74] https://www.epa.gov/ace/safe-drinking-water-information-system-federal-version-sdwisfed

was not completed. For general reference, population served data are presented in **Figure 11** based on the maximum all agricultural (AgNass) PCA. This figure shows that there are large populations (*i.e.*, 100,000 people) served by community water systems that use source surface water from intakes with watersheds with high PCAs (*e.g.*, 0.5). **Figure 12** compares watershed size to the maximum all agricultural (AgNass) PCA while **Figure 13** shows the watershed size compared to population served. This analysis shows that caution should be used when making generalities about the dataset. In general, small watersheds serve as source drinking water for smaller populations and smaller watersheds are more likely to have higher PCAs than larger watersheds. The assumption that all small watersheds with high PCAs only serve small populations should not be made. For example, PWSID IL1671200 serves a population of approximately 130,000 people. This system relies on two intakes that have PCAs of approximately 0.90.

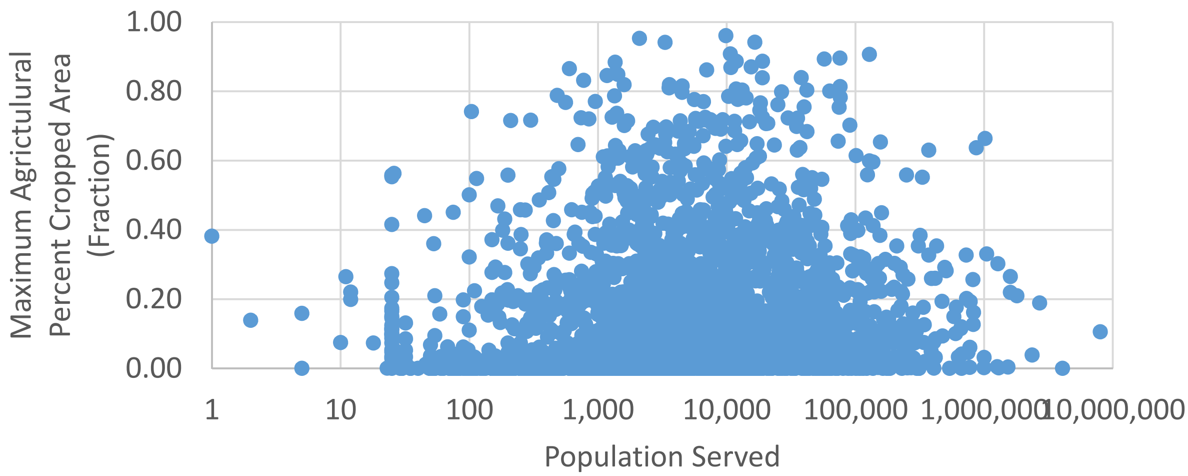


Figure 11. Community Water System Drinking Water Intake Percent Cropped Area and Population Served Comparison

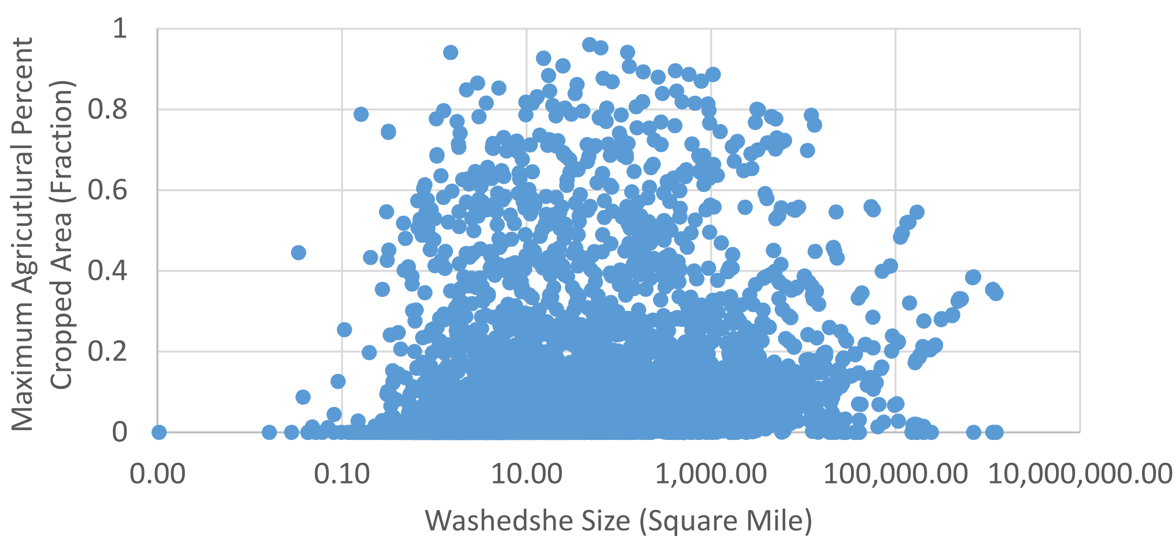


Figure 12. Community Water System Drinking Water Intake and Population Served Comparison

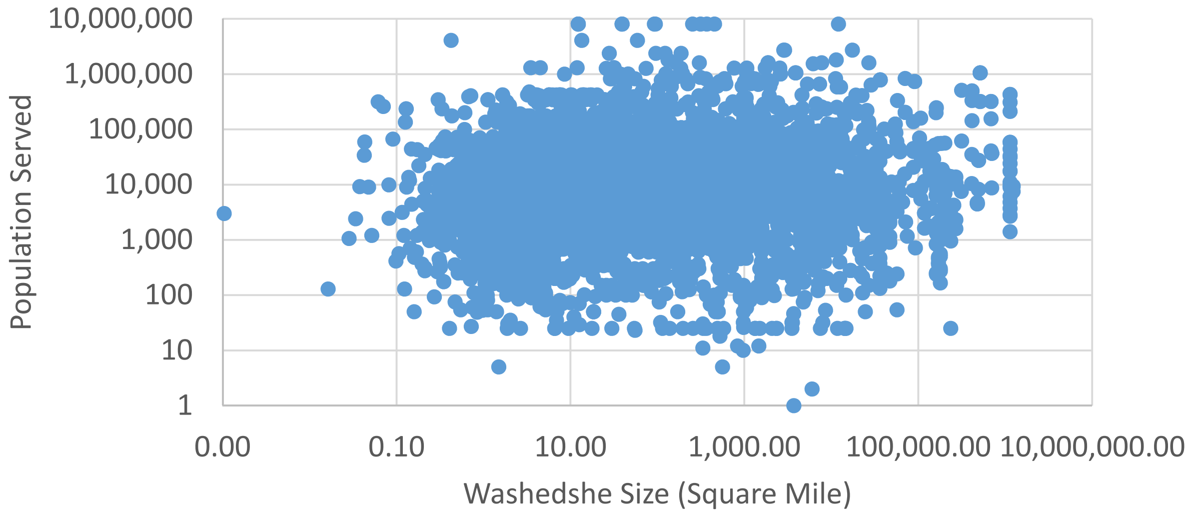


Figure 13. Community Water System Drinking Water Intake Watershed Size and Population Served Comparison

It took several years (2007-2013) to develop the DWI dataset and as such is potentially incomplete and/or obsolete as the universe of drinking water intakes is not fixed but inherently dynamic with existing intakes becoming inactive and new intakes being established continually. A random spot check of the intakes with the highest all agricultural PCA indicates that while a few intakes may no longer be active, the majority of the intakes in the DWI dataset remain. To investigate the scope of new intakes, EPA obtained a recent (Spring 2013) download of the SDWISFED data and identified approximately 700 (14%) drinking water intakes not included as part of the DWI dataset. The locations of these intakes are spatially diverse (see **Figure 14**). This figures does not provide insight into any trends. This may be the results of the underlying data or the factor that small watershed can serve large population and vise versa. For example, there are several examples within the dataset where multiple small watershed serve relatively large populations.

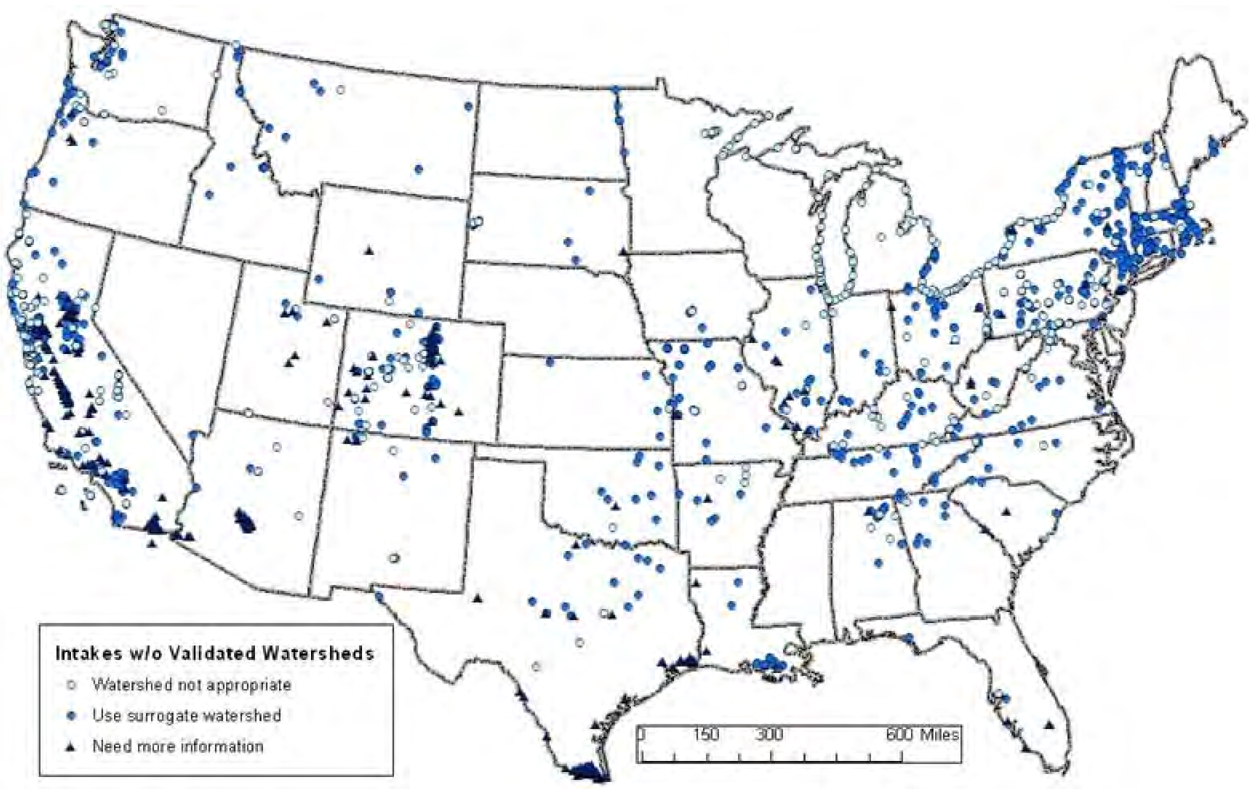


Figure 14. Locations of Quality-Assured Drinking Water Intake in the Conterminous U.S. Lacking Quality-Assured Watersheds

Use of the CWS PCA increases certainty of exposure with higher resolution information and projection of EDWCs. Based on this analysis, the CWS DWI dataset may be used at a regional level as recommended in the guidance document; however, if used at a smaller scale (*i.e.*, watershed) as presented in the 2014 assessment the data should only be used to identify areas where exposure concentrations are expected to be higher and not to dismiss areas not captured in the dataset. In absence of delineating the watersheds associated with the 700 new intakes, HUC-12 watersheds could be used as a surrogate similar to what was done for those intakes (666) previously identified where watersheds were not delineated and surrogate HUC-12 have been identified. HUC-12 watersheds range in size from 15.6 square miles (10,000 acres) to 62.5 square miles (40,000 acres). Based on the distribution of the current delineated CWS DWI dataset shown in **Figure 10** there are 258 CWS DWI watersheds smaller than 15.6 square miles and 328 CWS DWI watersheds smaller than 62.5**.** This suggests that for some systems, if a watershed approach were taken, there is potential the exposure could be underestimated for the drinking water intakes that HUC-12 watersheds were used as a surrogate. This is because a higher local maximum PCA value (*i.e.*, concentrated agricultural area) for a drinking water intake watershed (if smaller than HUC-12) may have be diluted when a larger scale (*i.e.*, HUC-12 watershed) is used.

Although there are a lot of data that can be utilized in deriving exposure estimates based on the CWS DWI PCA, given the current use profile of chlorpyrifos, a PCA of 1 is recommended for use on a national, regional and watershed basis. This is because chlorpyrifos may be used on turf (including sod farms, golf courses, road medians and industrial areas) as well as other wide areas including adult mosquito control anywhere in the watershed and multiple applications of chlorpyrifos to use sites within a watershed need to be considered. Although the CWS DWI PCAs are considered in this assessment, no refinement is possible at this time. If the chlorpyrifos use profile changes, the data are provided to easily facilitate investigation of the potential exposure without having to update this assessment.

It should also be noted that even if all wide area uses were excluded from the PCA selection process, there are a number of agricultural crops (*e.g.*, sorghum, triticale, alfalfa, sunflower) where the use of an all-agricultural PCA is recommended because reliable data are not available to derive individual crop specific PCAs. In addition, individual crops such as beets, asparagus, and cole crops PCAs cannot be derived using the available remote sensing data sources to develop the footprint, so for these crops an all-vegetable PCA is used. The crop group and crop specific PCAs provided in the CWS DWI PCA database are expected to reasonably represent chlorpyrifos use sites given the limitations of the data and therefore, chlorpyrifos specific PCAs are not needed.

Percent Use Treatment Adjustment Factors

Use of a percent cropped treated (PCT) or percent use treated (PUT) values to further refine the fraction representing the planted crop area treated with pesticide in a watershed was considered. PCT can be used to better understand actual exposure based on historical use, as well as provide a tool to facilitate the interpretation of model estimated exposure results compared to actual measured exposure concentrations. A limitation of this approach is that PCT values are typically aggregated at the State level and do not reflect local variations in areas treated (*e.g.*, regional/local pest pressures). For example, all the treatments could occur within one county/watershed or one farm within a county/watershed and that would be averaged out over an entire state potentially substantially underestimating exposure near the application sites. As a result, there would be an additional level of uncertainty in PCT/PUT values, particularly for smaller watersheds. While the incorporation of these factors has some merit in refining actual exposure estimate, the process needs to be evaluated further to insure potential exposure (change in use profile, aggregation of different crop uses) is captured and as such are not incorporated into this assessment. While data are generally limited for chlorpyrifos on the special scale necessary to conduct such an analysis, a case study for chlorpyrifos is presented in the **Data Interpretation and Extrapolation** section beginning on page 113.

b. <u>Monitoring Data</u>

i. Evaluation

Monitoring data provide snapshots of pesticide concentrations in time at specific locations under the conditions in which the data are collected. Supporting information or ancillary data are critical to understanding the monitoring data in context of overall pesticide exposures in the environment. Monitoring data where 1) sampling occurs in a high use area, 2) sampling occurs during the time frame in which pesticides are expected to be used, and 3) the sampling is frequent enough to estimate exposures for the endpoints of concern, are more informative to risk assessment, as compared to, monitoring data where these factors are unknown or did not occur.

Chlorpyrifos monitoring data are available for surface and groundwater. Groundwater data are not presented or further discussed in this assessment as exposure to chlorpyrifos and chlorpyrifos-oxon in groundwater is not expected to be higher than exposure in surface water based on the current chlorpyrifos use profile (**ATTACHMENT 1**). Surface water monitoring data for chlorpyrifos and chlorpyrifos-oxon are available from federal, state, local agencies, universities, and the registrant. Each database were examined independently and summarized. Evaluation considerations are outlined below.

- Study objective (*i.e.*, purpose and design of the monitoring study);
- Location description (latitude & longitude, if possible, or other reliable location information);
- Pesticide application sites;
- Monitoring station/sample site (and distance from pesticide application site)
- Date(s) sampled;
- Sample media (*e.g.*, water, filtered water, particulate);
- Water body type (stream, river or other flowing body; lake, reservoir, or other static body;
- Water body parameters (width, depth, flow rate);
- Pesticide(s) analyzed and reported concentration; and
- Analytical method and detection limit (LOD)/limit of quantitation (LOQ).

Other important information (*i.e.*, ancillary data) that may have aided in evaluating and interpreting monitoring data include:

- Quality assurance (QA)/quality control (QC) for sample collection and analytical methods, including a discussion of any limitations of the data (as referenced);
- Agronomic practices (*e.g.*, irrigation, land use, including cropping pattern, agriculture/urban; when data were easily accessible);
- Pesticide usage [application date, rate, and method (including release height, droplet spectrum; when data were easily accessible); and

All monitoring data were analyzed by program and by site-year for the various sample types listed in **Table 22**. To be considered a site-year there only needs to be one sample taken per year. A site-year analysis approach was employed because pesticide occurrence is dependent on spatially-dependent site conditions including pesticide use, agronomic practices, soil properties, meteorology, *etc*., as well as temporally-dependent conditions, including pesticide application timing and rainfall occurrence.

Table 22. Surface Water Sample Types Considered for Chlorpyrifos and Chlorpyrifos-oxon

Analyte	Sample Handling	Description of Sample Type
Chlorpyrifos	Unfiltered	Residue in unfiltered water (dissolved, suspended)
	Filtered	Residues in filtered water (dissolved)
	Finished	Residues in finished drinking water
	Particulate	Residues on suspended sediments
	Total	Residues in unfiltered water (dissolved, suspended)
	Recoverable	Residues detected in surface water
Chlorpyrifos oxon	Unfiltered	Residue in unfiltered water (dissolved, suspended)
	Filtered	Residues in filtered water (dissolved)
	Finished	Residues in finished drinking water
	Total	Residues in unfiltered water (dissolved, suspended)

As such, data from each monitoring location were analyzed using a custom Python program (Chemograph Generator[75] code provided in **ATTACHMENT 7**). Each site-year of monitoring data with four or more samples in a year were analyzed by generating a chemograph from the first sampling date to last sampling date. The concentrations for non-detections in the chemograph were expressed using

[75] Hook, James. 2015. Python Code for Chemograph Generator. Created on October 10, 2015.

three assumptions: the minimum reporting concentration (*i.e*., LOD or LOQ), ½ LOD, and LOD=0 (as described in the bullets below). This was done because the actual concentration of a sample reporting a non-detection of chlorpyrifos is unknown. The concentration can range from zero to the LOD or LOQ and the assumption may change the interpretation of the data.

- Assume samples below the LOD have chlorpyrifos concentrations equal to the LOD. This assumption is the most conservative assumption for estimating occurrence concentrations.
- Assume samples below the LOD have no chlorpyrifos in the sample. This assumption is the least conservative assumption for estimating occurrence concentrations.
- Assume samples below the LOD have chlorpyrifos concentrations at ½ LOD. This assumption is a compromise for assessing occurrence concentrations because it assumes the concentrations are between the LOD and zero.

Using the three different assumptions for the actual concentration permits the assessment of the impact of the low detection frequency in a monitoring dataset. Chemographs were not generated with monitoring data with less than 4 samples in the year.

Each chemograph was generated by stair-step imputation between measured values. The stair-step chemograph, therefore, provides a daily chemograph from the first sampling date to the last sampling date in the year. From this chemograph, maximum daily concentration, maximum 4-day average concentration, maximum 21-day average concentrations, maximum 60-day average concentrations, and maximum 90-day average concentrations, and the annual average concentrations were derived. Additionally, the Python program (Chemograph Generator) provides a count on the number of samples, number of non-detects, number of samples per quarter, and the average and median sampling intervals. For site years with less than four samples per year, the maximum concentration is only reported.

The calculation of time average concentrations for a site-year (*e.g*., maximum 4-day average concentration, maximum 21-day average concentrations, maximum 60-day average concentrations, and maximum 90-day average concentrations maximum, and annual average concentrations) requires, at a minimum, averaging concentrations over at least two samples. Because the sampling frequency varies among the various programs, the minimum number of samples in a site-year for time average concentration was calculated using the following equation: 365 divided by time average period. Using this equation, the minimum number of samples required for estimating a time average concentration from the monitoring data are shown in **Table 23**.

Table 23. Minimum Number of Samples in a Site-Year for Estimating Time Averaged Concentrations

Time Average Concentration	Samples Per Year
4 day average	91
21 day average	17
60 day average	6
90 day average	4
Annual Average	4

When daily time series were available, bias factors were developed using bootstrapping simulations of sampling frequencies to develop simple multiplicative factors for exposure estimates using the same chemograph generator mentioned above. The uncertainty of different sampling frequencies in estimating exposures of varying durations is characterized. Using various defined sampling windows (4 to 28-days) across a robust monitoring dataset, a random day within each sampling window is selected to simulate a monitoring event, and then 10,000 time series realizations are generated. For each of those time series, the 1-day peak and maximum rolling average for each of the averaging periods is calculated. A bias factor was then calculated by comparing the 5th percentile of the estimated maximums from the simulations to the actual maximums. The bias factor then becomes a multiplicative factor that can be applied to an exposure estimate, depending on the sampling frequency and the duration of exposure.

ii. Interpretation and Extrapolation

WARP Model

The Watershed Regression for Pesticides for multiple pesticides (WARP-MP) Map Application recently became available on the U.S. Geological Survey website (http://cida.usgs.gov/warp/home/). The WARP models for pesticides are developed using linear regression methods to establish quantitative linkages between pesticide concentrations measured at NAWQA and National Stream Quality Accounting Network (NASQAN) sampling sites and a variety of human-related and natural factors that affect pesticides in streams. Such factors include pesticide use, soil characteristics, hydrology, and climate - collectively referred to as explanatory variables. Measured pesticide concentrations, together with the associated values of the explanatory variables for the sampling sites, comprise the model-development data.

The WARP-MP Map Application is built upon the atrazine WARP models, in conjunction with an adjustment factor for each pesticide. The WARP model for estimating atrazine in streams is based on concentrations measured by NAWQA and NASQAN from 1992 to 2007 at 114 stream sites. The atrazine model actually consists of a series of models, each developed for a specific concentration statistic (annual mean and 4-, 21-, 30-, 60-, and 90-day annual maximum moving average). The models are built using the explanatory variables that best correlate with, or explain, the concentration statistics computed from concentrations observed in streams. Although explanatory variables included in the models are significantly correlated with pesticide concentrations, the specific cause-and-effect relations responsible for the observed correlations are not always clear, and inferences regarding causes should be considered as hypotheses.

