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MEMORANDUM

SUBJECT: Updated Chlorpyrifos Refined Drinking Water Assessment for Registration Review

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This memorandum transmits an update to the refined chlorpyrifos drinking water assessment completed in 2016 for registration review, as well as supporting documents and files. This update builds upon the 2016 DWA and focuses on a subset of currently registered chlorpyrifos uses – alfalfa, apple, asparagus, cherry, citrus, cotton, peach, soybean, sugar beet, strawberry, and wheat in specific areas of the country. These uses were identified as being high benefit crops to growers by the Biological and Economic Analysis Division in OPP, or the most important of all the currently registered uses by Corteva Agriscience. As in past assessments, this refined assessment considers usage data, upper bound, and average application rates. Furthermore, this update uses updated scenarios (i.e., uses new soil, weather, and crop data), applies new methods for considering the entire distribution of community water systems percent cropped area adjustment factors, integrates state level percent crop treated data, and includes quantitative use of surface water monitoring data.

The exposure estimates reported in this assessment and associated conclusions drawn are solely for those uses listed above. Adding additional uses would require reassessment and could change estimated drinking water concentrations and thus, exposure conclusions, and ultimately the risk conclusion relative to the drinking water level of comparison(s).

Chlorpyrifos

Drinking Water Assessment for Registration Review: Update

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Abstract

This refined drinking water assessment provides an update to the 2016 drinking water assessment for the registration review of chlorpyrifos. This assessment only evaluates a subset of currently registered chlorpyrifos uses – alfalfa, apple, asparagus, cherry, citrus, cotton, peach, soybean, sugar beet, strawberry, and wheat in specific areas of the country. This subset of uses was identified as being the most important of all the currently registered uses of chlorpyrifos.

This assessment utilizes new surface water model scenarios (i.e., soil, weather, and crop data), integrates the entire distribution of community water system percent cropped area adjustment factors, integrates state-level percent crop treated data, and considers the quantitative use of available surface water monitoring data. These methods have recently undergone external peer and public review.

Concentrations of chlorpyrifos and chlorpyrifos-oxon in drinking water are not likely to exceed the drinking water level of comparison (DWLOC) with or without the retention of the FQPA safety factor for the subset of uses considered. This conclusion is based on upper bound application rates determined from usage data.

Analysis of monitoring data shows that there are several monitoring sites across the United States that could have concentrations higher than the DWLOCs. However, the contribution of other currently registered uses of chlorpyrifos (i.e., uses not considered in this assessment), could not be ruled out, nor could a definitive conclusion be made that the measured concentration data correlated to one of the specific uses evaluated in this assessment.

Executive Summary

This drinking water assessment (DWA) updates and builds upon the 2016 drinking water assessment for chlorpyrifos (USEPA, 2016) completed as part of the registration review process. The focus of this assessment is surface water, as groundwater was determined to not be a potential route of exposure concern in prior assessments. The estimated concentrations from the 2016 DWA for the specific uses considered in this update were used as a gauge for determining the need for refinement.

Exposure estimates for chlorpyrifos and chlorpyrifos-oxon in drinking water sourced from surface water are provided for upper bound and average application rates and typical application timing for a subset of currently registered uses – alfalfa, apple, asparagus, cherry, citrus, cotton, peach, soybean, sugar beet, strawberry, and wheat in defined areas of the country (i.e., Hydrologic Unit Code (HUC)-2 regions). These uses encompass a large portion of the total amount of chlorpyrifos applied per year on a national basis, but there is also a lot of chlorpyrifos use that is not captured by these crops, including use on corn, almonds, grapes, peanuts, pecans, and walnuts, for example.

This subset of uses was selected based on discussion of critical uses with the registrant, Corteva Agriscience, and high benefit crops determined by the Biological and Economic Analysis Division (BEAD). As California is in the process of canceling most chlorpyrifos uses, this DWA does not consider use in California (HUC-18), except with respect to an evaluation of the monitoring data. Monitoring data from California reflects historical usage of chlorpyrifos that may also represent uses and environmental conditions relevant to the uses considered in this assessment.

This drinking water assessment integrates three recently developed and externally peer reviewed method improvements for conducting drinking water assessments.

1) ***New surface water model scenarios (i.e., soil, weather, and crop data):*** The Pesticide in Water Calculator (PWC) is a model that uses soil, hydrology, land cover/land use, weather, and waterbody properties to simulate environmental conditions to estimate pesticide concentrations for risk assessment purposes. The development of new PWC scenarios described in the methods document titled, *"Creating New Scenarios for Use in Pesticide Surface Water Exposure Assessments"* (USEPA, 2020) provides an opportunity to clearly and consistently identify field scenario inputs, and to rank the millions of new scenarios by vulnerability, thus providing a better understanding of estimated concentrations relative to environmental conditions and use.

2) ***Use of community water system percent cropped area (PCA) adjustment factors and state level percent crop treated (PCT) data:*** The recently completed methods document titled *"Integrating a Distributional Approach to Using Percent Crop Area (PCA) and Percent Crop Treated (PCT) into Drinking Water Assessment"* (USEPA, 2020) provides an approach to apply use and usage data to further refine estimated drinking water concentration (EDWCs) in higher-tier assessments for agricultural and non-agricultural uses individually or in combinations. The goal of the PCA and PCT refinements is to generate EDWCs that are appropriate for human health risk assessment, but more accurately account for the contribution from individual use patterns in the estimation of drinking water concentrations.

3) ***Quantitative use of surface water monitoring data:*** EPA recently evaluated the extent to which existing monitoring data can describe the range of possible pesticide concentrations, using updated tools for monitoring data analysis. The seasonal wave with streamflow adjustment and extended capability (SEAWAVE-QEX) model and sampling bias factors (SBFs) were evaluated for short-term and long-term exposure durations of interest and described in the White Paper titled *"Approaches for Quantitative Use of Surface Water Monitoring Data in Pesticide Drinking Water Assessments"* and presented to the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) Scientific Advisory Panel (SAP) in November 2019. The goal of this work is to use surface water monitoring data at higher tiers to confidently estimate pesticide concentrations in surface water that may be sourced by community water systems.

A description of how these methods fit into the overall tiered drinking water assessment process can be found in the Framework for Conducting Pesticide Drinking Water Assessments for Surface Water (DWA Framework) (USEPA, 2020).

Both chlorpyrifos and chlorpyrifos-oxon are considered residues of toxicological concern in drinking water in this assessment. Chlorpyrifos-oxon forms from the treatment, e.g., chlorination, of source water containing chlorpyrifos. While chlorination is the primary method of disinfection used in the United States, other methods are used such as chloramines. Generally, alternatives to chlorination are used by systems serving larger populations.

To address the multitude of water treatment possibilities across the country, a bounding approach is used in this assessment to capture the range of potential exposures to chlorpyrifos or chlorpyrifos-oxon in drinking water. To represent those facilities that use disinfectant processes not including 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, which is persistent over typical drinking water treatment distribution times.