The WARP models used on the Map Application web site to create maps and graphs are the models for the annual mean and annual maximum moving averages (4-, 21-, 30-, 60-, and 90-day durations). For each of these annual concentration statistics, the models can be used to estimate the value for a particular stream, including confidence bounds on the estimate, or the probability that a particular value will be exceeded, such as a water-quality benchmark. Each of these options for applying the model has advantages for specific purposes.

When used to estimate the value of a concentration statistic for a stream, such as the annual mean, the model computes the median estimate of the statistic for all streams with watershed characteristics that are similar to the stream in question. Thus, the computed estimate for a particular stream has an equal chance of being above or below the actual value of the statistic. The confidence that the estimated value is within a certain magnitude of the actual value is indicated by the 95-percent confidence limits, which encompass 95 percent of the actual values associated with the predicted value.

When used to estimate the probability that a particular stream has a pesticide concentration greater than a specific threshold, usually a water-quality benchmark, the model prediction and uncertainty are combined to estimate the probability for the stream.

This tool was used to estimated 4-day (surrogate for 1-day average concentration) and 21-day average concentration for chlorpyrifos. The estimated 4-day average concentration is still expected to underestimate the 1-day exposure but the 4-day average is the short duration of time available.

Bias Factor Development

The vast majority of pesticide monitoring data in the United States have limited sampling frequencies due to the cost associated with sampling and analysis. Additionally, pesticide use, as well as hydrologic patterns, are spatially and temporally variable. The net effect is a complex set of variables controlling pesticide occurrence in surface water. Because there is uncertainty in determining the exact pesticide occurrence pattern in any specific watershed, there is an inherent bias to underestimate actual pesticide concentrations because of the inability to capture peak or upper-bound concentrations through monitoring. Chlorpyrifos and chlorpyrifos-oxon occurrences in surface water are very sporadic as demonstrated by the low detection frequencies in the monitoring data (see **Monitoring Data** beginning on pg. 64). Low detection frequencies are expected to exaggerate the potential bias for underestimation of actual concentrations.

There has been several FIFRA SAP meetings discussing the uncertainty in deriving human health and ecological exposure to atrazine from the monitoring data (SAP April 2010,[76] SAP September 2010,[77] SAP July 2011[78] and SAP June 2012[79]). These SAPs have vetted different statistical approaches to account for uncertainty due to low sampling frequency, including the use of bias factors and kriging/ sequential stochastic simulation. The SAP recommended that OPP consider using sampling bias factors (BF), as well as SEAWAVEQ (a covariate model developed by USGS), for a quantitative estimate of uncertainty in the atrazine monitoring data. The analysis will present an estimation of BFs for chlorpyrifos. The BF serves as a protective multiplier of the actual concentration from monitoring data to account for uncertainty associated with sampling frequency.

---

[76] U.S. Environmental Protection Agency (USEPA). 2010a. FIFRA Scientific Advisory Panel: A Set of Scientific Issues Being Considered by the Environmental Protection Agency Regarding: Re- Evaluation of Human Health Effects of Atrazine: Review of Experimental Animal and In Vitro Studies and Drinking Water Monitoring Frequency. April 26-29, 2010. Document available at EPA-HQ-OPP-2010-0125

[77] U.S. Environmental Protection Agency (USEPA). 2010b. FIFRA Scientific Advisory Panel: A Set of Scientific Issues Being Considered by the Environmental Protection Agency Regarding: Re- Evaluation of Human Health Effects of Atrazine: Review of Non-cancer Effects and Drinking Water Monitoring Frequency. September 14-17, 2010. Document available at EPA-HQ-OPP-2010-0481

[78] U.S. Environmental Protection Agency (USEPA). 2011a. FIFRA Scientific Advisory Panel: A Set of Scientific Issues Being Considered by the Environmental Protection Agency Regarding: Re- Evaluation of Human Health Effects of Atrazine: Review of Cancer Epidemiology, Non-cancer Experimental Animal and *In vitro* Studies and Drinking Water Monitoring Frequency. July 26-29, 2011 FIFRA Scientific Advisory Panel. Document available at EPA-HQ-OPP-2011-0399

[79] U.S. Environmental Protection Agency (USEPA). 2012. FIFRA Scientific Advisory Panel: Problem Formulation for the Reassessment of Ecological Risks from the Use of Atrazine. September 11-14, 2012 FIFRA Scientific Advisory Panel. Document available at EPA-HQ-OPP-2012-0230

The general BF equation is as follows:

Ŷ=X*Bias Factor
Where:

Ŷ = Estimated chlorpyrifos concentration
X= Chlorpyrifos concentration obtained from monitoring data
Bias Factor=True chlorpyrifos conc./Estimated 5th percentile atrazine concentration estimated from 10,000 simulated chemographs

The statistical implication of the bias factor is that 95% of the time the bias factor adjusted chlorpyrifos concentrations from monitoring data will be equal to or greater than the true value in the monitoring data. As such it provides, an upper bound estimate on actual exposure.

BF for stratified random sampling are derived using a Monte Carlo sub-sampling process as presented to the 2011 FIFRA SAP (FIFRA SAP, 2011). A similar approach is used by Mosquin *et al*. 2011[80] to develop BFs from AEEMP and NCWQR data.

For stratified random sampling, each constructed chemograph was randomly subsampled 10,000 times using subsampling intervals of 4 days, 7 days, 14 days, and 28 days. The sampling simulation was conducted using a custom Pythron script software programs (Chemograph Generator version 2) starting with a random seed. For each sampling realization, a random value from the custom distribution of values within the designated time interval was selected to represent a value at each sampling interval within the chemograph. These selected concentrations were then used to construct simulated daily chemographs of chlorpyrifos concentrations using a linear interpolation. From a distribution of the 10,000 simulated chemographs, the 5th percentile maximum daily, 4 day average, 7 day average, 14 day average, 21 day average, 28 day average, 60 day average, and 90 day average chlorpyrifos concentrations were selected to derive the bias factors. Selection of the 5th percentile exposure chlorpyrifos concentration would provide development of conservative bias factors. The bias factor was calculated by dividing the true maximum value from the original chemograph by the 5th percentile maximum exposure atrazine concentration from the Monte Carlo simulation.

PWC Model Simulations

When use information was available for a given monitoring program, the data were further investigated to compare measured concentrations with model estimated concentrations. PWC model simulations were done using the standard model input parameters for chlorpyrifos, as well as available use information, including application rate and percent area treated. Representative PRZM scenarios were selected as appropriate.

[80] Mosquin, P., Whitmore, R., and Chen W. 2011. Impact of Alternative Monitoring Frequencies on Estimation of Atrazine Rolling Average Environmental Concentrations. Unpublished study from Syngenta Crop Protection, Inc. MRID 48470006

4. Results

a. <u>Modeling</u>

i. Pesticide Water Calculator

National

Several agricultural chlorpyrifos uses along with golf course use were screened using the PWC based on maximum labeled rates and minimum retreatment intervals. The results of this analysis are shown in **Figure 15** for the 1-in-10 year 1-day (or 24-hour) and 21 day average concentrations. The complete set of modeling results are available in **ATTACHMENT 7**. These results reflect the use of a DWI PCA of 1. Since chlorpyrifos is registered for use on turf (including sod farms, golf courses, road medians and industrial areas) a PCA of 1 (considers 100% of the watershed can and is treated) was applied to surface water modeling results for this national level analysis. The results presented in **Figure 15** only represent model output values and do not account for the potential conversion of chlorpyrifos to chlorpyrifos-oxon during drinking water treatment. The estimated chlorpyrifos concentrations presented in **Figure 15** are similar to what was presented in the 2011 assessment.

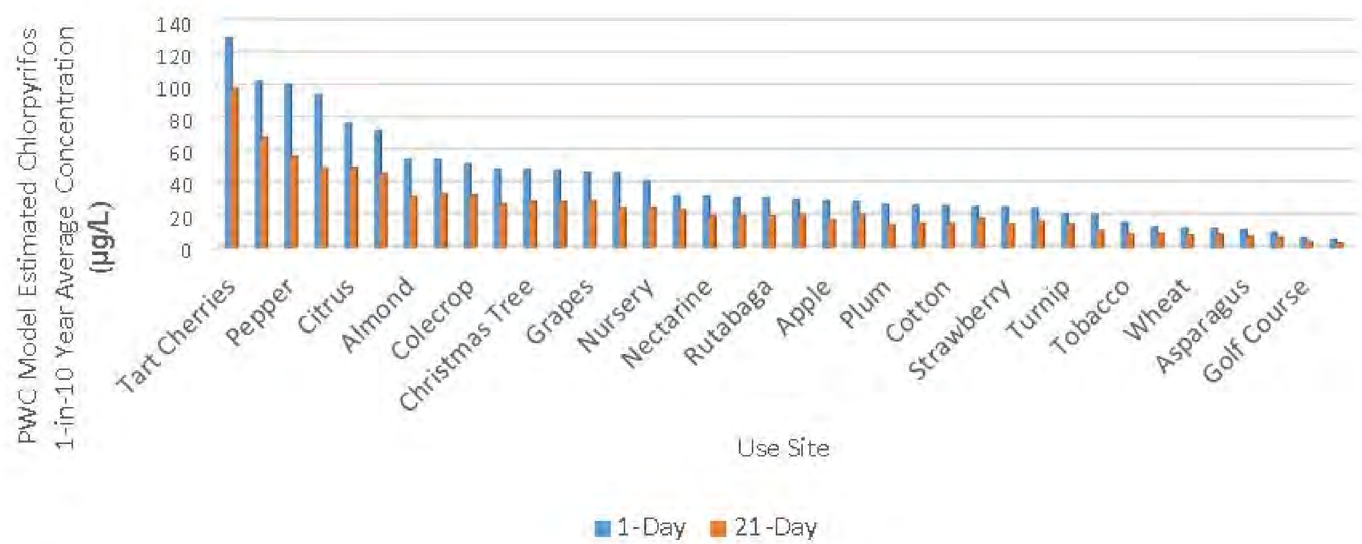


Figure 15. National Screening Level PWC Estimated Chlorpyrifos Concentrations Resulting from Maximum Labeled (single and yearly) Rates and Minimum Retreatment Intervals for Chlorpyrifos Uses on Agricultural Sites and Golf Courses

As previously reported in the 2011 and 2014 drinking water assessments, and for reasons described in the *National Level Assessment* section of this document, tart cherries and onions reasonably represent an upper and lower bound exposure potential based on maximum label (single and yearly) rates and minimum retreatment intervals. The EDWCs for chlorpyrifos and chlorpyrifos-oxon resulting from the use of surface water as sourced drinking water are presented in **Table 24** for these two exposure scenarios.

Table 24. PWC Estimated Chlorpyrifos Concentrations in Surface Water (Model Output Values; PCA 1.0)

Absolute Peak	1-in-10 Year Concentration (µg/L)				Relative Transport	Field to Water[a]
	Peak	21-day Average	Annual Average	30 Year Annual Average		
Michigan Tart Cherries						
172 (164)[b]	129 (123)	83.8 (80.0)	39.2 (37.4)	29.7 (28.3)	Runoff 18% Erosion 77% Drift 5%	1.2%
Georgia Bulb Onion						
8.5 (8.1)	6.2 (5.9)	3.1 (3.0)	1.2 (1.1)	0.8 (0.8)	Runoff 78% Erosion 18% Drift 3%	<1%

a. The relative amount of the material applied to the field that is transported off field and into the water body (*i.e.*, index reservoir).

Bracketed concentrations are for chlorpyrifos-oxon in treated drinking water assuming 100 percent conversion

The times series data for these simulations are shown in **Figure 16** and **Figure 17** for Michigan tart cherries and Georgia bulb onion, respectively. These data show that peak concentrations are not frequent, sometimes once per year (example shown in **Figure 18**). The magnitude of the peak concentrations correlate to the amount of chlorpyrifos present on the field at the time the runoff event occurs. The tailing concentrations following a peak concentration correlate to the volatilization, metabolism and washout (residence time) of the index reservoir. The residence time in a reservoir is expected to be longer than in a flowing water body, where the tailing concentrations may drop of quickly (hours to days). As such, the duration and magnitude of the tail is going to be water body specific. The sporadic nature of the exposure concentrations is consistent across scenarios for chlorpyrifos. Taken together these data suggest that unless monitoring studies are designed to target chlorpyrifos applications and unless sampling is taken frequently enough, it is unlikely that peak concentrations will be measured.

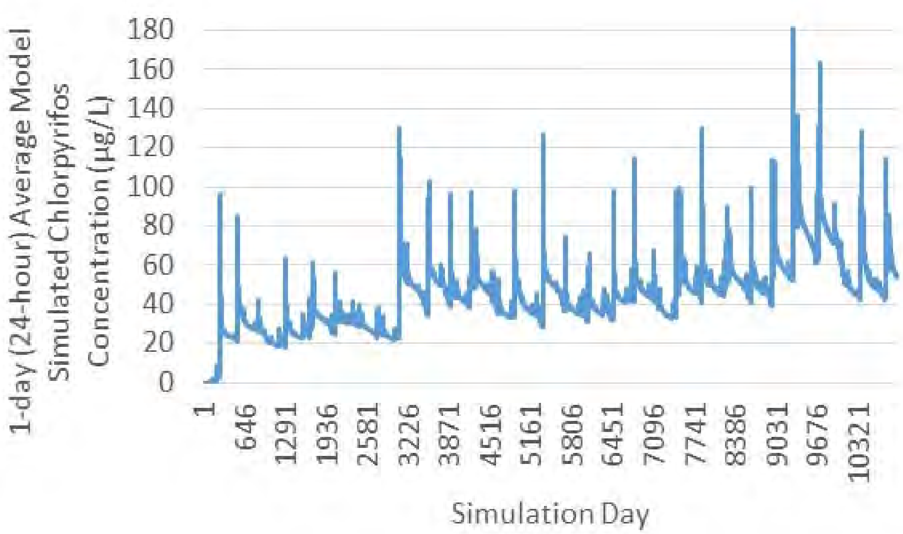


Figure 16. Time Series Data for Michigan Tart Cherries

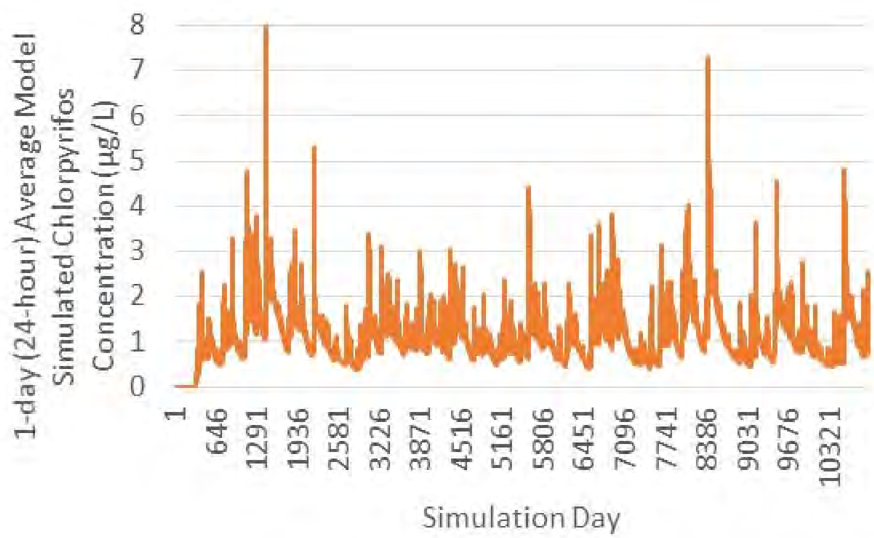


Figure 17. Time Series Data for Georgia Bulb Onion

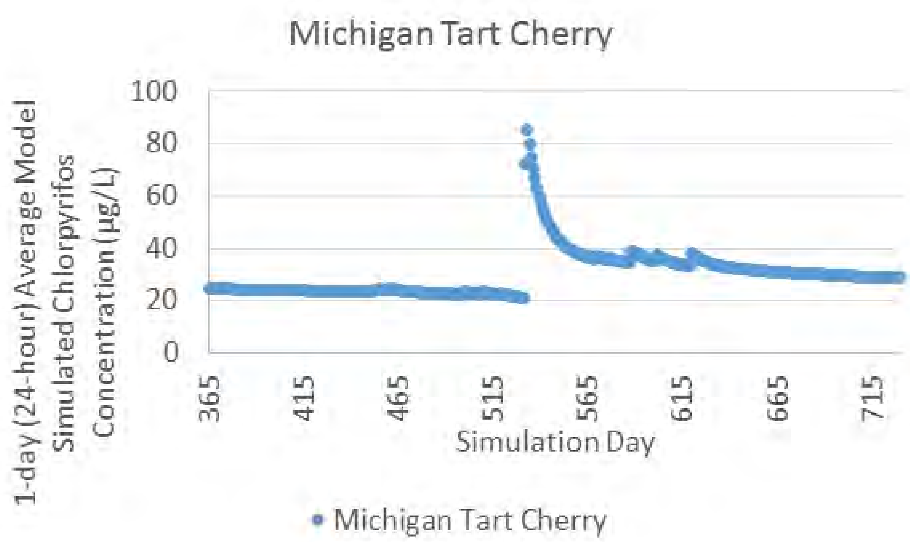


Figure 18. Time Series Data for the Second Simulation Year for Michigan Tart Cherries

As described in the drinking water treatment effects section of this document, a bounding approach was used in order to address the multitude of water treatment possibilities and potential exposures to chlorpyrifos and chlorpyrifos-oxon. Recall, chlorpyrifos converts to chlorpyrifos-oxon during some drinking water treatment processes (*e.g.*, free chlorine) while under other treatment processes it is not transformed. To represent those facilities that use disinfectant processes other than free chlorine, 100 percent of the chlorpyrifos entering the facility was assumed to be unchanged in the finished drinking water. In addition, to represent those facilities that employ chlorine as a disinfectant, 100 percent of the chlorpyrifos entering the facility was assumed to convert to chlorpyrifos-oxon. EDWCs for chlorpyrifos-oxon were derived from EDWCs for chlorpyrifos by multiplying chlorpyrifos EDWCs by 0.9541 (molecular weight adjustment factor) and 100% (maximum conversion of chlorpyrifos to chlorpyrifos-oxon during water treatment). It should be noted that an individual would not be exposed to both chlorpyrifos and chlorpyrifos-oxon at the same time at 100 percent of the EDWCs; however, both chemicals could be present in finished drinking water. Moreover, the conversion of chlorpyrifos to chlorpyrifos-oxon in the presence of chlorine may not always be quantitative. As such, an individual would be exposed to both chlorpyrifos and chlorpyrifos-oxon to some degree. In essence, complete conversion of chlorpyrifos to chlorpyrifos-oxon in the presence of chlorine is not a guarantee. For example, an individual could be exposed to 10 percent chlorpyrifos and 90 percent of chlorpyrifos-oxon.

Regional

The estimated chlorpyrifos concentration in surface water derived from the PWC modeling for maximum labeled (single and yearly) rates by HUC 2 are summarized in **Table 25**. Again, these results were corrected using the DWI PCA adjustment factor of 1 since chlorpyrifos is registered for use on turf (including sod farms, golf courses, road medians and industrial areas) as well as other wide areas uses including adult mosquito control a PCA of 1 (considers 100% of the watershed can and is treated). These results represent potential exposure to chlorpyrifos in drinking water treated using chlorine disinfectant alternatives. Results for chlorpyrifos-oxon, assuming 100 percent conversion as a result of chlorination during drinking water treatment, are also provided. While **Table 25** only provides results for the 1-in-10 year 1-day (24 hour) and 21-day average concentrations a complete set of modeling results are summarized in **ATTACHMENT 8**. This includes 1-in-10 year peak (instantaneous), 4-day, 60-day, 90-day, annual and simulation average concentrations. In addition, time series data for all simulations are available in **ATTACHMENT 9**. This is the case for all results/simulations conducted to support this assessment and presented in the sections below.