The drinking water estimates are compared with four different DWLOCs. The Health Effects Division (HED) provided EFED with drinking water levels of comparison based on 10% red blood cell acetylcholinesterase inhibition for both acute (1-day) and steady state (21-day) exposure. For each of these exposure durations, two DWLOCs are considered, one with, and one without retention of the 10X FQPA safety factor.

Acute DWLOCs were calculated by HED for infants, children, youths, and adult females both with and without the 10X FQPA SF. With the 10X FQPA SF retained, the lowest acute DWLOC calculated was for infants (<1 year old) at 23 ppb chlorpyrifos-oxon. With the FQPA SF removed (FQPA SF of 1X) the lowest acute DWLOC calculated was for infants (<1 year old) at 240 ppb chlorpyrifos-oxon. Steady state DWLOCs were calculated by HED for infants, children, youths, and adult females both with and without the 10X FQPA SF. With the 10X FQPA SF retained, the lowest steady state DWLOC calculated was for infants (<1 year old) at 4.0 ppb chlorpyrifos-oxon. With the FQPA SF removed (FQPA SF of 1X) the lowest steady state DWLOC calculated was for infants (<1 year old) at 43 ppb chlorpyrifos-oxon.

While this drinking water assessment is more refined than the 2016 assessment, it continues to demonstrate that 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.

Modeling results suggest EDWCs of either chlorpyrifos or chlorpyrifos-oxon in raw water (i.e., source water) or finished drinking water are not likely to exceed the DWLOCs for the 11 critical/high benefit uses included in this assessment, with or without the 10x FQPA safety factor. This conclusion only applies to these specific 11 uses in the areas of the country specified. It would be necessary to conduct a new DWA if additional uses were considered. Of note, this assessment does not account for potential residues in drinking water that may result from application on high usage crops such as corn, almonds, grapes, peanuts, pecans, and walnuts, as these crops were not identified by Corteva as critical uses or by BEAD as having high benefit to growers. This assessment also does not account for exposure from non-agricultural uses. If additional crops or non-agricultural use sites are considered, it is expected that model estimated concentration could be above the 10x DWLOC in some areas of the country, primarily driven by the increase in percent cropped area. It is possible with refinement that additional crops or non-agricultural use sites may result in concentrations below the 1x DWLOC; however, additional work would be necessary.

Evaluation of available surface water monitoring data and the application of SEAWAVE-QEX and sampling bias factors suggests chlorpyrifos-oxon concentrations may be above both the 1-day and 21-day DWLOCs with or without the FQPA safety factor. Additional analyses were completed as part of a weight-of-evidence to better understand what uses and environmental conditions are associated with these concentrations, however, the available monitoring data could not be specifically linked to the uses considered in this assessment.

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. Whether exposure is to chlorpyrifos or chlorpyrifos-oxon is highly dependent on local drinking water treatment processes.

a. Modeling Summary

A summary of the chlorpyrifos-oxon EDWCs resulting from upper bound (descriptions are provided by crop in supporting document provided in **ATTACHMENT 2**) application rates for each refinement step are presented in **Table 1** by 2-digit HUC region. Only chlorpyrifos-oxon EDWCs are provided here as the exposure and risk assessment conclusions are driven by exposure to chlorpyrifos-oxon.

Table 1. Surface Water Sourced Estimated Drinking Water Concentrations Resulting from Different Refinements for a Subset of Upper Bound Application of Chlorpyrifos Uses

2-digit HUC Name Overlapping States[1]	2-digit HUC Uses	Maximum 1-in-10 Year Estimated Chlorpyrifos-oxon Concentrations in Source Surface Water (µg/L)			
		Maximum 2-digit HUC Use Site-Specific Percent Cropped Area[2]		Percent Cropped Area Aggregation[3]	Percent Cropped Area-Percent Crop Treated Aggregation[4]
		1-day Average	21-day Average	21-day Average	21-day Average
Mid-Atlantic VT, NY, PA, NJ, MD, DE, WV, DC, VA	HUC-02 Apple and Peach	1.0	0.8	-	-
South Atlantic-Gulf VA, NC, SC, GA, FL, TN, MS	HUC-03 Cotton, Citrus, Peach, and Soybean	3.1	1.8	-	-
Great Lakes WI, MN, MI, IL, IN, OH, PA, NY	HUC-04 Alfalfa, Sugar beet, Apple, Cherry, Peach, Soybean, and Asparagus	22.8	19.6	3.4	-
Ohio IL, IN, OH, PA, WV, VA, KY, TN	HUC-05 Apple and Soybean	5.3	4.0	-	-
Tennessee VA, KY, TN, NC, GA, AL, MS	HUC-06 Apple	0.4	0.2	-	-
Upper Mississippi MN, WI, SD, IA, IL, MO, IN	HUC-07 Alfalfa, Sugar beet, and Soybean	9.9	7.2	5.4	3.2
Souris-Red-Rainy ND, MN, SD	HUC-09 Alfalfa, Sugar beet, Soybean, Spring Wheat, and Winter Wheat	8.3	5.6	5.2[4]	3.3
Missouri MT, ND, WY, SD, MN, NE, IA, CO, IA, KS, MO	HUC-10 Alfalfa, Soybean, Spring Wheat, and Winter Wheat	5.7	3.6	-	-
Arkansas-White-Red CO, KS, MO, NM, TX, OK, AR, LA	HUC-11 Alfalfa, Soybean, and Winter Wheat	3.9	3.9	-	-
Texas-Gulf NM, TX, LA	HUC-12 Citrus, Peach, and Winter Wheat	1.1	0.7	-	-
Pacific Northwest WA, ID, MT, OR, WY, UT, NV	HUC-17 Alfalfa, Sugar beet, Apple, and Strawberry	8.5	6.1	2.5	-

Green shading indicates concentrations are below the 10x DWLOC (1-day = 43 µg/L and 21-day = 4.0 µg/L) while red shading indicates concentrations are above the 10x DWLOC.
- indicates values are not calculated because the concentrations in the prior step were below the 10x DWLOC.
[1] Sites are listed that include any overlap with the HUC-2 region.
[2] Use site-specific PCA refers to the use of a percent cropped area adjustment factor to adjust EDWCs to account only for the potential use sites (e.g., for example for HUC-03 the PCA is the summation of individual percent cropped area for orchard, cotton, and soybean) within each individual community water system where chlorpyrifos is being considered (see column "2-digit HUC Uses").
[3] PCA aggregation refers to the use of individual percent cropped area adjustment factors to proportionally allocate pesticide residue contribution in the development of EDWCs based on potential chlorpyrifos use sites (i.e., land use data) for individual watersheds. This analysis was done using the model output 1-in-10 year values and does not account for temporal residue contributions.
[4] PCA-PCT aggregation refers to the use of individual percent cropped area adjustment factors to proportionally allocate pesticide residue contribution in the development of EDWCs based on known chlorpyrifos use for individual watersheds. This analysis was done using the model output 1-in-10 year values and does not account for temporal residue contributions.
[5] The use pattern specific PCA is higher (i.e., >1) than all-ag PCA (0.95). Therefore, the use pattern specific PCA is capped at all-ag value and the use pattern PCA should not exceed the all-agricultural PCA. However, when aggregating the individual use residue contributions results, this capping cannot be completed.

In summary, after the first refinement of applying use (usage rates, application dates and retreatment interval) data along with 2-digiti HUC maximum use site-specific percent cropped area (PCA), the EDWCs for upper bound application rates are below both the 1-day and 21-day 1x DWLOCs. However, EDWCs are above the 21-day 10x DWLOC in HUC-04 (considering use only on alfalfa, sugar beet, apple, cherry, peach, soybean, asparagus), HUC-07 (considering use only on alfalfa, sugar beet, soybean), HUC-09 (considering use only on alfalfa, sugar beet, soybean, and spring and winter wheat), and HUC-17 (considering use only on alfalfa, sugar beet, apple, and strawberry). These regions were further refined.

After the second refinement, which includes aggregation of the 1-in-10 year 21-day average concentrations (i.e., portioning the residue contribution from each use), only HUC-07 and HUC-09 have EDWCs greater than the 10x DWLOC. HUC-04 and HUC-17 are no longer considered for further refinement.

The third refinement, which utilized the application of percent crop treated data based on state level usage data in HUC-07 and HUC-09, suggests that concentrations are below the DWLOCs.

The exposure estimates reported in Table 1 and associated conclusions drawn are solely for those uses listed above. Consideration of fewer uses reduces the footprint (i.e., percent cropped area) where chlorpyrifos may be applied. Adding additional uses would require reassessment and could change estimated drinking water concentrations and thus, exposure conclusions, and ultimately the risk conclusion relative to the drinking water level of comparison(s).

It should be noted that in some cases the states included (or listed) in a region, as described in Table 1, may not entirely fall within one region. Therefore, the regional conclusions should not be assumed to occur across the entire state, but only part of the state with overlap.

b. Monitoring Summary

SEAWAVE-QEX analysis was completed for 11 sites across the country. SEAWAVE-QEX permits the estimation of pesticide concentrations between sampling events. Estimated chlorpyrifos and chlorpyrifos-oxon concentrations from SEAWAVE-QEX do not exceed the 1- or 21-day 1x or 10x DWLOCs.

Application of SBFs to sites with enough data to support a high confidence analysis indicate that concentrations may be higher than the DWLOCs in HUC-17. Sites with less data suggest concentrations could be higher than the DWLOCs in several HUCs for both the 1- and 21-day and 1x and 10x DWLOC. It should be noted that most available monitoring data for chlorpyrifos do not meet data quantity criteria for use in SEAWAVE-QEX or for the quantitative application of SBFs. Generally, the highest quality and quantity of chlorpyrifos data would be considered historical. The detection frequency for chlorpyrifos has generally gone down in recent years; however, often this is concurrently observed with a reduction in sample frequency, so it cannot be determined if occurrence frequency of chlorpyrifos is going down.

Problem Formulation

a. Background

Over the past 15 years, there have been four assessments of potential chlorpyrifos exposure in drinking water. In the 2001 Interim Reregistration Eligibility Decision (IRED), OPP considered exposure to chlorpyrifos in drinking water[1,2] and recommended the quantitative use of monitoring data to estimate exposure in groundwater. At the time of the IRED, measured chlorpyrifos concentrations in groundwater from termiticide uses (greater than 2000 µg/L) were the primary focus of drinking water exposure. The model groundwater 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 EDWCs for several agricultural uses of chlorpyrifos on a national basis and examined available monitoring data (USEPA, 2011). That assessment recommended the use of surface water 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 (USEPA, 2014) considered public comments received following release of the 2011 drinking water assessment. The 2014 assessment presented an approach for deriving more regionally specific estimated drinking water exposure concentrations for chlorpyrifos and chlorpyrifos-oxon for two 2-digit HUC regions (**Figure 1**).[3] A 2-digit HUC region is a hydrologically-based area that delineates contiguous drainage areas. There are 18 regions in the lower 48 states, plus 1 additional each for Alaska, Hawaii, and the Caribbean (21 regions total in the U.S.). 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

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[1] 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

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

[3] Hydrologic Units Codes are a hierarchical system developed by United States Geological Survey to catalogue hydrological units within the United States. In this system, there are 18 individual HUC-02 regions in the contiguous drainage areas in the United States with an average size of 177,560 mi^2. The U.S. is divided and sub-divided into smaller hydrologic units. These units are arranged within each other and identified by a unique code consisting of two to eight digits based on the levels of classification in the hydrologic unit system. Additional information can be found at https://water.usgs.gov/GIS/huc.html.
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)

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

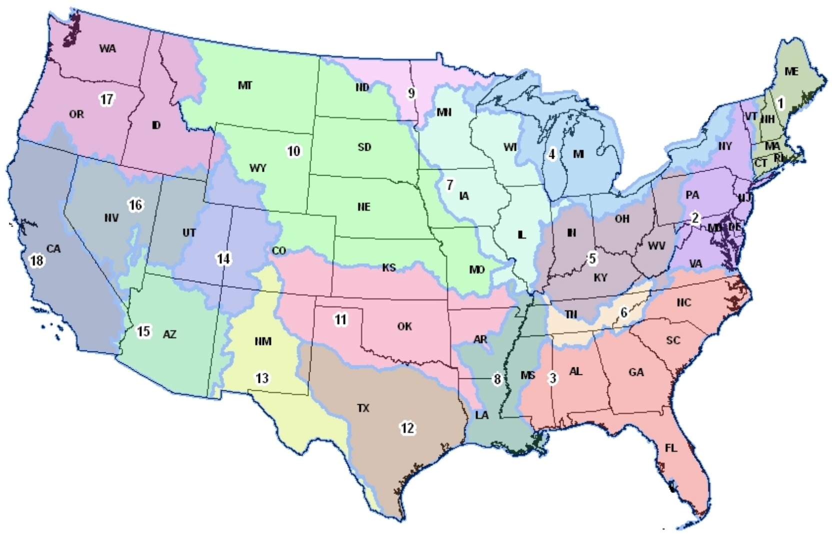

Figure 1. Spatial Distribution of HUC-02 Regions and U.S. State Boundaries

The 2016 DWA (USEPA, 2016) served to combine, update, and complete analysis for all 2-digit HUCs (or regions) presented in the 2011 and 2014 drinking water assessments for chlorpyrifos as part of the registration review process. The document specifically focused on the exposure estimates for surface water. Urban uses, that had not previously been assessed due to label ambiguities and challenges interpreting the label, were also included. PWC-modeled estimated concentrations indicated that chlorpyrifos and chlorpyrifos-oxon concentrations in drinking water vary over the landscape with potential for localized concentrations to be >100 µg/L for the 21-day average concentration based on maximum use rates provided on the Master Use Summary Table (see **ATTACHMENT 1**). Results were also provided for application rates reflective of typical usage practices, resulting in lower concentrations, though many concentrations are above the current DWLOCs (see **Residues of Concern and Drinking Water Level of Comparison** section beginning on **page 22**).