Table 25. The Range of PWC Estimated Chlorpyrifos Concentrations in Surface Water (Model Output Values) for Maximum Single <u>and</u> Yearly Label Rates on Golf Courses, Agricultural or Production Crops Excluding Seed Treatment Only Uses on a Regional Basis

HUC-02 Region	1-in-10 Year	
	1-day (24-hour) Average Concentration (µg/L)	21-day Average Concentration (µg/L)
HUC 1	8.14 – 243 (7.77 – 232)	5.04 – 159 (4.81 – 152)
HUC 2	5.11 – 110 (4.87 – 105)	2.95 - 75.6 (2.81 – 72.1)
HUC 3	4.41 - 135 (4.21 – 129)	2.24 - 84.7 (2.14 – 80.8)
HUC 4	2.04 – 241 (1.95 – 230)	1.33 – 166 (1.28 – 76.3)
HUC 5	6.02 – 111 (5.74 – 106)	3.31 - 68.3 (3.16 – 65.2)
HUC 6	2.5 – 141 (2.39 – 135)	1.34 – 80.0 (1.28 – 76.3)
HUC 7	5.7 – 123 (5.44 – 117)	3.78 - 77.1 (3.61 – 73.6)
HUC 8	6.97 – 181 (6.65 – 173)	3.42 – 106 (3.26 – 101)
HUC 9	4.14 - 250	2.52 – 166

HUC-02 Region	1-in-10 Year	
	1-day (24-hour) Average Concentration (µg/L)	21-day Average Concentration (µg/L)
	(3.95 – 239)	(2.40 – 158.4)
HUC 10a	6.88 – 109 (6.56 – 104)	4.42 - 76.2 (4.22 – 72.7)
HUC 10b	1.25 – 65.9 (1.19 – 62.9)	0.826 – 46.6 (0.788 – 44.5)
HUC 11a	4.15 – 167 (3.96 – 159)	2.15 – 97.5 (2.05 – 93.0)
HUC 11b	2.54 – 112 (2.42 – 107)	1.29 – 78.1 (1.23 – 74.5)
HUC 12a	2.44 – 145 (2.33 – 138)	1.51 - 94.9 (1.44 – 90.5)
HUC 12b	3.54 –174 (3.38 – 166)	1.96 – 94.3 (1.87 – 90.0)
HUC 13	1.42 - 69.8 (1.35 – 66.6)	0.81 – 45.7 (0.77 – 43.6)
HUC 14	1.02 - 60.7 (0.97 – 57.9)	0.719 - 34.8 (0.69 – 33.2)
HUC 15a	2.45 – 124 (2.34 – 118.3)	1.57 - 83.9 (1.50 – 80.1)
HUC 15b	0.604 - 72.5 (0.58 – 69.2)	0.445 - 39.3 (0.425 – 37.5)
HUC 16a	0.929 - 61.2 (0.89 – 58.4)	0.625 - 38.9 (0.60 – 37.1)
HUC 16b	0.607– 27.5 (0.58 – 26.2)	0.406 - 16.7 (0.39 – 15.9)
HUC 17a	5.23 – 302 (4.99 – 288)	3.46 – 214 (3.30 – 204)
HUC 17b	0.689 – 104 (0.66 – 99.2)	0.495 - 81.8 (0.47 – 78.1)
HUC 18a	2.28 – 367 (2.18 – 350)	1.39 – 269 (1.33 –257)
HUC 18b	1.31 – 249 (1.25 – 237)	0.814 – 161 (0.78 – 154)
HUC 19a	1.17 –207 (1.12 – 198)	0.817 – 160 (0.780 – 153)
HJC 19b	2.33 – 342 (2.22 – 326)	1.79 – 243 (1.71 – 232)
HUC 20a	13.7 – 1220 (13.1 – 1164)	6.88 – 613 (6.56 – 585)
HUC 20b	6.22 – 418 (5.93 – 398.77)	3.96 – 241 (3.78 – 230)
HUC 21	5.82 – 410 (5.55 – 391)	4.92 – 222 (4.69 – 212)
Bracketed concentrations are for chlorpyrifos-oxon in treated drinking water assuming 100 percent conversion.		

Note that **Table 25** does not include results for seed only treatments (*i.e.*, beans, cucumber, pea, pumpkin, and triticale), adult mosquito control or urban use scenarios. The PWC does not estimate exposure (0.0 µg/L) to chlorpyrifos or chlorpyrifos-oxon via drinking water for chlorpyrifos use as a seed only treatment. This is because of the assumed incorporation depth for each of these uses limits runoff of chlorpyrifos from the field to the adjacent waterbody. Other seed treatment uses may results in exposure depending on the planting depth. Results for chlorpyrifos use as an adult mosquito control are provided in **Table 26**. Urban use scenarios are provided in **Table 27** and **Table 28**.

Table 26. The Range of PWC Estimated Chlorpyrifos and Chlorpyrifos-oxon Concentrations in Surface Water (Model Output Values) for Chlorpyrifos Use as an Adult Mosquito Control on a Regional Basis

HUC-02 Region	1-in-10 Year			
	1-day (24-hour) Average Concentration (µg/L)		21-day Average Concentration (µg/L)	
	Chlorpyrifos	Chlorpyrifos-oxon[a]	Chlorpyrifos	Chlorpyrifos-oxon[a]
HUC 1	0.996	0.950	0.547	0.522
HUC 2	0.859	0.820	0.545	0.520
HUC 3	0.983	0.938	0.533	0.509
HUC 4	0.837	0.799	0.579	0.552
HUC 5	0.817	0.779	0.498	0.475
HUC 6	1.13	1.078	0.622	0.593
HUC 7	1.16	1.107	0.76	0.725
HUC 8	1.16	1.107	0.762	0.727
HUC 9	0.894	0.853	0.543	0.518
HUC 10a	1.18	1.126	0.733	0.699
HUC 10b	0.601	0.573	0.378	0.361
HUC 11a	1.02	0.973	0.593	0.566
HUC 11b	0.984	0.939	0.535	0.510
HUC 12a	1.11	1.059	0.583	0.556
HUC 12b	1.42	1.355	0.747	0.713
HUC 13	0.544	0.519	0.297	0.283
HUC 14	0.51	0.487	0.318	0.303
HUC 15a	0.748	0.714	0.49	0.468
HUC 15b	0.315	0.301	0.229	0.218
HUC 16a	0.373	0.356	0.259	0.247
HUC 16b	0.244	0.233	0.157	0.150
HUC 17a	1.55	1.479	1.04	0.992
HUC 17b	0.294	0.281	0.202	0.193
HUC 18a	1.15	1.097	0.767	0.732

HUC-02 Region	1-in-10 Year			
	1-day (24-hour) Average Concentration (µg/L)		21-day Average Concentration (µg/L)	
	Chlorpyrifos	Chlorpyrifos-oxon[a]	Chlorpyrifos	Chlorpyrifos-oxon[a]
HUC 18b	0.745	0.711	0.436	0.416
HUC 19a	0.585	0.558	0.366	0.349
HUC 19b	0.927	0.884	0.647	0.617
HUC 20a	0.585	0.558	0.366	0.349
HUC 20b	0.927	0.884	0.647	0.617
HUC 21	2.83	2.700	1.34	1.278

a. concentrations calculated by using a molecular weight adjustment factor of 0.9541 to convert chlorpyrifos to chlorpyrifos-oxon concentrations.

Table 27. The Range of Estimated 1-in-10-year 1-day (24-hour average) Chlorpyrifos Concentrations in Surface Water (Model Output Values) for Urban Chlorpyrifos Uses

HUC 2	Perimeter	Foundation and Walls	Trash Storage	Utility	Wood Treatment (*i.e.*, Fence)
	1-in-10 Year 1-day (24-hour) Average Concentration (µg/L)				
01	22.4	10.3	86.5	3.15	399
02	28.9	12.5	123	2.57	319
03	24.8	10.5	97.3	3.41	487
04	15.5	9.6	92.9	2.49	475
05	19	10.5	87.8	2.52	537
06	23.3	8.6	78.4	2.89	459
07	28.9	12.5	99.1	2.82	452
08	33.9	10.9	94.6	3.02	529
09	18.5	11.0	107	2.23	339
10a	18.8	13.9	131	3.23	425
10b	11.1	6.5	66.3	1.33	216
11a	30.4	11.0	104	3.84	547
11b	26.1	11.7	136	3.04	446
12a	28.2	14.0	160	3.56	505
12b	20.2	11.2	117	4.29	516
13	9.97	7.9	72.9	1.48	309
14	10.2	11.7	129	0.968	189
15a	23.1	10.6	116	1.64	350
15b	11.2	7.3	96.9	0.809	318
16a	9.79	6.6	73.6	0.849	225
16b	4.44	6.0	83.9	0.415	96
17a	34	11.4	84.7	4.92	304

17b	5.87	4.7	56	0.6	136
18a	20.1	10.3	94.3	2.91	443
18b	14.6	9.1	99.7	1.74	344
19a	8.54	3.5	28.4	6.28	188
19b	14.6	5.6	53.2	4.78	331
20a	36	11.4	73.5	3.87	953
20b	68.9	20.9	111	3.15	583
21	38.9	12.4	81.8	2.57	548

Table 28. The Range of Estimated 1-in-10-year 21-day Chlorpyrifos Concentrations in Surface Water (Model Output Values) for Urban Chlorpyrifos Uses (one 1 lb a.i./A/year)

HUC 2	Perimeter	Foundation and Walls	Trash Storage	Utility	Wood Treatment (*i.e.*, Fence)
	1-in-10 Year 1-day (24-hour) Average Concentration (µg/L)				
01	13.5	6.0	49.2	1.86	238
02	18.3	7.6	60.9	1.46	185
03	14.5	6.3	55.6	1.75	244
04	11.1	6.3	58	1.32	257
05	12.2	5.8	53.4	1.4	271
06	12	5.4	42.9	1.66	230
07	19	7.3	59.1	1.69	261
08	19.6	6.0	45.8	1.63	238
09	12.7	7.6	65.8	1.17	229
10a	11.7	8.1	81.6	1.79	243
10b	7.02	4.2	42.8	0.9	123
11a	14.9	6.4	58.1	1.95	313
11b	13.3	6.9	73.2	1.69	275
12a	15.4	7.2	70.7	2.05	301
12b	11.1	6.3	64.4	2.05	261
13	5.52	5.0	53.5	0.737	167
14	5.75	6.2	68.8	0.581	104
15a	14.5	6.2	58.6	1.09	175
15b	5.69	4.3	56.1	0.488	145
16a	5.7	4.3	44.9	0.545	135
16b	2.59	3.3	44.7	0.237	53
17a	23.7	7.1	49.5	3.04	196
17b	3.52	3.2	32.9	0.354	82
18a	13.8	6.9	56.8	1.7	252
18b	9.17	6.0	57.6	1.01	190
19a	5.68	2.5	21.7	3.21	127

19b	10.7	3.6	35.6	2.53	225
20a	16.5	5.6	42.2	2.23	409
20b	38.1	10.9	58.3	1.86	344
21	23.2	6.4	47.3	1.46	271

Aside from urban uses which are discussed in greater detail later in this document, the highest estimated chlorpyrifos and chlorpyrifos-oxon concentrations derived are generally estimated for vegetable crops, wide area uses and for tree fruits and nuts.

The highest estimated chlorpyrifos (and chlorpyrifos-oxon) concentrations based on the regional analysis are for the rutabaga scenario in locations. Current label restrictions for rutabaga are based on a crop cycle basis. As such, it is possible to have multiple crop seasons per year some regions. The highest concentration estimated as part of this regional analysis is for chlorpyrifos use on rutabaga in HUC-02 region 20 where multiple crops seasons per year are possible as well as heavy rainfall events.

Concentrations estimated for wide area uses scenarios are also generally high. This is the result of multiple applications per year considered in the model simulations. The current label does not specify the number of applications per year for wide area uses. Some labels state to apply as needed. As such, 12 applications were assumed for modeling purposes. Wide area uses were not considered in the previous drinking water assessments as previous work primary focused on agricultural uses sites and label clarification efforts.

Of the fruit and nut trees, the tart cherry scenario provides the highest exposure estimates. This is consistent with the national level assessment, as well as the previous drinking water exposure assessments. However, using the regional approach (representative crop group scenario and weather data) there are some regions with estimated exposures higher than that estimated using the standard Michigan Cherry scenario used in the national assessment. The range for estimated chlorpyrifos concentrations for tart cherries across all relevant HUC-02 regions is provided in **Figure 19**. This highlights the impact of different soil and weather combinations that exist across the landscape and the potential variation in concentrations that likely exist across the landscape. This also demonstrates that the standard scenarios represent vulnerable soil-weather combinations, but that they are not designed to capture the highest possible exposure scenario. Rather, the scenarios are intended to provide a reasonable upper bound.

It should be noted that the representative HUC-02 region 4 scenario (NYgrapes and w14839) results in higher concentrations than the standard Michigan Cherry (w14850) scenario. This is primarily due to the selection of the application date. As part of the regional approach, application dates were primarily selected based on the month with the highest cumulative precipitation. This was done to facilitate running the extensive number of model simulations in a batch mode. While the application date is a sensitive parameter, it is not expected to change the interpretation of this drinking water assessment and subsequent human health dietary risk assessment conclusions. To this end, as part of a sensitivity analysis the impact of application date was assessed over a 365 day window (**ATTACHMENT 10**).

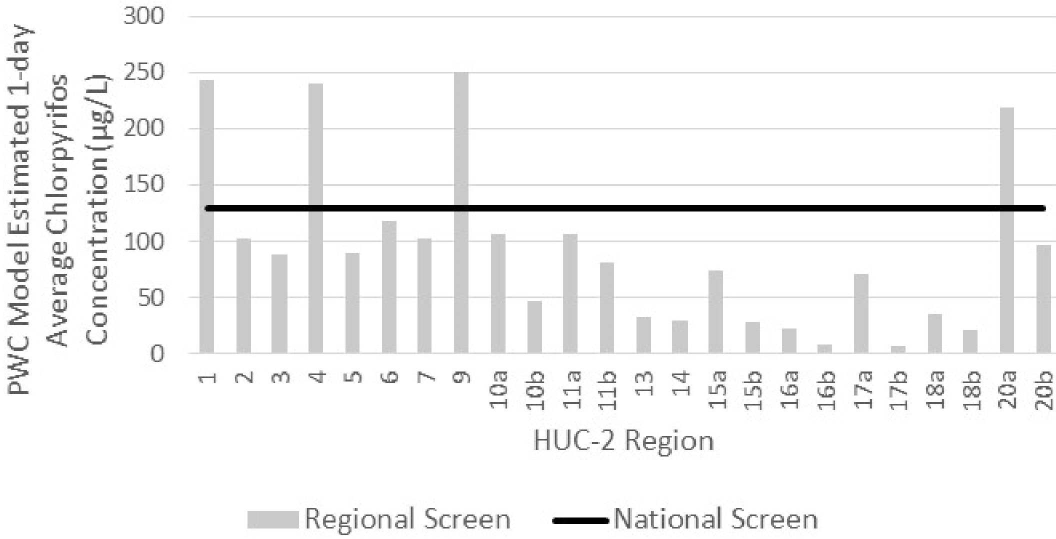


Figure 19. PWC Estimated 1-in-10 Year 1-day (24 hour) Average Chlorpyrifos Concentrations for Chlorpyrifos Use on Tart Cherries

The estimated chlorpyrifos and chlorpyrifos-oxon concentration in surface water derived from the PWC modeling based on a single application at 1 lb a.i./A are summarized in **Table 29** by HUC-02 region and chlorpyrifos use grouping. **Table 33** presents the EDWCs for one single adult mosquito control application per year. The complete set of modeling results are available in **ATTACHMENT 9**.

Table 29. The Range of Estimated 1-in-10-year 1-day (24-hour average) Chlorpyrifos Concentrations in Surface Water (Model Output Values) for Chlorpyrifos Use (one 1 lb a.i./A/year)

HUC 2	Range of Values	Impervious	Corn	Soybean	Cotton	Developed	Golf	Wide Area	Grassland	Pasture/ Hay/Rangeland/ Other Crops	Non-specified land cover
	1-in-10 Year 1-day (24-hour) Average Concentration (µg/L)										
01	3.86 - 147	147	12.9	12.9	[redacted]	23.4	3.86	23.4	9.51	9.65	7.47
02	2.52 - 135	135	7.94	7.94	16.3	19	2.52	19	2.71	2.52	9.11
03	2.1 - 256	256	8.36	8.36	22	25.3	2.1	25.3	9.69	9.76	7.64
04	2.48 - 238	238	6.08	6.08	[redacted]	18.5	2.48	18.5	2.95	2.48	6.53
05	3.1 - 230	230	18.2	18.2	17	18.9	3.1	18.9	7.71	7.57	9.29
06	1.22 - 176	176	7.93	7.93	18.7	21.4	1.22	21.4	8.31	8.41	8.13
07	3.21 - 242	242	17.9	17.9	18.3	20.9	3.21	20.9	9.06	9.25	8.74
08	3.35 - 287	287	16.9	16.9	16.8	22.4	3.35	22.4	11.7	12.1	9.27
09	1.85 - 183	183	6.11	6.11	[redacted]	16.6	1.97	16.6	2.29	1.85	5.61
10a	4.53 - 243	243	12.5	12.5	15.4	24	4.53	24	8.45	8.34	10.2
10b	0.611 - 113	113	6.53	6.53	6.65	9.95	0.611	9.95	3.06	2.77	4.33
11a	2.42 - 256	256	22.9	22.9	18.7	28.5	2.42	28.5	13.4	13.6	13.2
11b	1.16 - 216	216	14.8	14.8	15	22.6	1.16	22.6	9.75	9.53	9.39
12a	1.42 - 236	236	17.1	17.1	17.3	26.6	1.42	26.6	11.3	11.5	7.43
12b	1.79 - 181	181	17.5	17.5	15.7	32	1.79	32	12.2	11.9	7.55
13	0.77 - 110	110	11.4	11.4	6.12	11.1	0.77	11.1	4.32	3.67	2.71
14	0.511 - 127	127	8.29	8.29	5.38	7.27	0.511	7.27	2.29	1.91	4.04
15a	1.19 - 177	177	12.1	12.1	7.81	12.2	1.19	12.2	5.04	4.99	3.63
15b	0.35 - 132	132	6.37	6.37	5.48	6.06	0.35	6.06	1.78	1.66	1.28
16a	0.48 - 147	147	6.11	6.11	[redacted]	6.37	0.48	6.37	2.87	2.37	5.3
16b	0.377 - 66.3	66.3	4.12	4.12	[redacted]	3.17	0.377	3.17	1.89	0.659	3.52
17a	2.67 - 273	273	27.8	27.8	[redacted]	36.6	3.47	36.6	16	16.3	10.3

17b	0.415 - 89.4	89.4	3.64	3.64	[redacted]	4.56	0.415	4.56	2.08	0.85	1.32
18a	0.669 – 178	155	20.2	20.2	12.2	21.7	1.22	21.7	8.88	8.97	27.3
18b	0.651 – 182	182	10.1	10.1	6.93	12.9	0.651	12.9	4.79	4.69	13
19a	0.639 – 118	118	[redacted]	[redacted]	[redacted]	9.47	0.639	9.52	3.31	2.79	2.01
19b	1.02 - 169	169	[redacted]	[redacted]	[redacted]	17.0	1.25	17	7.56	7.5	3.47
20a	6.94 – 323	323	26.8	18.9	[redacted]	46.5	6.94	46.5	8.43	8.56	19.2
20b	3.12 – 230	230	15	10.4	[redacted]	35.4	3.12	35.4	4.31	4.23	9.45
21	3.5 – 274	274	12.1	[redacted]	[redacted]	24.4	3.5	24.4	[redacted]	[redacted]	11.1

Table 30. The Range of Estimated 1-day (24-hour average) Chlorpyrifos Concentrations in Surface Water (Model Output Values) for Chlorpyrifos Use (one 1 lb a.i./A/year) (continued)

HUC 2	Other Trees Christmas Tree	Orchards/ Vineyards	Other Grain	Other Row Crop	Wheat	Vegetables/ Ground Fruit
	1-in-10 Year 1-day (24-hour) Average Concentration (μg/L)					
01	22.5	22.5	7.66	20.1	7.66	20.5
02	7.64	7.63	6.52	8.13	6.52	17.5
03	7.53	7.52	10	19.8	9.69	9.06
04	19.9	24.4	6.45	6.63	6.64	6.38
05	8.02	8.01	16	16.6	16	10.1
06	11.3	11.3	8.31	7.93	8.31	10.1
07	7.43	7.42	9.06	17.9	9.06	21.4
08	8.51	8.5	17	13.3	9.9	13.7
09	14.8	22.1	5.52	4.55	5.86	4.19
10a	8.53	10.1	17.3	12.5	9.76	7.89
10b	2.85	3.12	9.79	6.53	5.98	3.89
11a	9.61	12.3	19.7	22.9	19.7	19
11b	7.15	8.63	16.4	14.8	16.4	15.4

12a	10.4	10.4	10.1	17.1	10.1	15.8
12b	11.4	11.4	11.1	17.5	11.1	19.5
13	3.22	3.2	3.4	6.9	3.4	8.2
14	1.94	1.92	2.38	4.42	2.38	5.43
15a	5.3	5.29	4.96	7.59	4.96	19.1
15b	1.7	1.69	2	2.94	2	8.41
16a	3.19	3.17	2.45	4.02	2.45	3.59
16b	0.583	0.57	1.9	2.06	1.9	1.41
17a	9.93	12.4	16	19.1	16	21.2
17b	0.483	0.575	2.08	2.15	2.08	2.66
18a	6.18	6.17	20.6	5.2	20.6	12.2
18b	3.37	3.36	12.9	2.76	12.9	6.63
19a	1.02	2.19	2.47	[redacted]	3.31	3.24
19b	2.77	4.44	3.65	[redacted]	7.65	7.41
20a	18.3	18.3	22.8	21.2	[redacted]	25.4
20b	10.3	10.3	10.8	11.9	[redacted]	17.5
21	18.1	17.4	[redacted]	[redacted]	[redacted]	13.4

Table 31. The Range of Estimated 1-in-10-year 21-day Average Chlorpyrifos Concentrations in Surface Water (Model Output Values) for Chlorpyrifos Use (one 1 lb a.i./A/year)

HUC 2	Range	Impervious	Corn	Soybean	Cotton	Developed	Golf	Wide Area	Grassland	Pasture/ Hay/Rangeland/ Other Crops	Non-specified land cover
	1-in-10 Year 1-day (24-hour) Average Concentration (µg/L)										
01	2.4 - 64.9	64.9	8.32	8.32		13.8	2.4	13.8	6.04	6.05	5.16
02	1.46 - 60.6	60.6	5.12	5.12	10.8	10.8	1.46	10.8	1.68	1.46	5.41
03	1.11 – 111	111	4.93	4.93	12.7	13	1.11	13	5.32	5.29	4.16
04	1.92 – 114	114	3.79	3.79		9.81	1.92	9.81	2.13	1.92	4.11
05	1.73 - 98.5	98.5	11.6	11.6	10.8	10.4	1.73	10.4	4.46	4.34	5.49
06	0.654 - 80.5	80.5	4.94	4.94	12	12.3	0.654	12.3	5.15	5.11	4.76
07	2.18 – 104	104	12	12	12	12.6	2.18	12.6	5.18	5.21	5.36
08	1.65 – 111	111	9.73	9.73	10.2	12.1	1.65	12.1	6.9	7.05	4.98
09	1.01 - 90.6	90.6	3.69	3.69		8.75	1.2	8.75	1.51	1.01	3.74
10a	2.51 – 114	114	8.09	8.09	8.91	13.3	2.51	13.3	5.63	5.52	6.15
10b	0.403 - 57.3	57.3	4.39	4.39	4.78	6.74	0.403	6.74	2.09	1.83	3.03
11a	1.36 – 113	113	12.8	12.8	10.4	14.5	1.36	14.5	7.34	7.37	6.99
11b	0.627 – 102	102	9.11	9.11	8.94	12.6	0.627	12.6	5.88	5.71	5.24
12a	0.783 – 103	103	11.7	11.7	11.5	15.3	0.783	15.3	7.45	7.34	4.4
12b	0.998 - 84.8	84.8	9.04	9.04	8.51	15.2	0.998	15.2	5.89	5.7	4.15
13	0.438 - 55.7	55.7	7.07	7.07	3.83	5.53	0.438	5.53	2.27	1.82	1.48
14	0.356 - 63.7	63.7	5.63	5.63	3.43	4.4	0.356	4.4	1.56	1.09	3.01
15a	0.755 - 79.4	79.4	7.91	7.91	5.33	8.15	0.755	8.15	3.38	3.25	2.31