In addition, a robust statistical analysis of all available surface water monitoring data for chlorpyrifos and chlorpyrifos-oxon was completed as part of the 2016 drinking water assessment. This included data from federal, state, and local agencies, universities, and the registrant.[4] The challenges and uncertainties in evaluating the chlorpyrifos and chlorpyrifos-oxon monitoring data were explained in detail. In summary, the data were determined to be inadequate to characterize the potential short-term exposure to chlorpyrifos and chlorpyrifos-oxon across the landscape. Though the model SEAWAVE-Q and SBFs were used to quantify the potential temporal uncertainty in the available monitoring data (i.e.,

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[4] Surface water monitoring programs considered as part of 2016 DWA include Dow Agrosciences California Monitoring Program (DACMP), 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 (WSDA).

from non-daily sampling) on a site-specific basis, the assessment concluded that concentrations in aquatic systems likely fall within the range of PWC model-estimated concentrations reported in the assessment and could be above the DWLOC discussed in this assessment (see **Residues of Concern and Drinking Water Level of Comparison** section beginning on **page 22**).

b. Assessment Scope

This document provides an update to the refined drinking water assessment completed in 2016. This update integrates three new methods for advancing how EFED conducts drinking water assessments. The three methods include:

1) incorporation of new PWC surface water model scenarios (i.e., soil, weather, and crop data);
2) presentation of the entire distribution of community water systems percent cropped area adjustment factors and integration of state level percent crop treated area data; and
3) quantitative use of surface water monitoring data.

This assessment focuses on a subset of currently registered chlorpyrifos uses. Specifically, this assessment focuses on critical and high benefit uses of chlorpyrifos on alfalfa, apple, asparagus, cherry, citrus, cotton, peach, soybean, sugar beet, wheat, and strawberry in specific 2-digit HUC regions except for HUC-18, -19, -20, and -21. HUC-18 is not considered because California which makes up most of the region is canceling most chlorpyrifos uses. The other HUCs are not typically considered in drinking water assessments. HUCs in the contiguous states are expected to cover these regions -19, -20, and -21 are not expected to have the same agricultural intensity as areas within the contiguous states.

This assessment builds upon prior assessments and begins at the Tier 3 assessment level and proceeds through a Tier 4 assessment level, the most highly refined assessment tier. Based on prior monitoring data analysis conducted as part of the 2016 DWA and preliminary analyses completed as part of this assessment, it was decided that a Tier 4 monitoring data analysis would be beneficial to the assessment and could be informative if additional crops were evaluated. EDWCs are compared to the DWLOC (for more information on the DWLOC see the Residues of Concern and Drinking Water Level of Comparison section on **page 22** on this document).

c. Use Characterization

Chlorpyrifos is an organophosphate used as an insecticide 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 July 2020), there are currently 112 active product labels (76 Section 3s and 36 Special Local Needs), which include formulated products (some with multiple active ingredients) and technical grade chlorpyrifos.

Several updates have been made to the chlorpyrifos registration over the years. For example, in the early 2000s, the registrants voluntarily agreed to eliminate and phase out some uses including eliminating most homeowner uses, as well as use on tomatoes, and restricting use on apples to pre-bloom and dormant applications. In addition, in 2002 label changes were made to include buffer zones to protect water quality as well as several reductions in application rates per season on a variety of crops including citrus and corn. More recent label updates have included spray drift buffers for sensitive sites (e.g., schools) to protect human health. In addition, in the early 2010s a master use summary table was developed in consultation with the technical registrants to ensure consistency across labels and further define the intended use of chlorpyrifos.

1. Master Use Summary Table

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 Table provided in **ATTACHMENT 1**). This summary reflects all currently registered labels and any agreed-upon changes to these labels from the registrants that have not been made to the labels to date.

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. Commitment letters from the chlorpyrifos registrants are available online as part of the Biological Evaluation Chapters for Chlorpyrifos ESA Assessment.[5] 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 except for 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 air blast, and chemigation) are allowed. Registered labels for liquid applications (i.e., flowable products) require 25-foot (ground boom and chemigation), 50-foot (orchard air blast), or 150-foot (aerial) no-spray buffer zones adjacent to waterbodies.

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].

[5] https://www3.epa.gov/pesticides/nas/final/chlorpyrifos/appendix-1-5.pdf

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).

2. Usage Data

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). Use on corn and soybean make up 20% of the total volume of chlorpyrifos used in the United States each year. However, both crops have low percent (≤5%) crop treated. 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 as shown in **Figure 2**.

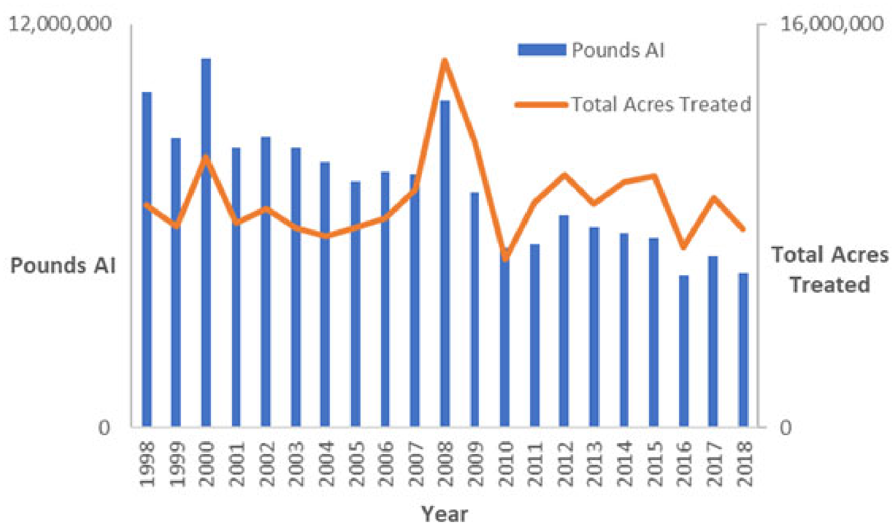


Figure 2. Chlorpyriphos Total Acres Treated and Total Pounds A.I. Applied (1998-2018)[6]

Limited national level chlorpyrifos usage data are available for registered non-crop use sites. These data not summarized here.