15b	0.215 - 69.9	69.9	3.97	3.97	3.03	3.65	0.215	3.65	1.18	1.03	0.84
16a	0.308 – 74	74	4.36	4.36		4.13	0.308	4.13	1.83	1.46	3.11
16b	0.216 – 34	34	2.67	2.67		1.85	0.216	1.85	1.1	0.449	2.15
17a	1.88 – 121	121	19.2	19.2		22.6	2.23	22.6	10.9	11.1	6.59
17b	0.258 - 46.5	46.5	2.53	2.53		2.72	0.258	2.72	1.3	0.624	1.23
18a	0.463 - 86.2	79	12	12	7.29	12.7	0.707	12.7	5.36	5.31	16.4
18b	0.409 - 91.1	91.1	6.27	6.27	4.23	7.5	0.409	7.5	2.89	2.73	8.45
19a	0.44 - 58.5	58.5				6.01	0.44	6.07	2.52	1.83	1.4
19b	1.01 – 77.7	77.7				11.2	1.01	11.2	5.64	5.52	2.65
20a	3.63 – 101	101	13.5	9.75		23.8	3.63	23.8	4.13	4.11	9.24
20b	1.89 – 101	101	8.29	7.97		18.8	1.89	18.8	2.73	2.55	5.16
21	1.79 – 110	110	6.97			14	1.79	14			6.58

Table 32. The Range of Estimated 1-in-10-year 21-day Average Chlorpyrifos Concentrations in Surface Water (Model Output Values) for Chlorpyrifos Use (one 1 lb a.i./A/year) (continued)

HUC 2	Other Trees Christmas Tree[a]	Orchards/ Vineyards	Other Grain	Other Row Crop	Wheat	Vegetables/ Ground Fruit
	1-in-10 Year 1-day (24-hour) Average Concentration (µg/L)					
01	14.4	14.4	4.91	14	4.91	14.3
02	4.65	4.65	3.83	4.71	3.83	10.3
03	4.31	4.3	6.01	11.3	5.32	5.54
04	12.2	15.7	3.88	3.92	4.16	3.89
05	5.08	5.06	9.78	10.4	9.78	6.29
06	7.45	7.44	5.15	4.94	5.15	6.19
07	4.82	4.81	5.18	12	5.18	13.9
08	5.06	5.06	10	8.15	5.74	8.32

09	8.88	14.5	3.2	3.01	3.79	2.63
10a	4.82	5.78	11.1	8.09	5.77	4.45
10b	1.96	2.25	6.64	4.39	3.86	2.54
11a	5.23	6.42	10.4	12.8	10.4	10.5
11b	4	4.64	9.67	9.11	9.67	9.15
12a	6.37	6.35	6.55	11.7	6.55	11
12b	6.81	6.8	5.51	9.04	5.51	10.2
13	1.76	1.75	2.16	3.93	2.16	4.76
14	1.1	1.09	1.59	2.83	1.59	3.31
15a	3.47	3.46	3.33	5.39	3.33	12
15b	0.976	0.97	1.29	1.94	1.29	5.88
16a	1.77	1.76	1.52	2.59	1.52	2.11
16b	0.367	0.355	1.14	1.26	1.14	0.902
17a	6.04	8.05	10.9	13.5	10.9	14.1
17b	0.302	0.376	1.3	1.35	1.3	1.63
18a	3.48	3.47	12.1	3.26	12.1	6.93
18b	1.88	1.87	7.8	1.62	7.8	4.05
19a	0.612	1.36	1.44	[redacted]	2.52	2.17
19b	2.06	3.46	2.64	[redacted]	5.64	4.95
20a	9.04	9.04	11.7	11.1	[redacted]	12.1
20b	6.11	6.1	7.75	7.48	[redacted]	9.24
21	10.6	9.64	[redacted]			7.01

Table 33. The Range of PWC Estimated Chlorpyrifos Concentrations in Surface Water (Model Output Values) for Chlorpyrifos and Chlorpyrifos-oxon Use as an Adult Mosquito Control (1 application per year) on a Regional Basis

HUC-02 Region	1-in-10 Year			
	1-day (24-hour) Average Concentration (µg/L)		21-day Average Concentration (µg/L)	
	Chlorpyrifos	Chlorpyrifos-oxon[a]	Chlorpyrifos	Chlorpyrifos-oxon[a]
HUC 1	0.04	0.04	0.02	0.02
HUC 2	0.03	0.03	0.02	0.02
HUC 3	0.05	0.04	0.03	0.02
HUC 4	0.04	0.04	0.02	0.02
HUC 5	0.04	0.04	0.02	0.02
HUC 6	0.05	0.04	0.03	0.03
HUC 7	0.05	0.04	0.03	0.03
HUC 8	0.05	0.05	0.03	0.03
HUC 9	0.04	0.04	0.02	0.02
HUC 10a	0.05	0.05	0.03	0.03
HUC 10b	0.02	0.02	0.02	0.01
HUC 11a	0.06	0.06	0.03	0.03
HUC 11b	0.05	0.05	0.03	0.03
HUC 12a	0.06	0.06	0.03	0.03
HUC 12b	0.07	0.07	0.03	0.03
HUC 13	0.03	0.03	0.01	0.01
HUC 14	0.02	0.02	0.01	0.01
HUC 15a	0.03	0.03	0.02	0.02
HUC 15b	0.01	0.01	0.01	0.01
HUC 16a	0.02	0.02	0.01	0.01
HUC 16b	0.01	0.01	0.01	0.01
HUC 17a	0.08	0.08	0.05	0.05
HUC 17b	0.01	0.01	0.01	0.01
HUC 18a	0.05	0.05	0.03	0.03
HUC 18b	0.03	0.03	0.02	0.02
HUC 20a	0.02	0.02	0.02	0.01
HUC 20b	0.04	0.04	0.03	0.03
HUC 21	0.10	0.09	0.05	0.05
a. concentrations calculated by using a molecular weight adjustment factor of 0.9541 to convert chlorpyrifos to chlorpyrifos-oxon concentrations.				

ii. PFAM

Cranberry

The PFAM modeled 1-in-10 year 1-day (24-hour average) concentrations associated with chlorpyrifos use on cranberries ranged from 36.1 to 55.7 µg/L for the Connecticut (HUC-02 region 1) and Wisconsin (HUC-02 Region 4) scenarios, respectively. The 1-in-10 year 21-day average concentration range from 35.1 to 61.1 µg/L. These results represent potential exposure from wet-harvested cranberry growing areas (*i.e.*, cranberry bogs). Peak concentrations occurred during the winter flood in January, and not during the three day harvest flood simulated in October. This is likely due to chlorpyrifos partitioning to the water phase from the sediment in the bog over the flood period. The winter flood is longer than the harvest flood providing more time for this partition process to occur, thus resulting in higher concentrations.

The PFAM estimates provided above may overestimate actual concentrations in drinking water as they represent the in-bog water concentrations of chlorpyrifos in a wet harvest environment. These concentrations are not expected to occur outside the cranberry bog. Although there are some drinking water intakes that are impacted by cranberry bogs, the intakes are not located within cranberry bogs. Water released from a cranberry bog will undergo some degree of dilution before reaching a drinking water intake. The extent of dilution is not known.

The PWC modeled 1-in-10 year 1-day (24-hour average) concentrations associated with chlorpyrifos use on cranberries ranged from 21.5 to 53.2 µg/L[81] for the HUC-02 regions 4 and 2. The 1-in-10 year 21-day concentrations range from 11.9 to 31.2 µg/L. These estimates are lower than those estimated for other chlorpyrifos use patterns, but are similar to those obtained using PFAM for bog water concentrations. It is reasonable to assume that based on the use scenario modeled (dry harvested cranberries at maximum labeled rates and minimum treatment intervals) these estimates represent the potential exposure to chlorpyrifos and chlorpyrifos-oxon (considering the molecular weight adjustment factor and complete conversion of chlorpyrifos to chlorpyrifos-oxon during drinking water treatment) in surface sourced drinking water. However, other uses within the watershed may actually result in a higher potential exposure.

Analysis of the locations of drinking water intakes in areas where cranberries are grown indicates that the area where drinking water is most likely to be influenced by pesticides used on cranberries is in Massachusetts.[82]

iii. Discussion and Conclusions

This refined drinking water assessment provides exposure estimates for chlorpyrifos and chlorpyrifos-oxon for all currently registered uses of chlorpyrifos at maximum label rates on a national as well as regional basis. **Table 34** provides a general overview of model refinement considered in this drinking

[81] HUC-02 Region 17b results in lower exposure estimates; however, the weather files used is associated with areas east of the Cascade Mountains and as such is not representative of the cranberry growing regions. Therefore, the results of this simulation are excluded from this analysis.

[82] Lafleur, J. 2002. Resource Planning for Cranberry Bogs within Drinking Water Supply Areas. Project Number 99-14SWT. June 14, 2002. Cape Cod Cranberry Growers' Association. Available at http://www.cranberries.org/pdf/resource_planning_2002.pdf (Accessed March 4, 2015).

water assessment. In addition, simulations were completed for alternative use scenarios, with application rates of one application at 1 lb. a.i./acre. All results of the model simulations are provided in **ATTACHMENT 8** and **ATTACHMENT 9** so that each application scenario can be evaluated and alternative use scenarios can be examined including altering PCA (*e.g.*, limiting chlorpyrifos to only agricultural crops, corn, or vegetables).

Table 34. Drinking Water Assessments Refinements

Parameter	Standard Approach	Refined Approach	Comments
Model Simulations			
Catchment area	1,728,000 m^2	Examine catchment areas with respect to range of drinking water intake watersheds.	Additional characterization is provided; however, use of the community water system drinking water data set is limited because of the extent of chlorpyrifos uses including adult mosquito control, golf course turf, and general wide area use.
Catchment soil conditions	Single, runoff prone (Hydrologic Soil Group C or D) soil type for entire field or watershed. Runoff driven by curve numbers (crop and no crop) that represents the single soil and crop use being modeled.	Same	Examine a range of scenarios with different runoff potentials (*i.e.*, curve numbers).
Pesticide inputs into catchment	Application according to label rates and timing, adjusted for crop area (assumes 100% of field for exposure)	Application of percent cropped area adjustment for drinking water intakes. Examination of alternative use rates.	Use of the community water system drinking water data set is limited because of the extent of chlorpyrifos uses including adult mosquito control, golf course turf, and general wide area use.
Pesticide fate in catchment (and amount available for transport)	First-order transformation and linear equilibrium sorption in soil. Finite difference solution to advection-dispersion equation.	Same	
Weather inputs	30 years (1961-1990) (SAMSON dataset)	Used regionally representative meteorological data.	Also examined different meteorological data within a region for those regions with substantial differences. Completed a sensitivity analysis looking at application date as well as applications occurring over a window of several days.
Water body	52,609 m^2 (area), 0.05 m (depth), 2630 m^3	Same	

Parameter	Standard Approach	Refined Approach	Comments
	(volume), 640 m (length), 82.2 m (width)		
Pesticide inputs to water	Pesticide mass flux in runoff (dissolved) and erosion (sorbed) by rain events. Spray drift mass based on application and required aquatic spray drift buffers.	Same	
Pesticide fate in water	Aerobic aquatic half-life (metabolism, hydrolysis, photolysis). First-order mass transfer between water column and sediment. Equilibrium partitioning to sediment	Same, sensitivity analysis (*i.e.*, bounding estimates) completed.	
Water body flow/dilution	Pesticide mass added instantaneously to fixed water body volume.	Same	

Based on maximum labeled rates, exposure to chlorpyrifos and chlorpyrifos-oxon in drinking water may be high (>100 µg/L) in some locations. Generally, exposure will be higher in areas with higher use intensity (higher application rates and more use sites); however, site vulnerability also plays a role. The residue of exposure concern depends on the treatment methods utilized by individual community water systems. A sensitivity analysis showed that adjustments to individual model input parameters, including environmental fate inputs and agronomical practices (exception being soil incorporation) do not substantially change EDWCs. Moreover, this is well within the range of the ranged of available monitoring data when bias factor adjustments are considered (see **Integration** section below for more discussion).

Although the model simulations suggest relatively high concentrations of chlorpyrifos in the receiving waterbody, previous analyses have shown that only a small amount (≤ 1.2%) applied to the field reaches the water body. This is consistent with a runoff study conducted by the registrant (MRID 00144906) that suggests that the amount of chlorpyrifos transported from a treated field (corn watersheds in Illinois) to proximal water bodies is generally less than one percent of the applied material.[83] Depending on the scenario used in the modeling simulations, the transport of chlorpyrifos from the field to the receiving water body is either primarily through runoff or erosion (**Table 24**) and the total mass transported from the field may be higher than 1.2% for other PRZM scenarios.

While model simulations consider the required aquatic spray drift buffers, these buffers may also reduce the transport of chlorpyrifos via runoff and erosion of chlorpyrifos from the field to the water body.

[83] McCall, P. J., Oliver, G. R., McKeller, R. L. Modeling the runoff potential and behavior of chlorpyrifos in a terrestrial aquatic watershed (DowElanco unpublished report GH-C 1964) 1984

Spray drift buffers provide distance between the field and the neighboring water body; however, it is unclear to what extent they may act like a filter strip. EFED does not currently have an exposure tool to assess the impact of vegetative filter strips (VFS) on reducing runoff and erosion; however, the development and maintenance of VFS is highly variable. Large runoff or erosion events are trigged by larger storm events, which are likely to overcome the buffer or VFS with sheet or channelized flow providing a direct conduit to the nearby water body. A U.S. Geological Survey (USGS) report suggests that sheet flow is expected at distances up to 100 feet.[84] Moreover, a review article on the reduction of herbicide concentrations from fields with VFS was not able to document a decline in herbicide concentrations in receiving water bodies as a result of VFS, and that data specifically on a watershed scale is lacking.[85] In addition, this review concluded that retention of sediment as a function of the VSF width was nonlinear, with most of the retention occurring within the first few meters.

Once in the water body, chlorpyrifos dissipation is scenario specific; however, the primary mechanisms of chlorpyrifos dissipation are volatilization, metabolism and washout. Based on laboratory studies, chlorpyrifos is expected to partition to sediment; however, this does not mean a complete reduction in chlorpyrifos in the water column is expected.

b. Monitoring

i. Monitoring Programs Summary

Surface water monitoring programs considered as part of this assessment include Dow Agrosciences California Monitoring Program, California Department of Regulation Surface Water Database (SURF), California Environmental Data Exchange Network (CEDEN), Central Coast Water Quality Preservation (CCWQP), Central Valley Irrigated Land Program **(**ILRP_5) , Central Valley Regional Water Control Board (CV_DNC_BPA), Oregon ELEM (OR ELEM), Registrants Organophosphate Monitoring Study, US EPA Storage and Retrieval Warehouse (STORET), USDA Pesticide Data Program (PDP), USGS National Water Information System (NWIS), USGS National Water Quality Assessment (NAWQA), USGS_EPA Stream Quality Index (USGS_MSQI), USGS State Data, USGS-EPA Pilot Monitoring Program (USGS-EPA reservoir), and Washington State Department of Agriculture (WDA). These data sources along with how the data were obtained are summarized below.

Dow Agrosciences California Monitoring Program MRID 44711601

Sampling was conducted at three locations on the lower reach of Orestimba Creek for one year (May 1, 1996 to April 30, 1997). Daily time-proportional composite samples[86] were collected, along with weekly samples. The report included chlorpyrifos use information for fields that drained into the creek or had the potential to contribute spray drift[87]. All chlorpyrifos applications were made to alfalfa and walnut by aerial equipment and were made during the irrigation season. The total mass of chlorpyrifos applied to all the fields that were identified to have the potential to impact the creek was 2.2 lb a.i./A (1308 kg).

---

[84] U. S. Department of Agriculture, National Resources Conservation Service, Small Watershed Hydrology WinTR-55 User Guide, January 2009.
[85] Krutz, L. J., Senseman, S. A., Zablotowicz, R. M., Matocha, M. A., Reducing Herbicide Runoff from Agricultural Fields with Vegetative Filter Strips: A Review, Weed Science, **2005**, *53*, 353-367.
[86] Hourly samples were collected and composited over a 24-hour period; relatively large fluctuations in stream flow were anticipated during unattended operation of the auto samplers
[87] Fields within 305 m buffer on either side of the mid-stream line

Applications occurred throughout the study period (or the day prior to study initiation) with, at most, three fields treated in the study area on the same day. The report suggests that typical chlorpyrifos use occurred during the study period, with the exception of dormant season applications to tree crops, which were limited due to the rainy weather during the study.

The measured concentrations at the three sample locations are provided in **Figure 20**. The highest measured concentration was 2.2 µg/L and was associated with a chlorpyrifos application to alfalfa followed by flood irrigation.

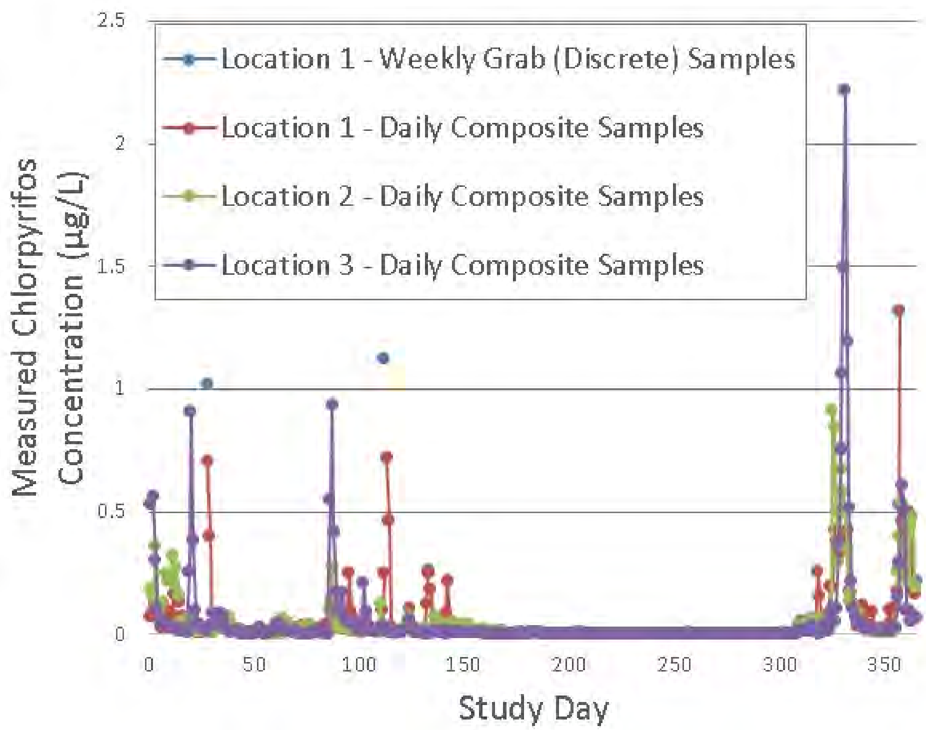


Figure 20. Orestimba Creek Water Monitoring Data (May 1, 1996 to April 30, 1997)

In several cases, the weekly grab samples were observed to have higher concentrations of chlorpyrifos. This suggests that the composite sampling methodology used in the study for daily samples resulted in the dilution of peak daily concentrations. Thirteen chlorpyrifos peak concentrations could be associated with specific events. The report authors suggest that nine of the events were related to spray drift (peak concentrations occurring within a three day window of application,) and were not linked to an irrigation event. The other four events were linked to irrigation tail water. Flood irrigation was reportedly used in the treated fields. Most of the peak concentrations were observed following chlorpyrifos applications to walnuts. The report noted that many of the walnut orchards are planted adjacent to the creek with an outside row located on the creek bank. This practice was done to maximize drainage from the orchard floor directly into the stream channel. It is unclear if any buffer zones were in place during application, but the observed concentrations suggest that the spray drift occurred during application even in the absence of adverse wind conditions.

Not all monitored concentrations were observed shortly after the application event. There is one example where the peak measured concentration (0.32 µg/L) associated with an application event occurred 56 days after application. The detection was associated with an irrigation event. This suggests that chlorpyrifos residues available for transport may persist on the field for several days (approximately two months) after application. No detections of chlorpyrifos were observed during the rainy season.

California Department of Regulation Surface Water Database

The California Department of Pesticide Regulation (CDPR) maintains a Surface Water Database (SURF) containing data from a wide variety of environmental monitoring studies designed to test for the presence or absence of pesticides in California surface waters. Monitoring data for pesticide in surface waters from California rivers, creeks, agricultural drains and urban streams are included in this dataset. In general, sample frequencies are sporadic and range from once per year to twice per month depending on the site and year.

California also maintains a Pesticide Use Reporting (PUR) database which can be coupled with the water monitoring data to correlate pesticide detections with specific uses/applications. The database provides use data for all agricultural pesticide applications and applications by licensed pesticide applicators.

California Environmental Data Exchange Network

The California Environmental Data Exchange Network (CEDEN) is a central repository containing information on California's water bodies, including streams, lakes, rivers, and the coastal ocean. Many groups in California monitor water quality including pesticide concentrations. CEDEN aggregates these data and makes it accessible to environmental managers and the public.