Critical Uses

In discussions with Corteva Agriscience, several crops were identified where chlorpyrifos is a critical pest management tool. This includes use of chlorpyrifos to combat alfalfa weevil in alfalfa, scale in citrus, cut

[6] Kynetec USA, Inc. 2019. "The AgroTrak® Study from Kynetec USA, Inc." Database Subset: 1998-2018

worms and lygus bug in cotton, two spotted spider mites in soybean, sugar beet root maggot in sugar beet and Russian wheat aphid in wheat. These uses have been cross walked with 2-digit HUC regions with BEAD's help. A summary of each critical use is provided in **APPENDIX A** and briefly summarized in **Table 2**, while more detailed information from BEAD is provided in **ATTACHMENT 2**. This table notes the only regions identified where the chlorpyrifos use is critical. It is noted that use of chlorpyrifos in California (HUC-18) is not considered in this assessment given the recent regulatory actions the State has taken regarding chlorpyrifos use.

Table 2. Critical (according to Corteva Agriscience) Chlorpyrifos Use Summary

Use	2-digit HUC	Maximum Single Rate (lb a.i./A)	Maximum Annual Rate (lb a.i./A)	Maximum of Average Surveyed Single Application Rate (lb a.i./A)[a]	Maximum of Surveyed Single Application Rate (lb a.i./A)[a]	Average Annual Pounds Chlorpyrifos Applied
Alfalfa	04, 07, 09, 10, 11, 13, 14, 15, 16, and 17	1.0 (l)	5.0	0.6	1.3	600,000
Citrus[b]	03, and 12	6.0 (l)	10.5	2.7	3.0	450,000
Cotton	03	1.0 (l)	3.2	0.2	1.0	70,000
Soybean	03, 04, 05, 07, 09, 10, and 11	2.2 (g)[b]	3.0	0.5	1.0	1,200,000
Sugar beet	04, 07, 09, and 17	2.0 (g)[b]	4.0	1.2	1.5	100,000
Wheat	09, 10, 11, and 12	4.0 (l)	12.0	0.4	0.8	600,000

a. Maximum across the noted 2-digit HUCs. Values for the individual HUCs are provided in **ATTACHEMNT 2**.
b. Includes data for all citrus crops including orange, lemon, and grapefruit.

Data summarized in this table are taken from **ATTACHMENT 2**.
(g) granular
(l) liquid application
1.0 for liquid applications

High Benefit Uses

In addition to the uses that Corteva Agriscience identified as critical, BEAD identified several uses where chlorpyrifos is a high benefit to growers. A high benefit signifies that there are no alternative pesticides available or the alternatives are expensive or not as efficacious for a pest on a specific crop. This includes apple, asparagus, tart cherry, peach, and strawberry. A summary of each critical use is provided **APPENDIX A** and briefly summarized in **Table 3,** while more detailed information from BEAD is provided in **ATTACHMENT 2**. This table notes the only regions identified where the chlorpyrifos use is high benefit to a subset of uses.

Table 3. High Benefit Chlorpyrifos Use Summary

Use	2-digit HUC	Maximum Single Rate lb a.i./A	Maximum Annual Rate lb a.i./A	Maximum of Average Observed Single Application Rate lb a.i./A[a]	Maximum of Observed Single Application Rate lb a.i./A[a]	Average Annual Pounds Chlorpyrifos Applied
Apple	02, 04, 05, 06, 17	2.0 (l)	2.0	1.5	2.8[b]	300,000
Asparagus	04	1.5 (g)	3.0	0.96	1.0	70,000
Tart Cherry	04	4.0 (l)	14.5	1.1[e]	3.0[d,e]	60,000[d]
Peach	02, 03, 04, 12	3.0 (l)	8.0[c]	1.3	3.0	30,000
Strawberry	17	2.0 (l)	4.0	1.24	2.0	<500

a. Maximum across the noted 2-digit HUCs. Values for the individual HUCs are provided in **ATTACHEMNT 2**.
b. 2.0 lb a.i./A is the 90th percentile application rate
c. 8.0 lb a.i./A per year is permitted in Georgia and South Carolina; however, the annual max application rate is 5.5 lb a.i./A in other areas of the county.
d. The maximum rate observed is 3.0 lb a.i./A with the 90th percentile at 2.0 lb/A.
e. Both sweet and tart cherry

Data summarized in this table are taken from **ATTACHMENT 2**.
(l) liquid application, (g) granular

d. Exposure Characterization

1. Conceptual Exposure Model

Chlorpyrifos will initially enter the environment via direct application (e.g., liquid spray and granular) to use sites. It may move off-site via spray drift, volatilization (primarily following foliar applications), and runoff (generally by soil erosion and to a lesser extent 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 desulfurization to form chlorpyrifos-oxon as shown in **Figure 3.** TCP may be converted to 3,5,6-trichloro-2-methoxypyridine (TMP) also shown in **Figure 3**. Most 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, phosphorus-sulfur double bond (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 desulfurization 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.

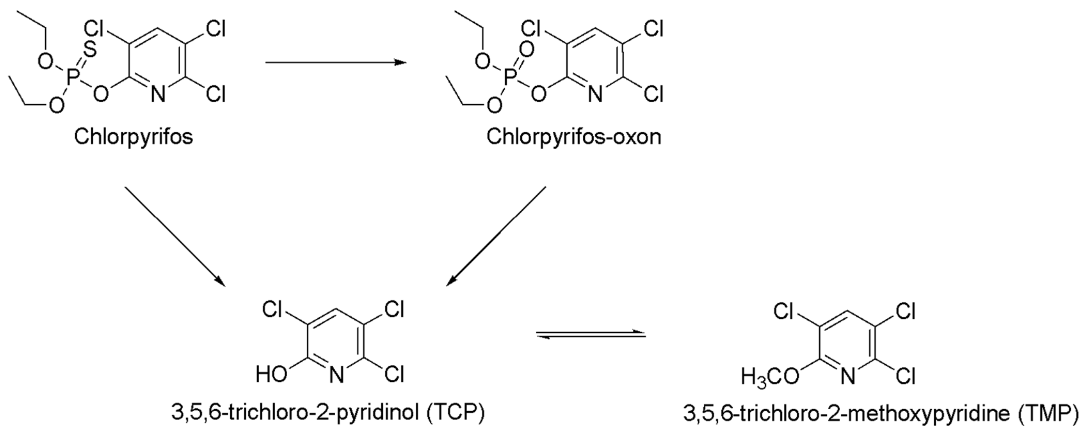


Figure 3. Environmental Transformation of Chlorpyrifos

2. Residues of Concern and Drinking Water Level of Comparison

Chlorpyrifos and chlorpyrifos-oxon are considered residues of toxicological concern for dietary exposure, including drinking water.[7] For this assessment, HED provided four different DWLOCs for both chlorpyrifos and chlorpyrifos-oxon based on 10% red blood cell acetylcholinesterase inhibition for both acute (1-day) and steady state (21-day) exposure. For each of these exposure durations, two DWLOCs are consider one with and one without retention of the 10X FQPA safety factor. This was done because the science addressing neurodevelopmental effects remains unresolved. The DWLOCs for chlorpyrifos are provided in **Table 4.** The DWLOCs for chlorpyrifos-oxon are provided in **Table 5**.[8] The DWLOCs may not be exactly 10-fold apart because the food and residential components of the aggregate exposure assessment completed by HED make up a different percentage of the risk cup depending on whether the 10x FQPA safety is retained or removed.