Central Coast Water Quality Preservation

Central Coast Water Quality Preservation, Inc. (Preservation, Inc.; (CCWQP)][88] is a non-profit organization that conducts a Cooperative Monitoring Program for surface water in accordance with Order No. R3-2012-0011, the Conditional Waiver of Waste Discharger Requirements for Discharges from Irrigated Lands, and the Monitoring and Reporting Program (http://www.ccwqp.org/CMP.html). This organization was formed by the Central Coast Regional Water Quality Control Board (RWQCB). The objectives of the monitoring program are to assess the impact of agricultural activities on surface water quality, identify problem areas where agricultural activities impact surface water quality, and provide a feedback loop for farmer on the impact of agricultural activities on surface water quality. The monitoring program has 50 monitoring sites in the Santa Cruz to Santa Barbara area including Santa Benito and Santa Clara Counties.

Central Valley Irrigated Land Program

The Irrigated Lands Regulatory Program (ILRP) was initiated in 2003 to prevent agricultural runoff from impairing surface waters. Water quality monitoring is conducted on irrigated agricultural discharges throughout the Central Valley as part of this program. Pesticides including chlorpyrifos are monitored as part of this program. Data from this program were obtained directly from the program.[89]

[88] Data obtained from Karen Worchester on 1/29/2015.
[89] Data obtained from Daniel J. McClure, PE on 1/27/2015

Central Valley Regional Water Control Board

The Central Valley Regional Water Control Board (CV_DNC_BPA)[90] is responsible to protect the quality of the waters within the California Central Valley Region (http://www.waterboards.ca.gov/centralvalley). This protection is accomplished by development of water quality plans for specific ground or surface water basins and by development of enforcement requirements on all agricultural, domestic and industrial waste discharges. The Central Valley Region in California encompasses 60,000 square miles, or about 40 percent of the State's total area. There are thirty-eight counties in the Central Valley Region. There are 11,350 miles of streams, 579,110 acres of lakes and the largest contiguous groundwater basin in California in this region of California. The major rivers include the Sacramento and San Joaquin Rivers, These two rivers furnish over half of the state's water supply. The southern third of the Central Valley contains the Tulare Lake Basin. The Central Valley is a very important agricultural area. Surface water monitoring projects under the control of the Central Valley Control Board include various agricultural regulatory programs (*i.e.*, Rice Pesticide Project), Basin Planning (*i.e.*, organophosphate pesticide control efforts on the San Joaquin River), non-point pollution sources (NPS), storm water, and total maximum daily load (TMDL) (*i.e.*, TMDL for organophosphate pesticides in the Sacramento and San Joaquin Rivers).

Oregon ELEM (OR ELEM)

The state of Oregon collects pesticide monitoring data as part of two different monitoring programs. The first program, the Statewide Toxics Monitoring Program,[91] began sampling in 2008 and continues today. The second program, the Pesticide Stewardship Partnerships Program[92] began sampling in 2000. Currently there are eight partnerships in seven watershed areas. Data from these programs were submitted directly to the EPA.[93]

Registrants Organophosphate Monitoring Study (MRID 45526201)

Monitoring data were provided on acephate, methamidophos, azinphos methyl, azinphos methyl-oxon, malathion, malaoxon, diazinon, diazoxon, chlorpyrifos, and chlorpyrifos-oxon in 44 community water systems utilizing sourced surface water.[94] The data were submitted by Syngenta Crop Protection, Inc. on October 23, 2001 on behalf of five companies: Bayer Corporation, Cheminova Agro A/S, Dow Agrosciences, Syngenta Crop Protection, and Valent U.S. The monitoring data for chlorpyrifos and chlorpyrifos-oxon provides some useful information, but failed to meet the stated objective of the study. Several study design issues are noted including site selection and quality control problems such as limited number of field spikes.

The study collected and analyzed 1103 samples from 44 different community water systems. Of the total, 731 of the samples were from 27 agriculturally influenced community water systems and 372 were from 17 urban influenced community water systems. All samples were taken from finished water.

---

[90] Data obtained from Daniel J. McClure, PE on 1/27/2015.
[91] http://www.deq.state.or.us/lab/wqm/toxics.htm
[92] http://www.deq.state.or.us/wq/pesticide/pesticide.htm.
[93] Data obtained from Brian Boling on March 16, 2015 via email to Tracy Perry
[94] Tierney, D.; Christensen, B.; Culpepper, V. (2001) Drinking Water Monitoring Study for Six Organophosphate Insecticides and Four Oxons from 44 Community Water Systems on Surface Water in the United States: Final Report: Lab Project Number: 1330-00: 00100. Unpublished study prepared by Syngenta Crop Protection, En-Fate, LLC, and EASI Laboratory. 880 p. (MRID 45526201)

In addition, 12 samples were taken from raw water, six samples each from two different sites. Chlorpyrifos and chlorpyrifos-oxon were not detected in any samples collected as part of the study. The analytical method of detection limit (MDL) was 0.0089 and 0.007 µg/L for chlorpyrifos and chlorpyrifos-oxon, respectively.

US EPA Storage and Retrieval Warehouse (STORET)

STORET is EPA's repository of the water quality monitoring data collected by water resource management groups across the country. These organizations, including states, tribes, watershed groups, other federal agencies, volunteer groups and universities, submit data to the STORET Warehouse in order to make their data publically accessible. Data in STORET are of documented quality, meaning that a certain level of metadata, including where, how, why, when and what was monitored must be included with all data submissions. Each sampling result in the STORET is accompanied by information on where the sample was taken (latitude, longitude, state, county, Hydrologic Unit Code and a brief site identification), when the sample was gathered, the medium sampled (*e.g.*, water, sediment, fish tissue), and the name of the organization that sponsored the monitoring. In addition, the STORET Warehouse contains information on why the data were gathered; sampling and analytical methods used; the laboratory used to analyze the samples; the quality control checks used when sampling, handling the samples, and analyzing the data; and the personnel responsible for the data. While STORET contains monitoring data for pesticides, it was not designed to collect only data on pesticides and does not contain information on pesticide use. Furthermore, sampling sites may not have been targeted to specific pesticide applications.

USDA Pesticide Data Program (PDP)

The PDP Water Monitoring Survey is designed to collect monitoring data on pesticide residues in drinking water. In 2001, PDP initiated a finished drinking water monitoring survey in California and New York. In 2002, PDP expanded its water program to include additional geographic regions within the United States, including Colorado, Kansas, and Texas. In 2004, the program was retooled to sample paired raw and finished water. The survey ended in April 2013. Throughout the survey, samples were collected by water treatment facilities that draw from surface water sources in 29 States plus the District of Columbia.

Samples from raw intake water (source water) as well as finished drinking water are analyzed as part of the PDP, typically on a bimonthly basis. Samples have been collected from 82 locations in 28 states and the District of Columbia; however, only a subset of these sampling locations are sampled each year. Although sampling sites fall within pesticide use areas, sample collection was not designed to specifically coincide with pesticide applications.

USGS National Water Information System (NWIS)

The United States Geological Survey (USGS) has collected water-resources data at approximately 1.5 million sites in all 50 States, the District of Columbia, Puerto Rico, the Virgin Islands, Guam, American Samoa and the Commonwealth of the Northern Mariana Islands. Surface water-quality data are available through NWIS include temperature, specific conductance, pH, nutrients, pesticides, and volatile organic compounds. The data are available for major rivers, lakes, and reservoirs and often include gage height (stage) and streamflow (discharge) data. The website includes current as well as historical data.

USGS National Water Quality Assessment (NAWQA)

The NAWQA program provides a nationally relevant dataset that includes analytes from a large list of pesticides and pesticide degradation products including chlorpyrifos and chlorpyrifos-oxon, larger than any other monitoring program in terms of scope and duration. The NAWQA surface water monitoring program is not designed to specifically target pesticide use. The sample timing and frequency are not designed to correspond with pesticide applications including chlorpyrifos applications. While sampling sites are distributed across the United States and include a wide-range of site vulnerabilities, the monitoring sites were not selected based on known pesticide treatment areas. However, there are some sampling locations that fall within in high pesticide use areas. In general, sample frequencies are sporadic and range from once per year to a couple times per month depending on the site and year. The NAWQA sampling program began in 1991 and continues today. Nevertheless, samples may not have been collected at all sample sites in all years. This dataset provides useful information on the geographical distribution of pesticides across the United States, trends in pesticide concentrations over time and establishes a baseline of water-quality conditions including pesticide concentrations.

USGS_EPA Stream Quality Index (USGS_MSQI)

The U.S. Geological Survey (USGS) National Water-Quality Assessment Program (NAWQA) and USGS Columbia Environmental Research Center (CERC) is collaborating with the U.S. Environmental Protection Agency (EPA) National Rivers and Streams Assessment (NRSA) to assess stream quality across the United States (http://water.usgs.gov/nawqa/studies/msqa/). Currently, the program has collected monitoring data from selected sites in the Midwest, Southeast, and Pacific Northwest. These data will used to characterize water-quality stressors including contaminants, nutrients, and sediment on ecological conditions in streams. These monitoring data are unique because they provide daily pesticide monitoring. Chlorpyrifos and chlorpyrifos oxon are analytes in this monitoring program.

USGS and State Monitoring Data

Monitoring data for chlorpyrifos and chlorpyrifos-oxon from the USGS as well as a number of state monitoring programs (USGS State Data) were compiles and analyses. States contributing data include: Florida Department of Regulatory and Economic Resources, South Dakota Department of Environment and Natural Resources, Kansas Biological Survey, Kentucky Watershed Watch, and New Hampshire Deportment of Environmental Services)

USGS-EPA Pilot Monitoring Program (USGS-EPA reservoir)

The USGS pilot reservoir monitoring program was designed to examine pesticide concentrations in twelve water-supply reservoirs and subsequent Community Water Systems (CWS). The reservoirs sampled ranged in size from 120 to 92,600 acre-foot normal capacity within watersheds ranging from about 3 to 785 square miles. The sites were located in California, Indiana, Louisiana, Missouri, New York, North Carolina, Ohio, Oklahoma, Pennsylvania, South Carolina, South Dakota, and Texas. Samples were collected from the raw-water intake and the finished-water tap located at the entry point to the distribution system. The correlation between raw and finished water detections are not adequate as finished water sampling generally occurred before raw water sampling. Each site generally was sampled every quarter, with biweekly sample collection during a four-month period coinciding with intensive pesticide applications. The program took place during 1999 and 2000. While sample timing and frequency were designed to target pesticide usage, the program was not specifically designed to correspond with specific pesticide applications events including chlorpyrifos applications. The monitoring sites were also not selected based on specific treatment areas, but rather areas where pesticides are generally applied and runoff is likely. This dataset provides useful information on pesticide concentrations in the tested systems during the sampling period.

Washington State Department of Ecology and Agriculture Cooperative Surface Water Monitoring Program (WDA)

Sampling focused on salmon-bearing streams in five different basins within Washington. Primarily weekly sampling was conducted during the pesticide use season; however, some daily sampling was also conducted. While the study did not specifically target chlorpyrifos use, nor did the report provide pesticide use information, some pesticide use survey data was obtained from WSDA. In addition, the report included information on the PCA for each of the basins included in the report.

The highest chlorpyrifos detections occurred within the Lower Yakima Agricultural Watershed (Table 35). The highest concentration (0.27 µg/L) was detected in Spring Creek in 2007. Within the Lower Yakima Agricultural Watershed, use of chlorpyrifos includes: wine grapes (early dormant spray), tree fruits (early dormant spray), and mint (late season). Chlorpyrifos detection frequencies ranged from 3 to 68% for weekly sampling. Daily samples were collected (mid-May-June) for one year at one location. When daily and weekly sampling frequencies of detection were compared, daily sampling detection frequency was more than 25% higher.

Table 35. Washington State Department of Agriculture Monitoring Summary for Chlorpyrifos (2006-2011)

Location	Spring Creek	Sulphur Creek Wasteway	Marion Drain	Mission Creek
Maximum Detected Chlorpyrifos Concentration	0.27 µg/L	0.28 µg/L	0.12 µg/L	2.1 µg/L
Sample Year[a]	2007	2009	2006 and 2007	2014
Watershed Size (acres)	27,373	103,010	80,491	Not reported
PCA[b]	50	42	66	Not reported
Primary Crops (PCA)[c]	Apples (4); Concord Grape (6); CRP (12%); Wine Grape (7); Hops[d] (3); Wheat (12)	Apples (5); Corn (8); Concord Grape (7); Wine Grape (4); Wheat (3)	Apples (9); Corn (12); Concord Grape (3); Hops (13); Mint (6); Wheat (8)	Tree Fruits Additional Data not provided

a. The exact sampling date is not provided in the report.
b. Percent cropped area provided for each basin in the report; includes grass, hay, and CRP (Conservation Reserve Program)
c. Survey data from report
d. Not a registered chlorpyrifos use

ii. Data Summary

Surface Water

Several sources of monitoring data were considered as part of this drinking water exposure assessment as described above. Analysis of these data are provided below for chlorpyrifos and chlorpyrifos-oxon.

Chlorpyrifos

Characteristics of surface water monitoring programs for chlorpyrifos from 1986 to 2016 are shown in **Table 36**. The monitoring represent 27,640 site-years in filtered surface water, 10,808 site-years in unfiltered surface water, 273 site-years in surface water with known particulates, and 166 site-years in finished surface source drinking water. A single site- year represents one sampling location with one sample collected. These monitoring data represent chlorpyrifos occurrence in 50 states, U.S. territories, tribal nations, and national parks. Based on available information on various monitoring programs, the registrant monitoring program (Dow Monitoring MRID 44711601) is the only program with targeted sampling in a watershed with known chlorpyrifos use. Additionally, this monitoring program had daily monitoring data to allow quantification of annual peak chlorpyrifos concentrations. Although the USGS reservoir monitoring program was focused on vulnerable watersheds with pesticide use, the monitoring program was not specifically focused on watersheds with chlorpyrifos usage. Other monitoring programs such as NWIS and NAWQA are associated with non-targeted monitoring throughout the United States. Monitoring data from EPA STORET database are an array of various monitoring data from local, state, tribal, and federal monitoring programs. Most of the monitoring data are from the state of CA. These monitoring data were obtained from the CCWQ, SURF, CV_DNc_BPA, and ILRP_R5 monitoring programs. Finished drinking water data for chlorpyrifos were obtained from the PDP and USGS Reservoir monitoring program. Collectively, these monitoring programs represent chlorpyrifos occurrence in filtered and unfiltered ambient surface water as well as finished drinking water.

Table 36. **Characteristics of Monitoring Programs and Databases Used for Assessing Chlorpyrifos Occurrence in Surface Water**

Study	Number of States and Territories	Number of Sampling Stations	Years	Targeted Monitoring	Water Sample Handling	Water Type
CCWQ	1	51	2001-2013	No	Filtered	Ambient
CEDEN	1	97	1993-2005	No	Dissolved	Ambient
	1	97	1993-2005	No	Particulate	Ambient
	1	1062	2001-2014	No	Total	Ambient
CV_DNC_BPA	1	435	2000-2011	No	Filtered	Ambient
ILRP_R5	1	69	2013-2014	No	Total	Ambient
Dow Monitoring (MRID 44711601)	1	3	1996-1997	Yes	Filtered	Ambient
NAWQA	15	48	1996 and 2014	No	Unfiltered	Ambient
	49	1713	1991-2013	No	Filtered	Ambient
OR_ELEM	1	288	2012-2015	No	Filtered	Ambient
PDP	29	74	2001-2012	No	Finished DW	Drinking
	27	49	2004-2012	No	Raw DW	Drinking

Study	Number of States and Territories	Number of Sampling Stations	Years	Targeted Monitoring	Water Sample Handling	Water Type
STORET	16(2)	1605	1988-2014	No	Total	Ambient
	7(2)	788	1996-2015	No	Dissolved	Ambient
SURF	1	339	1991-2014	No	Dissolved	Ambient
USGS Reservoir	12	12	1999-2000	No	Finished	Drinking
	12	17	1999-2000	No	Raw	Drinking
USGS_STATE	46	961	1986-2013	No	Unfiltered	Ambient
	1	5	1993-2013	No	Particulate	Ambient
WDA	1	24	2003-2012	No	Filtered	Ambient
NWIS	48	5297	1991-2015	No	Dissolved	Ambient
	44	1050	1986-2015	No	Recoverable	Ambient
	1	7	2005	No	Total	Ambient
USGS-MSQI	10	27	2013-2016	No	Filtered	Ambient

There were numerous issues to consider in the analysis of the monitoring data for chlorpyrifos. The monitoring data were evaluated to ensure the concentration units were corrected to parts-per-billion (µg/L) and that limits of detection (LOD) or limits of quantification (LOQ) were reported in the monitoring data. The monitoring data also were evaluated to ensure the range of chlorpyrifos concentrations are reasonable. Reasonable was determined using best professional judgement. For example, 2006 monitoring data in STORET database from the KAW Nation had LODs reported as 0.1 mg/L (100 µg/L). This LOD is so far above the other reported MRL that these data were excluded from analysis. The excluded surface water data are listed in **ATTACHMENT 11**. There is a potential for duplication of monitoring data among the various monitoring programs and databases because of the cooperative interaction of state and federal government monitoring programs. No attempt was made to eliminate duplication of monitoring data among the various monitoring programs.

Another issue is that the monitoring data are highly censored due to the high number of non-detections of chlorpyrifos among the various monitoring programs. The number of site-years with no chlorpyrifos detections was 9,583 from 10,808 site-years (11% detection frequency) for unfiltered water samples, 21,142 from 27,640 site-years (24% detection frequency) for filtered water samples, 166 from 166 site-years (0% detection frequency) for finished water samples, and 118 from 273 site-years (57% detection frequency) for water samples with known particulates.

Low detection frequencies indicate the occurrence pattern of chlorpyrifos is sporadic and/or that sampling was not targeted to chlorpyrifos use either in terms of geography or time. In any case, low detection frequencies suggest that monitoring data consist of low concentrations at or below the LOD or LOQ. Because the actual concentration of non-detections is unknown, the concentration can theoretically range from zero to the LOD or LOQ. Each monitoring program or database provided either a LOD or LOQ or minimum reporting limit (MRL). A sensitivity analysis was performed on several sites to assess the impact of the low detection frequency on the calculated 21-day average concentrations when the detection limit is at the MRL, 0 or ½ MRL (**Table 37**). For purposes of the data analysis in this section, the non-detections are assumed to be equal to ½ MRL.

Table 37. Sensitivity Analysis of MRL Assumptions on Distribution of 21-day Average Chlorpyrifos Concentration in Unfiltered Surface Water Samples

Program	LOD Condition	Percentile (as a fraction)						N
		0.5	0.75	0.9	0.95	0.99	1	
		Concentration (µg/L)						
CEDEN	MRL	0.028741	0.031565	0.0324	0.032678	0.032901	0.032957	4
	1/2 MRL	0.028548	0.031379	0.032218	0.032498	0.032721	0.032777	
	MRL=0	0.026173	0.029385	0.033481	0.034847	0.03594	0.036213	
	Mean	**0.027821**	**0.030776**	**0.0327**	**0.033341**	**0.033854**	**0.033982**	
	SD	**0.00143**	**0.001209**	**0.000683**	**0.001307**	**0.001808**	**0.001934**	
	CV	**5.140441**	**3.927725**	**2.088761**	**3.921329**	**5.341799**	**5.690417**	
NWIS	MRL	0.22	0.32	0.32	0.32	0.32	0.32	4
	1/2 MRL	0.11	0.16	0.16	0.16	0.16	0.16	
	MRL=0	0	0	0	0	0	0	
	Mean	**0.11**	**0.16**	**0.16**	**0.16**	**0.16**	**0.16**	
	SD	**0.11**	**0.16**	**0.16**	**0.16**	**0.16**	**0.16**	
	CV	**100**	**100**	**100**	**100**	**100**	**100**	
STORET	MRL	0.1	0.1	0.24	0.24	0.24	0.24	93
	1/2 MRL	0.05	0.05	0.12	0.12	0.127173	0.20966	
	MRL=0	0	0	0	0	0.016552	0.206902	
	Mean	**0.05**	**0.05**	**0.12**	**0.12**	**0.127908**	**0.218854**	
	SD	**0.05**	**0.05**	**0.12**	**0.12**	**0.111726**	**0.018365**	
	CV	**100**	**100**	**100**	**100**	**87.34831**	**8.391423**	
WDA	MRL	0.034619	0.037071	0.075244	0.108291	0.166527	0.726001	140
	1/2 MRL	0.020422	0.031061	0.075156	0.099994	0.165335	0.721583	
	MRL=0	0.009429	0.028259	0.075097	0.097691	0.164213	0.718833	
	Mean	**0.02149**	**0.03213**	**0.075166**	**0.101992**	**0.165358**	**0.722139**	
	SD	**0.012629**	**0.004503**	**7.37E-05**	**0.005576**	**0.001157**	**0.003616**	
	CV	**58.76794**	**14.01329**	**0.098021**	**5.466785**	**0.699695**	**0.500727**	

Another issue is the lack of uniformity associated with the type of samples and analytes in the chlorpyrifos monitoring data. The chlorpyrifos data are expressed as chlorpyrifos concentrations in unfiltered and filtered solution as well as on particulate fractions in surface water. These concentrations are expressed as particulate, total, dissolved, and recoverable. The reasons for the different sample and analytes is associated with the high sorption of chlorpyrifos on sediment and soil. Typically, the drinking water assessment is based on filtered water samples from monitoring data. The monitoring data for chlorpyrifos and chlorpyrifos oxon are divided into sample preparations of particulates, unfiltered and filtered water samples for dissolved chlorpyrifos or total chlorpyrifos**. Table 34** illustrates the sample categories considered in this assessment of monitoring data.

Chlorpyrifos monitoring data are discussed in terms of daily concentrations and 21-day average concentrations by sample type in the subsections below.

One-Day (composite, grab, etc.)

Filtered/Dissolved Samples

Thirteen monitoring programs with samples classified as dissolved or filtered were considered in this analysis. There are 27,640 site-years among the monitoring programs. The maximum daily chlorpyrifos concentration in filtered samples range from 0.0 to 7.5 µg/L (**Table 38**). The maximum daily chlorpyrifos concentration in filtered/dissolved water samples is 7.5 µg/L at a FL site (21FLSFWM-S65E) in 2000 from the STORET database. This concentration, however, is equal to ½ MRL of 15 µg/kg. This concentration is assumed to be equal and have units of µg/L using a density of water of 1 g/ml. The maximum confirmed daily chlorpyrifos concentration in filtered samples is 5.62 µg/L from a USGS monitoring site in New Jersey (USGS-01408460). This site is located in Ocean County, New Jersey on the Manapaque Branch at Lakehurst, New Jersey. The watershed of the sampling site has a watershed area of 6.32 mi^2 and appears to be surrounded by urban/suburban land use. The descriptive statistics for chlorpyrifos concentrations in each monitoring program is shown in **Table 38.**

Table 38. Descriptive Statistics of Daily Peak Chlorpyrifos Concentrations

Program	Mean	Median	Minimum	Maximum	Count
	Concentration (µg/L)				
CCWQ	0.0896	0.0090	0.0005	1.4943	75
CEDEN	0.0002	0.0001	5E-07	0.0065	241
CV_Dn_BPA	0.0596	0.0110	0.0005	3.7	970
MRID44711601	1.0788	0.9265	0.361	2.218	6
NAWQA	0.0098	0.0025	0.001	0.57	4223
NWIS	0.0252	0.0025	0.001	6	10472
OR_ELEM	0.0231	0.0119	0.0098	0.404	368
PDP	0.0000	0.0000	1.5E-09	1.35E-08	73
STORET	0.2023	0.0050	0	7.5	1303
SURF	0.1587	0.0520	0.000286	3.96	763
USGS_Reservoir	0.0043	0.0020	0.002	0.0341	27
USGS_State	0.0262	0.0025	0	5.62	9089
USGS_MSQI	0.1807	0.2045	0.003186	0.647	29

The minimum reporting limits (MRLs) for chlorpyrifos in samples classified as filtered or dissolved are shown in **Table 39**. The range of MRLs range from 0 to 15 µg/L. Typical MRLs, as indicated by the median, range from 0 to 0.409 µg/L among the monitoring programs.

Table 39. Descriptive Statistics for MRLs of Chlorpyrifos in Filtered Ambient Surface Water

Program	Mean	Median	Minimum	Maximum	Count
	Concentration (µg/L)				
CCWQ_CYP	0.0048	0.0010	0.0010	0.0500	95
CEDEN_ Dissolved_CYP	0.0003	0.0001	0.0000	0.0130	468
CV_DnC_CYP	0.0040	0.0030	0.0010	0.0100	162
Dow Monitoring	0.0100	0.0100	0.0100	0.0100	426

NAWQA_Filtered_CYP	0.0057	0.0040	0.0000	0.5000	25871
NWIS_Dissolved	0.0248	0.0050	0.0020	12.0000	41717
OR_ELEM_CYP	0.0328	0.0218	0.0184	0.2390	2030
PDP_unfinished[a]	0.0000	0.0000	0.0000	0.0000	1641
STORET_DISSOLVED_CYP	0.2278	0.0000	0.0000	15.0000	4473
SURF_DISSOLVED_CYP	0.0209	0.0092	0.0006	0.3000	546
USGS_Reservoir_CYP	0.0041	0.0040	0.0040	0.0100	375
USGS_State	0.015803	0.0025	0	2.5	43998
USGS_MSQI	0.3057	0.4090	0.0020	0.4090	1316
a. The MRLs range from $1.5E^{-8}$ to $1.5E^{-9}$ µg/L					

The majority of site-years have maximum daily chlorpyrifos concentrations in filtered water ranging from 0.001 to 0.01 µg/L (**Table 40**). There are 138 site-years with chlorpyrifos concentrations exceeding or equal to an arbitrary threshold of 1 µg/L. From these 10 site-years, there are only 42 site-years with confirmed chlorpyrifos concentrations at a concentration of ≥ 1 µg/L. These sites are located in California (36 sites-years), New Jersey (2 site-year), Oregon (1 site-year) and Texas (2 site-years). The only state with no confirmed chlorpyrifos detection is Alaska. The state with the highest chlorpyrifos detection frequency (55% site-years) is California. Other states with high detection frequencies (>25% site-years) include Arizona, Iowa, Illinois, Indiana, Nebraska, Ohio, Oregon, South Carolina, and Washington.

Table 40. Frequency of Site-Years According to Daily Peak Chlorpyrifos Concentrations in Filtered Ambient Surface Water

Concentration (µg/L)	Frequency of Site-Years
<0.00001	738
0.00001-0.0001	64
0.0001-0.001	283
0.001-0.01	**19879**
0.01-0.1	4664
0.1-1	1891
1-10	120
<10	0

Total, Recoverable, and Unfiltered

Seven monitoring programs with samples classified as total, recoverable, and unfiltered were considered in this analysis. There are 10,808 site-years among the monitoring programs. The maximum daily chlorpyrifos concentration in unfiltered samples range from 0.16 to 14.7 µg/L (**Table 41**). The maximum daily chlorpyrifos concentration of 14.7 µg/L at an Army Corp of Engineers monitoring site (COEOMAHA_WQX_YAKLND1) in Nebraska was confirmed.[95] This site has an agricultural watershed with

[95] Personal communication between Melanie Biscoe (EPA-OPP) and David Jensen (U.S. Army Corps of Engineers, Omaha District) August 5, 2015 at 10:35 am.

major production crops grown in the area including corn and soybeans. The descriptive statistics for chlorpyrifos concentrations in each monitoring program are shown in **Table 38.**

Table 41. Descriptive Statistics of Daily Peak Chlorpyrifos Concentrations in Unfiltered Ambient Surface Water

Program	Mean	Median	Minimum	Maximum	Count
	Concentration (µg/L)				
CEDEN	0.0617	0.0100	0.0000	3.7000	2278
ILRP_R5	0.0125	0.0013	0.0003	0.4200	95
NAWQA	0.0207	0.0050	0.0050	0.1600	68
NWIS	0.0591	0.0100	0.0000	11.3000	2575
STORET	0.0662	0.0250	0.0000	14.7000	3388
USGS-State	0.0948	0.0100	0.0002	2.4500	2229
WDA	0.0602	0.0250	0.0130	2.1000	175

The minimum reporting limit (MRL) for chlorpyrifos in samples classified as filtered or dissolved are shown in **Table 42**. The range of MRLs range from 0.0029 to 5.32 µg/L. Typical MRLs, as indicated by the median, range from 0.0023 to 0.1 µg/L among the monitoring programs.

Table 42. Descriptive Statistics for MRL Unfiltered Ambient Surface Water

Program	Mean	Median	Minimum	Maximum	Count
	Concentration (µg/L)				
CEDEN_ Total_CYP	0.0377	0.0026	0.0000	4.7000	6728
R5_ILRP_Total_CYP	0.0023	0.0026	0.0005	0.0029	344
NAWQA_Unfilter_CYP	0.0315	0.0100	0.0100	0.3200	110
NWIS_Total	0.1000	0.1000	0.1000	0.1000	38
NWIS_Recoverable	0.1046	0.0200	0.0060	5.3200	5284
STORET_TOTAL_CYP	0.0811	0.0500	0.0000	5.0000	10112
USGS_State_unfiltered_CYP	0.1976	0.1000	0.0004	4.9000	6146
WDA_Total_CYP	0.0327	0.0330	0.0120	0.1300	3724

The majority of site-years have chlorpyrifos concentrations in the range of 0.1 to 1 µg/L (**Table 43**). States with confirmed chlorpyrifos concentrations exceeding or equal to an arbitrary threshold concentration of 1 µg/L are Arkansas (1 site-year), California (1 site-year), Florida (2 site-years), Iowa (1 site-year), Missouri (2 site-year), Nebraska (1 site-year), New Hampshire (2 site-years), New York (1 site-year), Utah (46 site-years), Washington (1 site-year). The states with no confirmed chlorpyrifos detections are Alabama, Connecticut, District of Columbia, Georgia, Idaho, Massachusetts, Maryland, Michigan, Montana, New Jersey, Ohio, Pennsylvania, South Carolina, Tennessee, West Virginia, and Wyoming. Further analysis indicate that 18 states had approximately 10% of site-years with chlorpyrifos detections. States with the highest site-year detection frequencies (≥50% site-years) include Virginia and Nebraska. Other states with high detection frequencies (25 to 50% site-years) include Indiana, Kansas, Kentucky, Missouri, Utah, and Washington.

Table 43. Frequency of Site-Years According to Daily Peak Chlorpyrifos Concentrations in Unfiltered Ambient Surface Water

Concentration (µg/L)	Frequency of Site-Years
<0.00001	16
0.00001-0.0001	22
0.0001-0.001	34
0.001-0.01	205
0.01-0.1	4505
0.1-1	**4945**
1-10	1017
<10	62

Particulate

Two monitoring programs had samples classified as particulates in this analysis. There are 273 site-years among the monitoring programs (**Table 44**). The maximum chlorpyrifos concentration is 0.00074 µg/L. This concentration, as reported in both the CEDEN and USGS_State monitoring programs, is associated with a monitoring site on the Guadalope River (BW15) in California.

Table 44. Descriptive Statistics of Daily Peak Chlorpyrifos Detections in Surface Water with Known Particulates

Program	Mean	Median	Minimum	Maximum	Count
	Concentration (µg/L)				
CEDEN	4.91E-05	0.000018	5E-07	0.00074	237
USGS_State	0.00011	0.000049	5E-07	0.00074	36

The MRL for chlorpyrifos in samples with particulates are shown in **Table 45**. The range of MRLs range from 3.1E-7 to 0.000109 µg/L. Typical MRLs, as indicated by the median, range from 1.44E-6 to 3.59E-6 µg/L among the monitoring programs.

Table 45. Descriptive Statistics for MRLs for Chlorpyrifos in Ambient Surface Water with Reported Particulates

Program	Mean	Median	Minimum	Maximum	Sum	Count
	Concentration (µg/L)					
Cedan_Part_CYP	2.26E-05	1.44E-06	3.1E-07	0.000109	0.003998	177
USGS_STATE_PART_CYP	2.97E-05	3.59E-06	0.000001	0.000109	0.000504	17

The majority of site-years have chlorpyrifos concentrations in the range of 0.00001 to 0.0001 µg/L (**Table 46**). Unlike the monitoring data for filtered and unfiltered water samples, 57% of the site-years in the monitoring programs had detectable concentrations of chlorpyrifos in the water samples with known particulates. Possible reason(s) for the high percentage of chlorpyrifos detections may be associated with the low analytical detection limits as well as the high sorption affinity (K_{oc}) of chlorpyrifos to soil and sediments.

Table 46. Frequency of Site-Years According to Daily Peak Chlorpyrifos Concentrations in Surface Water with Known Particulates

Concentration (µg/L)	Frequency of Site-Years
<0.00001	102
0.00001-0.0001	**134**
0.0001-0.001	37
0.001-0.01	0
0.01-0.1	0
0.1-1	0
1-10	0
<10	0

Finished Drinking Water

The monitoring data for finished drinking water samples was derived from the USDA_ PDP and USGS_Reservoir and the registrant monitoring program (MRID 45526201). There are 166 site-years in USDA_PDP and USGS_Reservoir monitoring programs. The registrant monitoring program (MRID 45526201) has monitoring data from 44 community water systems with watersheds influenced by agricultural and urban activities. Unlike the other water samples in the monitoring programs, there are no detections of chlorpyrifos in finished drinking water. The maximum 1-day and 21-day average chlorpyrifos concentrations, therefore, are estimated at 0.0089 µg/L (**Table 47**). This concentration represents the highest MRL in the monitoring programs.

Table 47. Descriptive Statistics of Chlorpyrifos Detection Limits in Finished Surface Sourced Drinking Water

Program	Mean	Median	Minimum	Maximum	Count
	Concentration (µg/L)				
PDP	5.28E-09	3.76E-09	1.5E-09	1.5E-08	147
USGS_Reservoir	0.004	0.004	0.004	0.006	19
MRID 45526201	0.0089				1103[a]
a. Indicates number of samples in the analysis					

Although these monitoring data represent finished surface source drinking water from 32 states, the spatial-temporal distribution of data are generally sparse. States with a highest number of site-years of monitoring data are California with 37 site-years and New York with 36 site-years. The other states have a substantially lower number of site-years (1 to 8 site-years) of monitoring data. The lack of chlorpyrifos detections in finished drinking water could be due to water chlorination as well as low detection frequencies. It is known that chlorpyrifos is oxidized to form chlorpyrifos-oxon during water chlorination (See **Drinking Water Treatment Effects** section beginning on page 29). However, this situation is not likely in the current data because there were no detections of chlorpyrifos-oxon in paired finished water samples from the PDP monitoring program. Tierney et al., 2003[94] also did not detect chlorpyrifos in finished water at community water systems.

21-day Average Concentration

The monitoring data for 21-day average concentrations were censored to include only site-years with 17 or more samples per year. This censoring was conducted because a minimum of two samples in any 21 day interval in a year are required for estimating a 21-day average concentration. The censoring process eliminated assessing 21-day average chlorpyrifos concentrations in samples with particulates due to low sampling frequencies. Additionally, the high number of samples with non-detections in the monitoring data requires the consideration of the LOD. Each monitoring program or database provided either a limit of quantification (LOD) or limit of quantification (LOQ) or minimum reporting limit (MRL). For purposes of this data analysis, the LOD and LOQ are assumed to be equal to the MRL. In the analysis for 21-day average concentrations, the data were analyzed assuming non-detections were equal to 0, ½ Limit of Detection (MRL), or the MRL. A sensitivity analysis was conducted to assess the impact of using different assumptions for quantification of the MRL on calculation of the 21-day average concentration in unfiltered surface water (**Table 37**).

The impact of the MRL assumptions on calculation of 21-day average concentrations varies among the different monitoring programs. The highest coefficient of variations (100%) are associated with monitoring programs (*i.e.*, NWIS and STORET) with a high number of non-detections. In contrast, monitoring programs (*i.e.*, CEDEN and WDA) with a low number of non-detections have coefficients of variations of less than 10%. These data illustrate that a high percentage of non-detections are expected to invoke a considerable amount of uncertainty regarding estimating 21-day average concentrations. The extent of variation in the 21-day average concentrations could vary by as much as 100% in site-years with a high number of non-detections (≥ 17 per year).

Filtered/Dissolved Samples

Ten monitoring programs had site-years with ≥17 filtered samples per year to allow determination of 21 day average concentrations. There are 1,558 site-years in this analysis. The maximum 21-day average chlorpyrifos concentration in filtered samples range from 0.00 to 0.3633 µg/L (**Table 48**). The maximum 21-day average chlorpyrifos concentration in filtered/dissolved water samples is 0.3623 µg/L at a CA site (Orestimba Creek) in 1997 from the SURF database. Similar concentrations are reported in the Dow monitoring program (MRID 44711601). These data represent targeted monitoring on Orestimba Creek with chlorpyrifos use and high sampling frequencies (57-120 days in a site-year). Monitoring programs with no detections include PDP, STORET, and OR_ELEM.

Table 48. Descriptive Statistics of 21-day Average Chlorpyrifos Concentrations in Filtered Surface Source Drinking Water

Program	Mean	Median	Minimum	Maximum	Count
	Concentration (µg/L)				
CV_DnC_BPA	0.0285	0.0152	0.0058	0.1597	32
MRID44711601	0.2082	0.1879	0.1075	0.3586	6
NAWQA	0.0159	0.0050	0.0018	0.2133	437
NWIS	0.0134	0.0049	0.0018	0.2159	432
OR_ELEM	0.0525	0.0613	0.0122	0.1111	8
PDP	1.56E-09	1.5E-09	1.5E-09	5.79E-09	66
STORET	0	0	0	0	3

SURF	0.1552	0.1481	0.0068	0.3633	14
USGS_Reservoir	0.0033	0.0020	0.0020	0.0112	8
USGS_State	0.0177	0.0052	0.0018	0.2500	531
USGS_MSQI	0.1421	0.2045	0.0012	0.2950	21

The minimum reporting limit (MRL) for 21 day average chlorpyrifos concentrations in samples classified as filtered or dissolved are shown in **Table 49**. The range of MRLs range from 0 to 15 µg/L. Typically, MRLs, as indicated by the median, range from 0 to 0.409 µg/L among the monitoring programs.

Table 49. Descriptive Statistics for MRLs of Chlorpyrifos in Filtered Ambient Surface Water

Program	Mean	Median	Minimum	Maximum	Count
	Concentration (µg/L)				
CV_DnC_CYP	0.0040	0.0030	0.0010	0.0100	162
MRID44711601	0.0100	0.0100	0.0100	0.0100	426
NAWQA_Filtered_CYP	0.0057	0.0040	0.0000	0.5000	25871
NWIS_Dissolved	0.0248	0.0050	0.0020	12.0000	41717
OR_ELEM_CYP	0.0328	0.0218	0.0184	0.2390	2030
PDP_unfinished[a]	0.0000	0.0000	0.0000	0.0000	1641
STORET_DISSOLVED_CYP	0.2278	0.0000	0.0000	15.0000	4473
SURF_DISSOLVED_CYP	0.0209	0.0092	0.0006	0.3000	546
USGS_Reser voir_CYP	0.0041	0.0040	0.0040	0.0100	375
USGS_State	0.015803	0.0025	0	2.5	43998
USGS_MSQI	0.3057	0.4090	0.0020	0.4090	1316

a. The range in MRL is $1.5E^{-8}$ to $1.5E^{-9}$ µg/L

The majority of site-years have chlorpyrifos concentrations in the range of 0.001 to 0.01 µg/L (**Table 50**). The highest number of site-years with detectable chlorpyrifos include California (139 site-years) Washington (36 site-years), Oregon (35 site-years), Nebraska (33 site-years), Pennsylvania (31 site-years), North Carolina (27 site-years), Indiana (25 site-years), Georgia (23 site-years), and Iowa (21 site-years).

Table 50. Frequency of Site-Years According to 21-day Average Chlorpyrifos Concentrations in Filtered Surface Source Drinking Water

Concentration (µg/L)	Frequency of Site-Years
<0.00001	69
0.00001-0.0001	0
0.0001-0.001	0
0.001-0.01	**997**
0.01-0.1	423
0.1-1	69
1-10	0
<10	0

Unfiltered Samples

Five monitoring programs had site-years with ≥ 17 unfiltered samples per year to allow determination of 21-day average concentrations. There are 251 site-years in this analysis. The maximum 21-day average chlorpyrifos concentration in unfiltered samples range from 0.0328 to 0.7216 µg/L (**Table 51**). The maximum 21-day average chlorpyrifos concentration in unfiltered water samples is 0.7216 µg/L at a Washington site (MI-1) in 2014 from the Washington Department Agriculture monitoring program. This monitoring site is located on Mission Creek in central Washington.[96] The main agricultural activities in this watershed are associated with tree fruit production.

Table 51. Descriptive Statistics of 21-day Average Chlorpyrifos Concentrations in Unfiltered Ambient Surface Water for Monitoring Programs

Program	Mean	Median	Minimum	Maximum	Count
	Concentration (µg/L)				
CEDEN	0.0252	0.0285	0.0108	0.0328	4
NWIS	0.1100	0.1100	0.0600	0.1600	4
STORET	0.0543	0.0500	0.0200	0.2097	93
USGS_State	0.0829	0.0600	0.0050	0.1600	10
WDA	0.0379	0.0204	0.0128	0.7216	140

The minimum reporting limit (MRL) for chlorpyrifos in samples classified as filtered or dissolved are shown in **Table 52**. The range of MRLs range from 0.1 to 5.00 µg/L. Typical MRLs, as indicated by the median, range from 0.0026 to 0.1 µg/L among the monitoring programs. These MRLs represent a range of 21-day average concentrations in monitoring data with not chlorpyrifos detections such CEDEN, NWIS, and USGS_State. The only monitoring program with high detection frequencies is the Washington Department of Agriculture. The other programs, however, had very low or no detections of chlorpyrifos. These data suggest the highest certainty in estimation of the "true" 21-day average chlorpyrifos concentrations is from the Washington Department of Agriculture monitoring program.

Table 52. Descriptive Statistics for MRL Unfiltered Ambient Surface Water Monitoring Programs

Program	Mean	Median	Minimum	Maximum	Count
	Concentration (µg/L)				
Cedan Total_CYP	0.0377	0.0026	0.0000	4.7000	6728
NWIS_Total	0.1000	0.1000	0.1000	0.1000	38
NWIS_Recoverable	0.1046	0.0200	0.0060	5.3200	5284
STORET_TOTAL_CYP	0.0811	0.0500	0.0000	5.0000	10112
USGS_State_unfiltered_CYP	0.1976	0.1000	0.0004	4.9000	6146
WDA_Total_CYP	0.0327	0.0330	0.0120	0.1300	3724

[96] Tuttle, George. 2015. Surface Water Monitoring Program for Pesticides in Salmoid-Bearing Streams, 2014: A Study by the Washington Department of Agriculture. AGR PUB 104-494.

The majority of site-years have 21 day average chlorpyrifos concentrations in the range of 0.01 to 0.1 µg/L (**Table 53)**. States with confirmed detectable chlorpyrifos include Minnesota (1 site-year) and Washington (85 site-years).

Table 53. Frequency of Site-Years According to 21-day Average Chlorpyrifos Concentrations in Unfiltered Surface Source Drinking Water

Concentration (µg/L)	Frequency of Site-Years
<0.00001	0
0.00001-0.0001	0
0.0001-0.001	0
0.001-0.01	2
0.01-0.1	**217**
0.1-1	32
1-10	0
<10	0

Chlorpyrifos-oxon

Monitoring data for chlorpyrifos-oxon occurrence in surface water were available from NAWQA, PDP, USGS_EPA Stream Quality Index, USGS_State Data, and WDA.

Characteristics of surface water monitoring programs for chlorpyrifos oxon from 1991 to 2016 are shown in **Table 54**. The monitoring programs represent 2,011 site-years in filtered surface water, 114 site-years in unfiltered surface water and 147 site-years in finished surface source drinking water. These monitoring data represent chlorpyrifos oxon occurrence in 47 states. Although several of the monitoring programs are targeted to pesticide use areas such as Washington Department of Agriculture, these monitoring programs are generally not targeted monitoring for chlorpyrifos use areas. Finished drinking water data for chlorpyrifos were obtained from the PDP. Collectively, these monitoring programs represent chlorpyrifos occurrence in filtered and unfiltered ambient surface water as well as finished drinking water.