Table 4. Chlorpyrifos Drinking Water Level of Comparison

Safety Factor	Acute (1-day) μg/L	Steady State (21-day) μg/L
Retained (10x DWLOC)	180	17
Removed (1x DWLOC)	1000	100

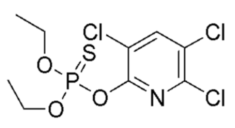
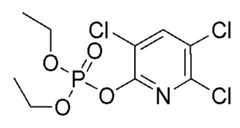
Table 5. Chlorpyrifos-oxon Drinking Water Level of Comparison

FQPA 10x Safety Factor	Acute (1-day) μg/L	Steady State (21-day) μg/L
Retained (10x DWLOC)	23	4.0
Removed (1x DWLOC)	230	43

Physical chemical properties for chlorpyrifos and chlorpyrifos-oxon are provided in **Table 6** (USEPA, 2016). TCP and TMP are not considered residues of toxicological concern based on analysis by HED and, therefore, are not discussed in detail in the remaining sections of this document.

[7] Email from Danette Drew (EPA/HED) to Rochelle Bohaty (EPA/EFED), September 21, 2010.
[8] Email from Kristin Rickard (EPA/HED) to Rochelle Bohaty (EPA/EFED), June 3, 2020.

Table 6. Physical/Chemical Properties of Chlorpyrifos and the Transformation Product of Concern, Chlorpyrifos-oxon

Parameter	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)(OC C)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
Table is taken directly from the 2016 DWA (USEPA, 2016)		

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 100 percent. Therefore, an individual would be exposed to both chlorpyrifos and chlorpyrifos-oxon to some degree. For example, an individual could be exposed to 10 percent chlorpyrifos and 90 percent chlorpyrifos-oxon. More discussion is provided in **Drinking Water Treatment Effects** subsection of this document (pg. 26).

3. Environmental Fate

A detailed discussion of the fate and transport of chlorpyrifos and chlorpyrifos-oxon in the environment is provided in the 2016 drinking water assessment. This includes data submitted to the U.S. EPA, as well as open literature data obtained prior to the assessment. Environmental fate parameters for chlorpyrifos are provided in **Table 7** and **Table 8**, respectively. No additional environmental fate data were submitted since the completion of the 2016 drinking water assessment. 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. Chlorpyrifos-oxon is expected to be more mobile but far less persistent in the environment than chlorpyrifos.

Table 7. Summary of Environmental Fate and Transport Characteristics of Chlorpyrifos

Parameter	Test System Name or Characteristics	NAFTA Representative Half-life Values (fitting model)[a] days	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
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) 25 ˚C	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 (DFOP)	MRID 42144911	Acceptable
Aerobic Aquatic Metabolism half-life (days) at 25 ˚C	Water, pH 8.1 Sediment, pH 7.7	30.4 (SFO)	MRID 44083401	Supplemental
Anaerobic Soil Metabolism half-life (days) 25 ˚C	Commerce, loam	78 (IORE)	MRID 00025619	Acceptable
	Stockton, clay	171 (SFO) Values represent only anaerobic phase		
Anaerobic Aquatic Metabolism half-life (days) 25 ˚C	Commerce pH 7.4	50.2 (IORE)	MRID 00025619	Supplemental
	Stockton pH 5.9	125 (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		
Mobility Data				

Parameter	Test System Name or Characteristics	NAFTA Representative Half-life Values (fitting model)[a] days	Study ID	Study Classification
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		

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 DT_{50} 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.
K_d = adsorption coefficient (mL/g)
Koc = organic carbon normalized adsorption coefficient (mL/g_{OC})

Table 8. 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) 25 ˚C	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)		

Test System Name or Characteristics	K_f (regressed)	K_{foc} µg/g	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		

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 Agency, December 21, 2012. The same model used to estimate the value used to derive a model input, is used to describe the DT_{50} 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.

%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

4. Drinking Water Treatment Effects

Because drinking water for a large percentage of the population is derived from community water systems that treat raw water (USEPA, 1989) prior to consumption, the impact of water treatment on pesticide removal and transformation are considered, when possible, in estimating drinking water exposure (USEPA, 2000, 2001, 2011). Community water systems across the national use a wide range of water treatment processes including disinfection, coagulation/flocculation, sedimentation, and filtration (USEPA, 2006). The effect of various processes has been investigated for several pesticides (USEPA, 2011) including chlorpyrifos. These results are detailed in the 2016 DWA.

In summary, in the presence of free chlorine, the most common disinfection process utilized by community water systems, chlorpyrifos transforms to chlorpyrifos-oxon via rapid oxidation by the oxychlorine species. This transformation can yield almost 100% oxon. Reduction of chlorpyrifos in the presence of monochloramines, often used as an alternative to chlorine to avoid transformation biproducts, is low (<10%). Use of monochloramines is more common by community water systems serving larger (>100,001) populations. 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) with a half-life of 12 days under typical water purification conditions (pH 8) due to stabilization .[9] Very limited data on physical removal processes such as coagulation/flocculation, sedimentation, and filtration are available for chlorpyrifos or chlorpyrifos-oxon. However, such processes, except for granular activated carbon,[10] have been shown to be ineffective for select organic pesticides (USEPA, 2001). Based on the physical-chemical properties of chlorpyrifos and chlorpyrifos-oxon, granular activated carbon likely reduces the amount of both chemicals to some extent. However, data are not available on the removal efficiency for either compound. Use of activated carbon is not a common treatment practice for treatment facilities.

Therefore, 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,

[9] pH 8 and residual chlorine concentration of 1 ppm.

[10] U.S. Environmental Protection Agency. 1998. Small System Compliance Technology List for the Non-Microbial Contaminants Regulated Before 1996. EPA 815-R-98-002.

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.

Analysis

a. Approach

This document provides EDWCs by 2-digit HUC using a bounding approach to address the multitude of drinking water treatment possibilities across the country and potential exposures to chlorpyrifos and chlorpyrifos-oxon in drinking water. This assessment begins at Tier 3 and only considered those uses previously described as being a critical use (CU) or high benefit (HB) and are summarized by 2-digit HUC in **Table 9**. Empty cells indicate that the use is not assessed in the respective HUC. Alfalfa use in HUC-13, 14, 15, and 16 are not modeled in this update because prior estimated concentrations indicate that for usage rates provided by BEAD for this assessment, the estimated concentrations would be below the DWLOCs.