Table 54. Characteristics of Monitoring Programs and Databases Used for Assessing Chlorpyrifos-oxon Occurrence in Surface Water

Study	Number of States and Territories	Number of Sampling Stations	Years	Targeted Monitoring	Water Sample Handling	Water Type
NAWQA	7	13	1991-2013	No	Filtered	Ambient
PDP	29	74	2001-2012	No	Finished DW	Drinking
	27	49	2004-2012	No	Raw DW	Drinking
USGS_STATE	44	881	1999-2013	No	Unfiltered	Ambient
	1	2	2009	No	Total	Ambient
	44	732	1999-2013	No	Filtered	Ambient
WDA	1	17	2003-2014	No	Total	Ambient

Study	Number of States and Territories	Number of Sampling Stations	Years	Targeted Monitoring	Water Sample Handling	Water Type
USGS-Stream Index	10	27	2013-2016	No	Filtered	Ambient

There are numerous issues to consider in the analysis of the monitoring data for chlorpyrifos-oxon. The monitoring data were evaluated to ensure the concentration units were corrected to parts-per-billion (µg/L) and that LOD or LOQ were reported in the monitoring data. The monitoring data also were evaluated to ensure the range of chlorpyrifos oxon concentrations are reasonable. There is a potential for duplication of monitoring data among the various monitoring programs and databases because of the cooperative interaction of state and federal government monitoring programs. No attempt was made to eliminate duplication of monitoring data among the various monitoring programs.

Another issue is that the monitoring data are highly censored due to the high number of non-detections of chlorpyrifos oxon among the various monitoring programs. The number of site-years with chlorpyrifos oxon detections was 72 in 114 site-years (63 % detection frequency) for unfiltered water samples, 23 in 2,011 site-years (1.1% detection frequency) for filtered water samples, 0 in 147 site-years (0% detection frequency) for finished water samples. As discussed in the previous sections, the assumption on quantification of MRL is an important consideration for calculation of 21-day average concentrations due to low detection frequencies.

One-Day (composite, grab, etc.)

Filtered/Dissolved Samples

Two monitoring programs with samples classified as dissolved or filtered are considered in this analysis. There are 2,011 site-years among the monitoring programs. The maximum daily chlorpyrifos-oxon concentration in filtered samples ranged from 1.28E-7 to 0.291 µg/L (**Table 55)**. The maximum daily chlorpyrifos oxon concentration in filtered/dissolved water samples is 0.291 µg/L at a Wisconsin site (Station No. 40869416) in 2013 from the USGS_Stream Quality Index monitoring program. This sampling program is unique because of daily sampling during part of the year.

Table 55. Descriptive Statistics of Daily Peak Chlorpyrifos-oxon Concentrations for Filtered Ambient Surface Water

Program	Mean	Median	Minimum	Maximum	Count
	Concentration (µg/L)				
NAWQA	0.0025	0.0025	0.002	0.0025	13
PDP	7.15E-08	6.6E-08	5.25E-09	1.28E-07	73
USGS_state	0.0285	0.0281	0.008	0.241	1896
USGS_MSQI	0.0313	0.012	0.001	0.291	29

The MRL for chlorpyrifos-oxon in samples classified as filtered or dissolved are shown in **Table 56**. The range of MRLs range from 2.55E-7 to 0.3302 µg/L. Typical MRLs, as indicated by the median, range from 1.32E-7 to 0.056 µg/L among the monitoring programs.

Table 56. Descriptive Statistics for MRLs of Chlorpyrifos-oxon in Filtered Ambient Surface Water

Program	Mean	Median	Minimum	Maximum	Count
	Concentration (µg/L)				
PDP-unfinished_CYPOX	1.32E-07	1.32E-07	6E-09	2.55E-07	1641
USGS_Stream_CYPOX	0.0181	0.024	0.002	0.024	1341
USGS_States_CYPOX	0.0559	0.0562	0.007	0.3302	11653

The majority of site-years have chlorpyrifos-oxon concentrations in the range of 0.01 to 0.1 µg/L (**Table 57**). Sites with confirmed chlorpyrifos-oxon concentrations are in California (1 site-year), Colorado (1 site-year), Iowa (1 site-year), Indiana (3 site-years), Kentucky (1 site-year), Missouri (3 site-years), Mississippi (2 site-year), Nebraska (3 site-years), New Jersey (1 site-year), Ohio (1 site-year), Oregon (2 site-years), South Carolina (1 site-year), Washington (1-site-year), and Wisconsin (1 site-year). These detections are found in the USGS_Stream and USGS_state monitoring programs.

Table 57. Distribution of Daily Peak Chlorpyrifos-oxon Concentrations in Filtered Ambient Surface Water by State

Concentration (µg/L)	Frequency of Site-Years
<0.00001	73
0.00001-0.0001	0
0.0001-0.001	4
0.001-0.01	132
0.01-0.1	**1793**
0.1-1	9
1-10	0
<10	0

Unfiltered Samples

Two monitoring programs with samples classified as total, recoverable, and unfiltered were considered in the analysis. There are 114 site-years among the monitoring programs. The maximum daily chlorpyrifos-oxon concentration in unfiltered samples range from 0.05 to 0.29 µg/L (**Table 58**). The maximum chlorpyrifos-oxon concentration of 0.29 µg/L was detected at a Washington site (Peshastin Creek) in 2014 from the WA_Ag monitoring program. This sampling site is located in a watershed with agricultural tree fruit production.[96]

Table 58. Descriptive Statistics of Daily Peak Chlorpyrifos-oxon Concentrations for Unfiltered Ambient Surface Water

Program	Mean	Median	Minimum	Maximum	Count
	Concentration (µg/L)				
USGS_state	0.05	0.05	0.05	0.05	2
WDA	0.0878	0.1	0.0493	0.29	111

The minimum reporting limit (MRL) for chlorpyrifos-oxon in samples classified as unfiltered are shown in **Table 59**. The range of MRLs range from 0.033 to 0.3 µg/L. Typical MRLs, as indicated by the mean, range from 0.07 to 0.1001 µg/L among the monitoring programs.

Table 59. Descriptive Statistics for MRLs of Chlorpyrifos-oxon in Unfiltered Ambient Surface Water

Program	Mean	Median	Minimum	Maximum	Count
	Concentration (µg/L)				
USGS_State_Total_CYPOX	0.070833	0.0795	0.033	0.1	6
WDA-Total_CYPOX	0.100946	0.1	0.096	0.3	2223

The majority of site-years have chlorpyrifos-oxon concentrations in the range of 0.01 to 0.1 µg/L (**Table 60**). These monitoring are representative of monitoring data from Washington.

Table 60. Distribution of Daily Peak Chlorpyrifos-oxon Concentrations in Unfiltered Ambient Surface Water by State

Concentration (µg/L)	Frequency of Site-Years
<0.00001	0
0.00001-0.0001	0
0.0001-0.001	0
0.001-0.01	0
0.01-0.1	**81**
0.1-1	32
1-10	0
<10	0

Finished Water

The monitoring data for finished drinking water samples represent only the PDP monitoring program. There are 146 site-years in this analysis. There are no detections of chlorpyrifos-oxon in finished drinking water. The maximum daily and 21-day average chlorpyrifos-oxon concentrations, therefore, are estimated at 2.75E-12 µg/L. This concentration represents ½ MRL in the monitoring program. Based on this analysis and considering the impact of the assumptions for using different MRLs, the highest chlorpyrifos-oxon concentration in finished drinking water would equal a MRL of 5.5E-12 µg/L

21-day Average Concentration

Filtered Samples

Two monitoring programs had 267 site-years with ≥17 samples to allow estimation of 21-day average concentrations for chlorpyrifos-oxon. The maximum 21-day average chlorpyrifos-oxon concentration in filtered samples ranged from 1.28E-7 to 0.0541 µg/L (**Table 61**). The maximum 21-day average chlorpyrifos-oxon concentration is 0.054 µg/L at a Missouri site (USGS 3.92E+14) in 2013 from the USGS_stream quality index monitoring program. This monitoring program is unique because it has daily sampling during part of the year.

Table 61. Descriptive Statistics of 21-Day Average Chlorpyrifos-oxon Concentrations in Filtered Ambient Surface Water

Program	Mean	Median	Minimum	Maximum	Count
	Concentration (µg/L)				
PDP	7.51E-08	6.6E-08	4.58E-09	1.28E-07	66
USGS_state	0.0301	0.0281	0.0080	0.1141	180
USGS_MSQI	0.0121	0.0120	0.0010	0.0545	21

The minimum reporting limit (MRL) for chlorpyrifos-oxon in samples classified as filtered or dissolved are shown in **Table 62**. The range of MRLs range from 2.55E-07 to 0.3302 µg/L. Typical MRLs, as indicated by the mean, range from 1.32E-7 to 0.0559 µg/L among the monitoring programs.

Table 62. Descriptive Statistics for MRL for Chlorpyrifos-oxon Filtered Ambient Surface Water

Programs	Mean	Median	Minimum	Maximum	Count
	Concentration (µg/L)				
PDP-unfinished_CYPOX	1.32E-07	1.32E-07	6E-09	2.55E-07	1641
USGS_Stream_CYPOX	0.018078	0.024	0.002	0.024	1341
USGS_Stat_CYPOX	0.0559	0.0562	0.007	0.3302	11653

The majority of site-years have 21-day average chlorpyrifos-oxon concentrations in the range of 0.1 to 1 µg/L (**Table 63**). States with confirmed chlorpyrifos-oxon concentrations and site-years with ≥ 17 samples are Colorado (1 site-year), Indiana (1 site-year), Missouri (1 site-year), Mississippi (1 site-year), Nebraska (2 site-years), Ohio (1 site-year), Oregon (2 site-years), Washington (1 site-year) and Wisconsin (1 site-year). The other states had no confirmed detections of chlorpyrifos-oxon. These states, therefore, have chlorpyrifos-oxon concentrations dependent on the assumption used for quantification of the MRL. In this analysis, the non-detections are assumed to be equal to ½ MRL.

Table 63. Distribution of 21-day Average Chlorpyrifos-oxon Concentrations in Filtered Ambient Surface Water

Concentration (µg/L)	Frequency of Site-Years
<0.00001	66
0.00001-0.0001	0
0.0001-0.001	0
0.001-0.01	4
0.01-0.1	7
0.1-1	**190**
1-10	0
<10	0

Unfiltered Samples

Two monitoring programs had 92 site-years with ≥17 samples per year to allow for estimation of 21-day average chlorpyrifos-oxon concentrations. The maximum 21-day average chlorpyrifos-oxon concentration in unfiltered samples ranged from 0.0498 to 0.1298 µg/L (**Table 64**).
The maximum 21-day average chlorpyrifos-oxon concentration is 0.1298 µg/L at a Washington site (Peshastin Creek) in 2014 from the WDA monitoring program. This sampling site is located in a watershed with agricultural tree fruit production [93].

Table 64. Distribution of 21-Day Average Chlorpyrifos-oxon Concentrations in Unfiltered Ambient Surface Water

Program	Mean	Median	Minimum	Maximum	Count
WDA	0.0747	0.07	0.0498	0.1298	92

The MRL for chlorpyrifos-oxon in samples classified as unfiltered, total or recoverable are shown in **Table 65**. The range of MRLs range from 0.096 to 0.3 µg/L. The typical MRLs, as indicated by the median, is 0.1 µg/L.

Table 65. Descriptive Statistics for MRL for Chlorpyrifos-oxon in Unfiltered Ambient Surface Water

Program	Mean	Median	Minimum	Maximum	Count
WDA-Total_CYPOX	0.1009	0.1	0.096	0.3	2223

The majority of site-years have 21-day average chlorpyrifos-oxon concentrations in the range of 0.01 to 0.1 µg/L (**Table 66**). There are 68 site-years in Washington with confirmed chlorpyrifos-oxon detections.

Table 66. Distribution of 21-day Average Chlorpyrifos-oxon Concentrations in Unfiltered Ambient Surface Water

Concentration (µg/L)	Frequency of Site-Years
<0.00001	0
0.00001-0.0001	0
0.0001-0.001	0
0.001-0.01	0
0.01-0.1	**80**
0.1-1	12
1-10	0
<10	0

iii. Data Interpretation and Extrapolation

WARP Model

For 2012 (one year), **Table 67** provides the range of the estimated 4-day moving average concentrations and the estimated upper bound 4-day moving average concentrations for chlorpyrifos by HUC-02. The 4-day averages are reported, as peak concentrations are not provided by the Map Application. **Table 68** provides the corresponding results for the 21-day average concentration. Recall, that these estimated concentrations are derived based on monitoring data and as such reflect actual use data. These values are approximately within an order of magnitude of the PRZM5/VVWM modeled concentrations for most maximum labeled rate simulations and compare reasonably well with typical use scenarios as well as the other monitoring data discussed in this document. The highest 4-day average concentration is 2.06 µg/L for HUC-02 region 12 while the upper bound 4-day average concentration is 86.8 µg/L also in HUC-02 region 12. HUC-02 region 12 also has the highest average and upper bound value for the estimated 21-day average concentrations.

Table 67. WARP Map Application Estimated 4-day Moving Average Concentrations for Chlorpyrifos

HUC 2	Count of Detects (Total Count)	Range of Estimated 4-day Moving Average Concentrations (µg/L)	Range of Estimated Upper Bound[a] 4-day Moving Average Concentrations (µg/L)
1	720 (891)	< 0.001 – 0.03	< 0.001 – 1.04
2	1432 (1631)	< 0.001 – 0.42	< 0.001 – 15.29
3	3434 (4058)	< 0.001 – 0.53	< 0.001 – 20.86
4	955 (1227)	< 0.001 – 0.28	< 0.001 – 10.14
5	2278 (2758)	< 0.001 – 0.17	< 0.001 – 6.25
6	593 (728)	< 0.001 – 0.10	< 0.001 – 3.64
7	2403 (2579)	< 0.001 – 0.50	< 0.001 – 19.93
8	307 (697)	< 0.001 – 0.06	< 0.001 – 2.19
9	417 (441)	< 0.001 – 0.59	< 0.001 – 23.18
10	4493 (6177)	< 0.001 – 1.18	< 0.001 – 46.52
11	2173 (2402)	< 0.001 – 0.92	< 0.001 – 36.27
12	1321 (1560)	< 0.001 – 2.06	< 0.001 – 86.75
13	283 (470)	< 0.001 – 0.06	< 0.001 – 2.37
14	445 (707)	< 0.001 – 0.04	< 0.001 – 1.61
15	202 (495)	< 0.001 – 0.08	< 0.001 – 3.21
16	198 (397)	< 0.001 – 0.03	< 0.001 – 1.26
17	1839 (3327)	< 0.001 – 0.13	< 0.001 – 5.19
18	573 (750)	< 0.001 – 0.44	< 0.001 – 17.89
a. 95th upper confidence limit value of the mean value			

Table 68. WARP Map Application Estimated 21-day Moving Average Concentrations for Chlorpyrifos

HUC 2	Count of Detects (Total Count)	Range of Estimated 21-day Moving Average Concentrations (µg/L)	Range of Estimated Upper Bound[a] 21-day Moving Average Concentrations (µg/L)
1	720 (891)	<0.001 - 0.02	<0.001 - 0.78
2	1432 (1631)	<0.001 - 0.32	<0.001 - 10.82
3	3434 (4058)	<0.001 - 0.39	<0.001 - 14.17
4	955 (1227)	<0.001 - 0.21	<0.001 - 7.12
5	2278 (2758)	<0.001 - 0.13	<0.001 - 4.53
6	593 (728)	<0.001 - 0.08	<0.001 - 2.61
7	2403 (2579)	<0.001 - 0.38	<0.001 - 13.92

8	307 (697)	<0.001 - 0.05	<0.001 - 1.65
9	417 (441)	<0.001 - 0.44	<0.001 - 15.97
10	4471 (6177)	<0.001 - 0.89	<0.001 - 32.17
11	2173 (2402)	<0.001 - 0.70	<0.001 - 25.35
12	1321 (1560)	<0.001 - 1.61	<0.001 - 62.02
13	283 (470)	<0.001 - 0.05	<0.001 - 1.82
14	421 (707)	<0.001 - 0.03	<0.001 - 1.14
15	197 (495)	<0.001 - 0.06	<0.001 - 2.35
16	192 (397)	<0.001 - 0.03	<0.001 - 0.93
17	1744 (3327)	<0.001 - 0.10	<0.001 - 3.53
18	558 (750)	<0.001 - 0.33	<0.001 - 12.13
a. 95th upper confidence limit value of the mean value			

Bias Factors

The development of BF for chlorpyrifos are based on selected monitoring data from the USGS_MSQI, registrant monitoring, and state monitoring programs. These monitoring data were selected because the data have high sampling frequency (daily) are representative of different locations (California, Pacific Northwest, Midwestern, and Southeastern Streams) within the United States (**Table 69**). It is important to note that chlorpyrifos was not detected at all sampling sites in the USGS_ MSQI. In fact, chlorpyrifos was detected only at monitoring sites in Oregon, Washington, and Missouri in the USGS_MSQI monitoring program.

Table 69. Description of Monitoring Data Used for Bias Factor Estimation

Monitoring Program	Shortest Sampling Interval	Number of Years	Site	States	Surface Water Classification
USGS Stream Quality Index	Daily	1	27	MO,IA,IN,WI,NE, WA, OR, GA, NC, SC, VA	Flowing Water Stream
California (Registrant Monitoring Program MRID 44711601)	Daily	2	3	CA	Flowing Water Stream

BF statistics for USGS_MSQI sites with daily sampling are shown in **Table 70**. The impact of sampling interval on BF was not important in the USGS_MSQI monitoring sites because the chlorpyrifos occurrence was essentially a single daily maximum concentration with the remaining samples in the time series at the MRL. Therefore, the short duration of chlorpyrifos occurrence did not overlap the short sampling interval of 7 days. This situation prevents an assessment on the impact of sampling interval on bias factor. The BFs for the daily peak concentration from USGS_MSQI data is 1.0 to 221 with an average of 11. In contrast, BFs for the 21-day average concentration range from 0.9 to 11.50 with an average of 1.73. In general, these bias factors are equivalent to the maximum observed concentration divided by ½ MRL.

Table 70. Statistical Description of Bias Factors for Chlorpyrifos from the USGS_ MSQI

Statistics	BF for Daily Peak	BF for 21-day Average
	Sampling Interval	Sampling Interval
	7 days to 28 days	7 to 28 days
Mean	10.92	1.73
Median	1.00	1.00
Minimum	1.00	0.85
Maximum	221.42	11.50
Count	29	29

BFs calculated for the Orestimba Creek data are provided in **Table 71**. For the daily peak concentration from Orestimba Creek, data range from 2.26 to 20.92 with an average of 8.01 for a 7 day sample interval, 4.87 to 40.33 with an average of 15.47 for a 14 day sample interval, 9.76 to 105.62 with an average of 38 for a 21 day sample interval, and 4.87 to 44.36 with an average of 23.39 for a 28 day sampling interval. In contrast, bias factors for the 21-day average concentration from the Orestimba Creek data range from 1.38 to 4.45 with an average of 2.27 for a 7 day sample interval, 1.67 to 8.24 with an average of 3.56 for a 14 day sample interval, 3.47 to 17.68 with an average of 7.91 for a 21 day sample interval, and 1.40 to 7.83 with an average of 4.90 for a 28 day sample interval. The BFs reported in **Table 71** are slightly different than those reported in the 2014 assessment because the current BFs were calculated based on site year as opposed to the study period (May 1, 1996 to April 30, 1997) as done previously. Additionally, the Python program (Chemograph Generator 2) was modified to eliminate extrapolation at the time series beyond the last stratified random interval in site-year chemograph. This code modification was conducted to ensure when there are no detections of pesticide in the site-year time series the BF is equal to 1.

Table 71. Statistical Description of Bias Factors for Chlorpyrifos from the Registrant Monitoring on Orestimba Creek

Statistic	BF for Daily Peak				BF for 21-day Average			
	Sampling Interval				Sampling Interval			
	7 days	14 days	21-days	28 days	7 days	14 days	21 days	28 days
Mean	8.01	15.47	38.00	23.39	2.27	3.56	7.91	4.90
Median	6.22	10.17	27.38	21.20	1.92	2.50	5.06	5.49
Minimum	2.26	4.87	9.76	4.87	1.38	1.67	3.47	1.40
Maximum	20.92	40.33	105.62	44.36	4.45	8.24	17.68	7.83
Count	6	6	6	6	6	6	6	6

Although there are an insufficient number of sites-years with daily monitoring data to derive regression equations for estimation of bias factors, the descriptive statistics provide an indication on the extent of bias for different sampling intervals. The average BFs for the daily peak chlorpyrifos concentrations range from 8 to 38 for the 7-day sampling interval, 11 to 15 for the 14-day sampling interval, 10 to 38 for the 21-day sampling interval, 10 to 23 for a 28-day sampling interval. These data indicate that daily peak BF for chlorpyrifos is generally greater than 10.

The average BF for a 21-day average chlorpyrifos concentrations range from 1.7 to 2 for the 7 day sampling interval, 1.7 to 3.6 for the 14-day sampling interval, 1.7 to 7.9 for the 21-day sampling interval, and 1.7 to 4.9 for the 28-day sampling interval. These data indicate that daily peak BF for chlorpyrifos is less than 10.

The NAWQA data for filtered water samples were examined and the bias factor needed to result in a 1-day average concentration of 0.01, 0.1, 1, and 10 µg/L was determined by sampling site. Mean BFs, as derived from selected daily monitoring data in Oregon, Washington, and California, range from 5 to 20. The use of BFs on the NAWQA data shows that the majority of number of site-years with concentrations from BF adjustment range in concentration from 0.01 to 0.1 µg/L (**Table 72**). However, the application of bias factors substantially increased number of site-years with concentration of 0.1 to 1 µg/L.

Table 72. Bias Factor Analysis for NAWQA sites for Filtered Water Samples

Bias Factor	Number of Site-Years with 1-day (24 hour) Average Concentration Exceeding The referenced Concentration				
	<0.01	0.01-.1 µg/L	0.1-1 µg/L	1-10 µg/L	>10 µg/L
1	3637	507	79	0	0
5	1819	2081	284	39	0
10	1	3636	507	79	0
15	0	3366	739	118	0
20	0	3209	864	147	1

PWC Model and Interpretation of Monitoring Results

<u>*California (Registrant Monitoring Program MRID 44711601)*</u>

For comparative purposes, representative model simulations were completed for Orestimba Creek and are presented in Table 73. The scenarios used in this analysis are also provided in Table 73 while chemical specific model input values are provided in **Table 15.** The estimated peak concentrations are higher than the measured concentrations; however, the estimated concentrations are within an order of magnitude of the measured concentrations.

Table 73. Surface Water Concentration Calculator Simulation Results Comparison with California Registrant Monitoring Program Surface Water Monitoring Data[a]

Represented Location	Represented Crop Use	Estimated Drinking Water Concentration µg/L (PCA adjusted concentration)			Maximum Detected Chlorpyrifos Concentration (associated use)
		1-in-10 Year Peak	1-in-10 Year Annual Average	30 Year Average	
1	Walnut	13.4 (2.68)	2.35 (0.47)	1.73 (0.35)	1.32 µg/L (walnut, spray drift) April 22, 1997 (day 357)
2	Alfalfa	5.66-12.9 (1.13-2.58)	0.69-1.56 (0.14-0.31)	0.61-1.39 (0.12-0.28)	0.92 µg/L (alfalfa, spray drift) March 22, 1997 (day 325)
3					2.22 µg/L (alfalfa, flood irrigation) March 28, 1997 (day 331)

a. MRID 44711601

CA Almond, 1/2.2 lb a.i./A(assumes total annual application of chlorpyrifos was made to the single field on one day), June 10, aerial application [0.95; 0.135 (spray drift assuming no buffer zones or droplet size restrictions)
CA Alfalfa, 1/2.2 lb a.i./A (assumes total annual application of chlorpyrifos was made to the single field on one day) or 1/1.0 lb a.i./A (maximum currently registered application rate), May 6, aerial application [0.95; 0.135 (spray drift assuming no buffer zones or droplet size restrictions)

The estimated concentrations are expected to be highly conservative for a few reasons. A PCA adjustment factor was not applied and it is known that the entire watershed was not treated on the same day or planted with crops that chlorpyrifos may be applied. The report noted that approximately 80 percent of the watershed was forest. If the remaining watershed was assumed to be treated (PCA = 0.20) the peak estimated concentrations are in reasonable agreement with the measured concentrations. This suggests the standard modeling approach employed, although a likely over simplification of reality, does not provide unreasonable highest estimated chlorpyrifos concentrations. Also, the amount of chlorpyrifos applied to the entire area of influence was only 2.2 lb a.i./A spread out over the course of the study. The model simulations assumed all the chlorpyrifos applied over the course of the study (one year) was applied as a single application event. This would suggest that the model approach reasonably accounts for applications even if spread out over time. Lastly, the model simulation also considered a worst case spray drift scenario. It is unclear if any drift reduction technologies (spray drift buffer, large droplet sizes, etc.) were utilized; however, spray drift reduction strategies (*i.e.*, buffers) were not added to the chlorpyrifos labels until the Interim Registration Eligibility Decision in February 2002.

This analysis suggests that the model estimated concentrations of chlorpyrifos compare well with monitoring data when the model is parameterized to reflect the actual use and a PCA representative of all use sites is utilized. Therefore, it is expected that the model estimated chlorpyrifos concentrations provide a reasonable upper bound of concentrations that may occur in the environment based on the modeled use and PCA applied. In addition, this dataset indicates sporadic detections and rapidly fluctuating concentrations of chlorpyrifos, further supporting the use of model EDWCs for deriving a reasonable upper bound estimation of chlorpyrifos exposure in drinking water.
The highest measured concentration of chlorpyrifos of 2.2 µg/L was measured on March 28, 1997 (Day 331 of the study). This peak measured concentrations was associated with a chlorpyrifos application to

alfalfa on March 22, 1997 (day 325 of the study) followed by flood irrigation. Application information obtained from the California Pesticide Use Reporting database (**Table 74**) indicate eight chlorpyrifos applications on alfalfa occurred in Stanislaus County on March 22, 1997. The total number of 390 acres were treated with an average application rate of 0.58 lb a.i./A (range of 0.5 to 1.0 lb a.i./A). The only reported applications of chlorpyrifos that occurred in the county were to alfalfa with the exception of an area of outdoor containerized flower garden plants (0.06 lb a.i./0.25A). The Orestimba Creek watershed is 134 square miles or approximately 84,760 acres. Assuming all the applications that occurred in Stanislaus County occurred within the Orestimba Creek watershed, the corresponding PCT is 0.005 for March 22, 1997. Considering all chlorpyrifos applications for the month of March for Stanislaus County the PCT is 0.16. This suggests that while use of a PCA seems to provide an estimated exposure that reasonably compares to measured concentrations, use of a PCT may substantially underestimate exposure and as such should not be applied without further in-depth analysis of monitoring data where pesticide use information is available.

Table 74. Chlorpyrifos Application in Stanislaus County

1997		March		March 22	
Total Use lb a.i./A	Area Treated (A)	Total Use lb a.i./A	Area Treated (A)	Total Use lb a.i./A	Area Treated (A)
114,218	92,940	8,445	13,186	225	390

<u>Washington State Department of Ecology and Agriculture Cooperative Surface Water Monitoring Program</u>

PWC model simulations were completed to compare measured concentrations of chlorpyrifos from the WSDA for comparative purposes. These simulations and the resulting exposure concentrations reflect chlorpyrifos use information (type/timing of application), maximum label rates, and PCAs provided in the report associated with the various sampling locations. The use scenarios used in model simulations for this analysis are provided in **Table 75**, while chemical specific model input values are provided in **Table 15**. Note that a range of application dates was examined and the date that provided the highest concentration is reported. The results of this analysis are shown in **Table 75**. The monitoring data presented in **Table 75** do not reflect use of a BF. In general, based on the results presented in **Bias Factors** beginning on page 115, a BF of 10 or higher is needed to capture a peak concentration unless daily sampling is available.

Table 75. Surface Water Concentration Calculation Simulation Comparison with Washington State Department of Ecology and Agriculture Cooperative Surface Water Monitoring Program

Represented Location	Represented Crop Use	Model Output *PCA Corrected for Total Cropland (PCA Corrected for Specific Crop[a])*				Maximum Detected Chlorpyrifos Concentration
		Absolute Peak	1-in-10 Year Peak	1-in-10 Year Annual Average	30 Year Average	
Spring Creek	Apples[b]	4.0 *2.0* *(0.16)*	2.6 *1.3* *(0.10)*	0.35 *0.18* *(0.01)*	0.23 *0.12* *(0.01)*	0.27 µg/L
	Grape[c,d]	4.3 *2.2* *(0.56)*	1.7 *0.85* *(0.22)*	0.25 *0.13* *(0.03)*	0.15 *0.08* *(0.02)*	

Sulphur Creek Wasteway	Apples[b]	4.0 *1.7* *(0.20)*	2.6 *1.1* *(0.13)*	0.35 *0.15* *(0.02)*	0.23 *0.10* *(0.01)*	0.28 µg/L
	Grape[c,d]	4.3 *1.8* *(0.47)*	1.7 *0.71* *(0.19)*	0.25 *0.11* *(0.03)*	0.15 *0.06* *(0.02)*	
Marion Drain	Apples[b]	4.0 *2.6* *(0.36)*	2.6 *1.7* *(0.23)*	0.35 *0.23* *(0.03)*	0.23 *0.15* *(0.02)*	0.12 µg/L
	Grape	4.3 *2.8* *0.13*	1.7 *1.1* *0.05*	0.25 *0.17* *0.01*	0.15 *0.01* *<0.01*	
	Mint	6.1 *4.0* *(0.37)*	3.0 *2.0* *(0.18)*	0.36 *0.24* *(0.02)*	0.22 *0.15* *(0.01)*	

a. PCA adjusted EDWCs reflect EDWCs if only the crop specified is treated within the watershed
b. ORApple, w24243 (Yakima), 1/2.0 lb a.i./a, dormant 1/14 (dates examined: 1/1-3/31 based on emergence date in scenario), ground application
c. CAGrape, w24243 (Yakima), 2/2.0 lb a.i./a, 7-day application retreatment, dormant 1/13 (dates examined: 1/1-1/23 based on emergence date in scenario), ground application
d. Individual and combined PCA for concord and wine grapes.
e. ORMint, w24243 (Yakima), 1/2.0 lb a.i./a, 8/17 (8/1-9/31), ground application

Current national spray drift restrictions were considered as part of this analysis.

The estimated peak concentrations are generally higher but never greater than an order of magnitude higher if a BF is applied to maximum observed concentrations when a total cropland PCA is applied to the output values. The estimated concentrations may be higher than the measured values because 1) the sampling program missed the peak concentration (underscores the need of applying a BF), 2) the monitored locations were less vulnerable than the standard "scenarios" used in the model simulations, and/or 3) the application rate and dates were different between the monitoring program and model simulations.

When individual crop PCAs are considered, the estimated peak concentrations in some cases underestimate the measured maximum concentrations. This may be the result of multiple chlorpyrifos applications (*i.e.*, multi-crop) contributing to the measured concentration.

This analysis demonstrates that the model estimated concentrations reasonably compare to measured concentrations. This suggests that if the maximum labeled rates were applied, as simulated using the PWC, the model EDWCs provide a reasonable upper bound on the potential exposure and are not overly conservative.

iv. Discussion and Conclusions

Chlorpyrifos and chlorpyrifos-oxon monitoring data from 16 monitoring programs including site-years from 1992-2016 were considered in the assessment. Although the objective and design of each monitoring program are different, the monitoring data, in total, provide information on the spatial and temporal context on the magnitude and occurrence patterns of chlorpyrifos and chlorpyrifos-oxon in surface water in the United States. In general, measured concentrations of chlorpyrifos [and chlorpyrifos-oxon] varied greatly across the landscape. Higher concentrations are generally found in areas with higher chlorpyrifos use and environmental conditions that make the site more vulnerable to runoff. The monitoring data confirm the potential exposure to chlorpyrifos and chlorpyrifos-oxon via surface water used as source drinking water.

The monitoring data analysis considered all the available monitoring data. Because of the difference in monitoring program designs, including site selection, sample collection, sample frequency, and analytical methods among the sampling programs, statistical interpretation of monitoring data was limited to descriptive statistics (mean, median, minimum, and maximum) for site-year maximum daily concentrations and site-year 21-day average concentrations.

There are several challenges in evaluating the chlorpyrifos and chlorpyrifos-oxon monitoring data. The sample classification among the various monitoring programs included dissolved chlorpyrifos, filtered sample, total chlorpyrifos, unfiltered sample, recoverable chlorpyrifos, finished water, raw intake water, and particulate. These sample designations have different implications for potential drinking water exposure because some chlorpyrifos sorption is expected on suspended sediments. The exposure to chlorpyrifos found in samples with particulates or suspended sediments, as expected in samples classified as total chlorpyrifos, unfiltered sample, recoverable chlorpyrifos, particulates, may be removed in the water treatment processes such as flocculation/sedimentation and filtration. However, there are no data available to assess the potential reduction by these processes for chlorpyrifos or chlorpyrifos-oxon. In contrast, dissolved chlorpyrifos in filtered waters have a higher potential to result in drinking water exposure. Chlorpyrifos-oxon is not expected to bind to sediment as readily as chlorpyrifos. Sample classification was not considered in the chlorpyrifos monitoring data analysis completed by Mosquin, et al. 2015 (Summary provided in **ATTACHMENT 14**).[97]

The highest detection of chlorpyrifos was 14.7 µg/L in an unfiltered water sample and 5.61 µg/L in dissolved/filtered water samples. The vast majority of chlorpyrifos concentrations are below 1 µg/L. The highest frequency of chlorpyrifos concentrations in site-years is 0.01 to 1 µg/L (4945 site-years) and 0.001 to 0.01 µg/L (19879 site-years) for unfiltered water samples and filtered water samples, respectively. These concentration ranges are approaching the minimum reporting limit (MRL) in the monitoring programs.

c. Integration

The integration of modeling and monitoring data for chlorpyrifos and chloropyrifos-oxon requires consideration of numerous factors including pesticide use, watershed properties, hydrology, monitoring site location, sampling frequency, temporal and geographic extent of monitoring data, etc.

Model simulations were completed to represent two different water monitoring datasets - Washington State Department of Ecology and Agriculture Cooperative Surface Water Monitoring Program and Dow AgroSciences (MRID 44711601) Orestimba Creek. For both of these water monitoring programs, enough information was available, including chlorpyrifos use information as well as the PCA, to parameterize the model and post process the model output values. In these simulations, the modeled EDWCs were within an order of magnitude of the measured concentrations. The modeling approach, although a simplified reflection of reality, provides sufficient estimates of chlorpyrifos concentrations in the aquatic systems

[97] Mosquin, P.L., J. Aldworth, N. N. Poletika. 2015. Peak centiles of chlorpyrifos surface-water concentrations in the NAWQA and NASQAN programs. Water Resources 69:261-273.

when the model input values are selected based on known chlorpyrifos use conditions. This suggests that the modeling results are not overly conservative and supports the use of the model to estimate chlorpyrifos and chlorpyrifos-oxon concentrations in drinking water.

In addition, the USGS-WARP modeling output values are also presented in this assessment to characterize the magnitude of chlorpyrifos concentrations in streams and rivers according to USGS monitoring data and actual chlorpyrifos use data. The results, as expected, provide a range of estimated concentrations across the landscape which reasonably compare with modeling results when the model is parametrized to reflect typical use information.

In general, the monitoring data include sampling sites that represent a wide range of aquatic environments including small and large water bodies, rivers, reservoirs, and urban and agricultural locations, but are limited for some areas of the United States where chlorpyrifos use occurs. Also, the sampling sites, as well as the number of samples, vary by year. In addition, the vulnerability of the sampling site to chlorpyrifos contamination varies substantially due to use, soil characteristics, weather and agronomic practices. With the exception of targeted monitoring programs, the quantification of chlorpyrifos concentrations according to chlorpyrifos use is a major uncertainty with understanding the relationship of monitoring data and modeling. A comparison of modeling and monitoring data was conducted according to state and HUC-02 regions for the maximum 1-day chlorpyrifos concentrations in filtered water samples (**Attachment 11**). This analysis provides some spatial delineation of the modeling (PWC and WARP) and monitoring data. The analysis show positive correlations between monitoring data and model predictions for PWC and WARP modeling. A positive correlation of monitoring and model prediction is expected because higher use rates lead to higher chlorpyrifos concentrations. The use rate is a significant variable in both PWC and WARP modeling.[98,99]

The BF analysis shows the potential extent of underestimation in monitoring data due to low sampling frequency. The BF is approximately greater than or equal to ten for daily maximum chlorpyrifos concentration and less than or equal to ten for the 21-day average chlorpyrifos concentration. Additional analysis using a significant regression equation for the relationship of WARP UCB concentration verses unadjusted monitoring data [Log WARPUCB = 0.1781(log monitoring data) + 1.3151, p=0.0537; R2=0.0769] shows the estimated WARP UCB predictions for the 4-day maximum chlorpyrifos concentration ranges from 2.65 to 31 µg/L for monitoring data ranging from 0.00001 to 10 µg/L (**Attachment 11**). Given most of the monitoring data are below 0.1 µg/L, this analysis indicates substantial uncertainty in assessing 1-day maximum chlorpyrifos concentrations from highly censored monitoring data with low sampling frequency. Additionally, a distributional analysis of NWIS data was used to estimate the upper percentile concentrations (0.90^{th} 0.95^{th}, 0.99^{th}, and 0.999^{th}) at sites with more than 10 years of monitoring data. Based on a lognormal distribution assumption, mean and median maximum daily chlorpyrifos concentrations among site-years range from 1 to 2 µg/L from the 90^{th} to the 99^{th} percentile in filtered and unfiltered water samples. At the 99.9^{th} centile, however, the mean maximum daily chlorpyrifos concentration increases by orders of magnitudes from 1 to ≥ 400

---

[98] Stone, Wesley W., C. G. Crawford, and R. J. Gilliom. Watershed Regressions for Pesticides (WARP) Models for Predicting Stream Concentrations of Multiple Pesticides. J. Environ. Qual. 42: 1838-1851.
[99] U.S. Environmental Protection Agency (USEPA). 1998. FIFRA Scientific Advisory Panel: Proposed Methods for Basin-Scale Estimation of Pesticide Concentrations in Flowing Water and Reservoirs for Tolerance Reassessment. July 29 – 30, 1998. Document available at https://archive.epa.gov/scipoly/sap/ meetings/web /html/072998_mtg.html.

µg/L, yet the median 99.9th percentile maximum daily chlorpyrifos concentration is only 1 µg/L. The range of predicted 90th to 9th centile maximum daily chlorpyrifos concentrations is from 1 to 66 µg/L. The highest confirmed chlorpyrifos concentration is 14.7 µg/L in unfiltered water samples and 5.61 µg/L in filtered water samples. Applying a BF of ten to these maximum 1-day chlorpyrifos concentrations, the maximum daily chlorpyrifos concentration increase to 147 µg/L in unfiltered water and 56.1 µg/L in filtered water. The use of various approaches including BF, regression analysis, and distributional analysis for predicting daily maximum chlorpyrifos concentrations suggests considerable underestimation of upper bound concentrations from available monitoring data. More importantly, the modeling and monitoring data are comparable when considering the estimation of upper percentile chlorpyrifos concentrations.

Another consideration in assessing the modeling and monitoring data is the correlation of general monitoring data in ambient surface water and monitoring data at CWSs. The available data on chlorpyrifos and chlorpyrifos-oxon for CWSs indicate no detections of chlorpyrifos or chlorpyrifos-oxon in raw or finished water. This situation is not predicted by the PWC modeling or ambient surface water monitoring data. The apparent disconnect in these data suggest some variables are not being considered in the assessment. The monitoring data for the CWSs in this assessment may not be from sampling locations in vulnerable watersheds with high chlorpyrifos use. Also, the impact of water treatment has not been fully explored. Also, the sampling frequency in the drinking water monitoring was not daily. This is expected to increase the probability of missing peak chlorpyrifos concentrations. Although there is ample evidence to suggest oxidation of chlorpyrifos during chlorination, there is no information on the impact of filtration and sedimentation on chlorpyrifos removal.

The assessment suggests that monitoring data are biased low due to low sampling frequency as well as the non-targeted monitoring program designs. The PWC modeling with regional PCA adjustments, however, provides a reasonable yet conservative estimate of daily and 21-day average chlorpyrifos concentrations. Correction of the sampling bias align the model predictions with monitoring data.

5. Conclusions

In summary, examination of chlorpyrifos use across the United States indicates that there are a number of uses that may result in potential exposure to chlorpyrifos and chlorpyrifos-oxon in finished drinking water. The concentrations are expected to vary across the country with the highest potential for exposure in high use areas in vulnerable (*i.e.*, runoff prone) watersheds. This is supported by both model estimated and measured concentrations of chlorpyrifos and chlorpyrifos-oxon in surface water in the United States.

While chlorpyrifos and chlorpyrifos-oxon have not been detected in drinking water supplies to date, there is the exposure potential. There are several reasons why chlorpyrifos and chlorpyrifos-oxon may not have been detected in drinking water, including sample site location, sampling frequency, as well as drinking water treatment. There is insufficient data available to determine if the community water systems sampled for chlorpyrifos to date are located in watersheds vulnerable to chlorpyrifos contamination. Although the median sampling frequencies in the monitoring programs at CWSs was high (24 samples per year), this sampling frequency is insufficient to capture upper centile chlorpyrifos concentrations. As previously described, chlorpyrifos is converted to chlorpyrifos-oxon in the presence of chlorine. As such, monitoring for chlorpyrifos in chlorinated drinking water does not provide information on the potential exposure to chlorpyrifos-oxon. Finally, the impact of physical removal processes such as flocculation/sedimentation and filtration is not known.

Examination of all available monitoring data, most of which is non-targeted monitoring data, indicates relatively low chlorpyrifos and chlorpyrifos-oxon concentrations with a large number of non-detections on a national scale. However, there are several detections of chlorpyrifos greater than 1 µg/L. Further analysis of the available monitoring data suggests that measured chlorpyrifos and chlorpyrifos-oxon concentrations do not reflect upper bound exposure concentrations nor do the measurements reflect the upper bound of potential exposure (*i.e.*, maximum label rates as chlorpyrifos is not generally used at maximum label rates). To account for this potential underestimation of exposure to chlorpyrifos in the available monitoring data BFs were developed from several sites with daily chlorpyrifos concentration. Although the sites used for BF development are limited to a few sites in California, Oregon, and Washington, the estimated BFs provide a measure on the extent of underestimation (bias) due to low sampling frequencies. The mean BF for the 1-day average concentration for a 7 day sampling frequency is 23. For sampling frequencies greater (14, 21, and 28 days) the mean BF is 43. WARP modeling suggest a BF of 30. This is consistent with the BFs calculated in this assessment.

When measured chlorpyrifos concentrations, which reflect typical chlorpyrifos use rates, are multiplied by BFs the resulting concentrations are within the range of the model estimated chlorpyrifos concentrations for maximum labeled rates and are generally higher than model estimated concentrations based on typical use data. As such, use of BF adjusted measured concentrations or the use of model estimated concentrations of chlorpyrifos and chlorpyrifos-oxon as an estimated upper bound exposure is expected to result in similar dietary risk assessment conclusions.

To assess the potential exposure (maximum label rates) for individual chlorpyrifos uses, model estimated concentrations are recommended. The model estimated drinking concentrations provided in this assessment are considered highly refined (**Table 34**) based on the current use profile for chlorpyrifos. However, if the chlorpyrifos use profile changes, all the model results are provided to quickly facilitate estimating the potential exposure. A sensitivity analysis was completed to address uncertainties associated with, as well as to investigate, the conservative nature of the model input parameters, and demonstrated that the resulting EDWCs were not different enough to alter the dietary risk assessment conclusions.

It should also be noted that depending on the drinking water level of concern, measured concentrations of chlorpyrifos and chlorpyrifos-oxon may exceed the level of concern in some locations across the country. Moreover, consideration of the MRL and BF adjusted MRLs should be considered in comparison to the established drinking water level of concern.