Table 9. Chlorpyrifos Use and 2-digit HUC Region Crosswalk

Name of 2-digit HUC Overlapping States	2-digit HUC	Alfalfa	Apple	Asparagus	Tart Cherry	Cotton	Citrus	Peach	Soybean	Sugar Beet	Wheat, Spring	Strawberry	Wheat, Winter
Mid-Atlantic VT, NY, PA, NJ, MD, DE, WV, DC, VA	02	-	HB	-	-	-	-	HB	-	-	-	-	-
South Atlantic-Gulf VA, NC, SC, GA, FL, TN, MS	03	-	-	-	-	CU	CU	HB	CU	-	-	-	-
Great Lakes WI, MN, MI, IL, IN, OH, PA, NY	04	CU	HB	HB	HB	-	-	HB	CU	CU	-	-	-
Ohio IL, IN, OH, PA, WV, VA, KY, TN	05	-	HB	-	-	-	-	-	CU	-	-	-	-
Tennessee VA, KY, TN, NC, GA, AL, MS	06	-	HB	-	-	-	-	-	-	-	-	-	-
Upper Mississippi MN, WI, SD, IA, IL, MO, IN	07	CU	-	-	-	-	-	-	CU	CU	-	-	-
Souris-Red-Rainy ND, MN, SD	09	CU	-	-	-	-	-	-	CU	CU	CU	-	CU
Missouri MT, ND, WY, SD, MN, NE, IA, CO, IA, KS, MO	10	CU	-	-	-	-	-	-	CU	-	CU	-	CU
Arkansas-White-Red	11	CU	-	-	-	-	-	-	CU	-	-	-	CU

Name of 2-digit HUC Overlapping States	2-digit HUC	Alfalfa	Apple	Asparagus	Tart Cherry	Cotton	Citrus	Peach	Soybean	Sugar Beet	Wheat, Spring	Strawberry	Wheat, Winter
CO, KS, MO, NM, TX, OK, AR, LA													
Texas-Gulf NM, TX, LA	12	-	-	-	-	-	CU	HB	-	-	-	-	CU
Rio Grande CO, NM, TX	13	<[a,b]	-	-	-	-	-	-	-	-	-	-	-
Upper Colorado WY, UT, CO, AZ, NM	14	<[a,c]	-	-	-	-	-	-	-	-	-	-	-
Lower Colorado NV, UT, AZ, NM, CA	15	<[a,d]	-	-	-	-	-	-	-	-	-	-	-
Great Basin CA, OR, ID, WY, NV, UT	16	<[a,e]	-	-	-	-	-	-	-	-	-	-	-
Pacific Northwest WA, ID, MT, OR, WY, UT, NV	17	CU	HB	-	-	-	-	-	-	HB	-	HB	-

a. 2016 drinking water assessment indicates EDWCs will be below the DWLOC.
b. HUC-13: 1.0 lb a.i./A (upper-bound); 2.3 µg/L (no PCA adjustment) chlorpyrifos concentration
c. HUC-14: 1.0 lb a.i./A (upper-bound); 1.6 µg/L (no PCA adjustment) chlorpyrifos concentration
d. HUC-15: 0.75 lb a.i./A (upper-bound) 2.5 µg/L (no PCA adjustment) chlorpyrifos concentration
e. HUC-16: 1.0 lb a.i./A (upper-bound) 1.8 µg/L (no PCA adjustment) chlorpyrifos concentration
\- Use not assessed

Critical use (CU)
High benefit (HB)
< Indicates where concentrations are expected to be below the 10xDWLOC
Empty cells with - indicate that the use is not assessed the respective HUC

The 2-digit HUCs considered in this assessment are shown in **Figure 4**. Regions considered in this assessment are shown in green shading while those not considered are shown in gray shading in **Figure 4**.

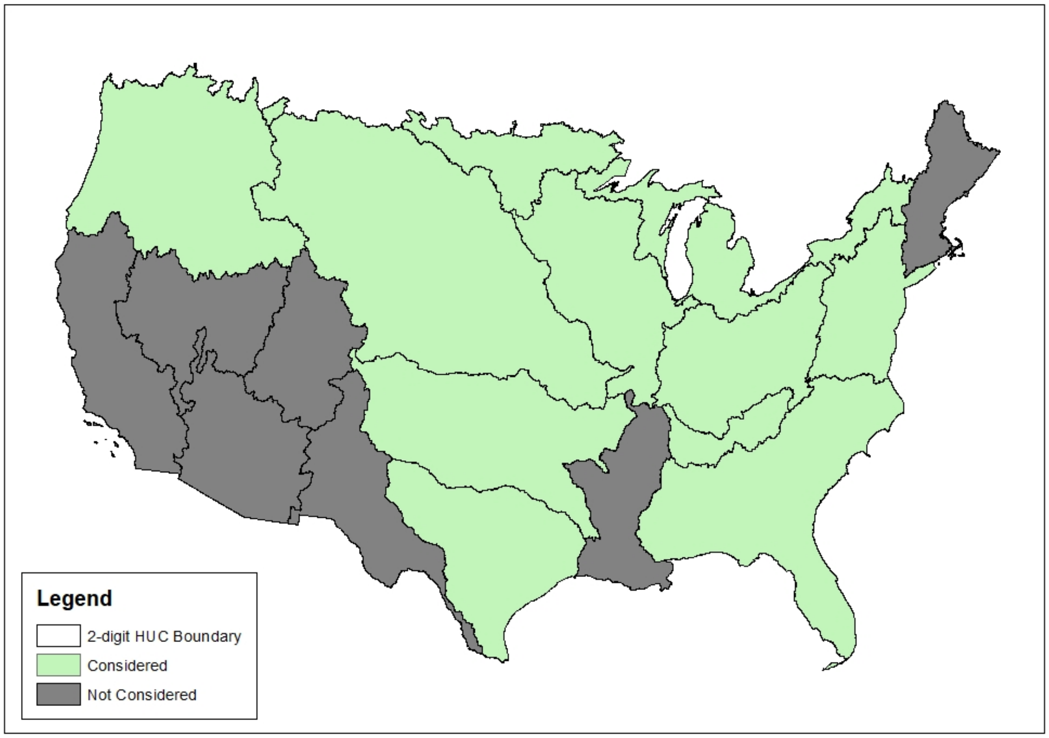


Figure 4. Summary of 2-Digit HUCs with Chlorpyrifos Uses Considered and Assessed in this Assessment

Consistent with the DWA Framework (USEPA, 2019), usage data, regional PCAs, and new methods for considering available surface water monitoring data are utilized. A detailed discussion of the methods and refinement strategies used in this assessment are described in the sections below. The general methods and refinements are well-established and have undergone FIFRA Scientific Advisory Panel (SAP) review or other external review process including formal public comment period and follow currently approved guidance.

b. Model Simulations

1. Pesticide in Water Calculator (PWC)

The Pesticide Root Zone Model (PRZM5) (Young and Fry, 2014) and the Variable Volume Water Model (VVWM) (Young, 2014) 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). The PRZM5 and VVWM documentation, installation files, and source code are available at the USEPA Water Models website.[11]

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

[11] 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.[12]

All model simulations were run using the external batch function within the provisional version of PWC (v.1.89) for chlorpyrifos. This version of the model accommodates use of the new scenarios along with new weather files. A final updated version of PWC is scheduled for release in late 2020. Model outputs for chlorpyrifos were compared to the DWLOCs for chlorpyrifos. In addition, the model outputs for chlorpyrifos are converted to chlorpyrifos-oxon equivalents for comparison to the chlorpyrifos-oxon DWLOCs to complete the bounding approach.

2. Scenario Selection

PWC uses soil, hydrology, land cover/land use, weather, and waterbody properties to simulate environmental conditions. Prior to this assessment, a suite of PRZM5 scenarios were used to estimate pesticide concentrations. These scenarios were developed over time by different groups in EFED and for different purposes. As a result, the previous scenarios represented a range of conditions spanning a range of agricultural and non-agricultural pesticide use sites.; however, the percentile of vulnerability for these scenarios is unknown.

To develop scenarios consistently across the landscape, EFED developed a new method to generate PRZM5 scenarios. These scenarios include the use of more recent weather data (1961-2014) (Fry, et. al, 2016). In addition, a process was developed to compare and rank the millions of new scenarios (combinations of soil, land cover, and weather) in order to evaluate relative vulnerability.

New scenarios available at the time of this assessment include: cotton, hay (surrogate for alfalfa), evergreen orchards (for citrus), row and field crop (for sugar beet), soybean, fresh market (for strawberry), spring wheat, and winter wheat based on the regions where these crops are grown and uses considered in this assessment.

The existing scenario for asparagus was updated with new weather data. A new asparagus scenario is not planned as the existing asparagus scenario is suitable for modeling exposure to pesticides asparagus because asparagus largely occurs in a few isolated areas of the country. Furthermore, use of the fresh market scenario is not appropriate as the growth/management practices of asparagus is different from the other vegetables – harvest of the spears occurs before canopy growth starts; the fern canopy continues to grow until frost, when it is removed.

The existing scenarios for apple, cherry, and peach were updated with new weather data and used in this assessment to cover these respective crops, except for peach in HUC-12 (Texas-Gulf) where the evergreen orchard scenario was expected to be a better surrogate than use of the previous GA Peach scenario. a deciduous orchard scenario was not available at the time this assessment was completed.

The new scenarios were created to be the 90th percentile as ranked by the long-term average concentration in the receiving waterbody. Because rankings are sorption-dependent, scenarios were

[12] 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

created for 3 bins of chemicals: those carried primarily by runoff, those carried primarily by erosion, and those carried by both mechanisms. For more information see USEPA (2020b*)

3. *Chemical Specific Input Parameters*

Although limited environmental fate data are available for chlorpyrifos-oxon, the data suggest that in the environment, there is little or no formation of chlorpyrifos-oxon by routes other than photolysis. Therefore, it is only necessary to conduct aquatic modeling for chlorpyrifos. To address the exposure to chlorpyrifos-oxon in drinking water as a result of formation during drinking water treatment with chlorine (described in the *Water Treatment Effects* section of this document) aquatic modeling results for chlorpyrifos can be used to estimate concentrations of chlorpyrifos-oxon (see **Drinking Water Treatment** on **page 35**).

Summaries of the environmental fate input parameters used in the PWC modeling of chlorpyrifos are presented in **Table 10**. These values are the same as those used in the 2016 DWA and more details on the rational for selection is provided in that assessment. 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[13] (USEPA, 2009),
- *Guidance for Evaluating and Calculating Degradation Kinetics in Environmental Media*[14] (NAFTA, 2012; USEPA, 2012c), and
- *Guidance on Modeling Offsite Deposition of Pesticides Via Spray Drift for Ecological and Drinking Water Assessmen*t[15] (USEPA, 2013)

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

Table 10. 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_{OC}) 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 91.2 days. This half-life value 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 metabolism half-life of 91.2 days will not result in substantially different model-estimated concentration 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	203	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 °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), 25 °C	170.6	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 °C	1.87×10^{-5}	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)	0	Default value	
Application Efficiency	0.99 (ground; air-blast) 0.95 (aerial)	Default Values	
Application Drift	See **Table 12**	AgDRIFT modeling based on label restrictions	Labels contain aquatic buffer distances of 25, 50 and 150 ft for ground, airblast and aerial applications.

All PWC model input files, and output files are provided in **ATTACHMENT 3**.

Use Scenarios

Chlorpyrifos-specific modeling scenarios used in this assessment reflect usage data for chlorpyrifos for the critical and high benefit uses based on information provided by BEAD. This includes application rate, method, and timing. **ATTACHMENT 2** includes all the information provided by BEAD for this assessment while **Table 11** provides the application rates modeled by crop at the 2-digit HUC level. Formulation and application methods are considered in the context of the reported usage data when developing use scenarios and multiple scenarios may be modeled. For example, most applications for sugar beet occur by ground with 20% being the highest percentage of survey applications made by air. Furthermore, the maximum average application rate of 1.2 lb a.i./A and the upper bound rate of 1.5 lb a.i./A exceed the maximum permitted application (1 lb a.i./A) for aerial applications and only granular applications are permitted above 1 lb a.i./A. This is due to how usage rates are estimated. For example, usage rates are estimated across all application methods and formulations. In addition, usage rates are not calculated specifically for the critical or high benefit target pest but for all use on the specified critical or high benefit crop. Generally, the usage data would not be robust enough to estimate usage rates for specific target pests.

Table 11. Chlorpyrifos Use Rates Modeled

Use	2-digit HUC	Average Single Application Rate (lb a.i./ acre)	Upper-bound Single Application Rate (lb a.i./ acre)
Critical Uses			
Alfalfa	04	0.25	1.25
	07	0.53	1.00
	09	0.56	1.00
	10	0.50	1.00
	11	0.58	1.00
	13	0.50	1.00
	14	0.6	1.00
	17	0.52	1.00
Citrus	03	1.88	3.0
	12	2.7	3.5
Cotton	03	0.21	0.5
Soybean	03	0.53	1.00
	04	0.41	0.75
	05	0.33	0.75
	07	0.40	1.0
	09	0.33	0.75
	10	0.35	0.75
	11	0.37	0.75
Sugar beet	04	0.50	1.25
	07	1.16	1.50
	09	0.69	1.25
	17	0.66	1.25
Wheat, spring	09	0.36	0.75
	10	0.27	0.75
Wheat, winter	09	0.44	0.75
	10	0.32	0.50
	11	0.39	0.75
	12	0.21	0.75

High Benefit Uses			
Apple	02	1.5	2.0[1]
	04	1.5	2.0[1]
	05	1.5	2.0[1]
	06	1.5	2.0[1]
	17	1.5	2.0[1]
Asparagus	04	0.964	1.0
Tart Cherry	04	1.5	2.0[1]
Strawberry	17	1.24	2.0
Peach	03	1.3	3.0[1]
[1]The BEAD documents (**ATTACHMENT 3**) reported maximum rates; however, when the 90th percentile is lower it was reported. The 90th percentile use rates were used for modeling in this assessment. For peach, the maximum and the 90th percentile were reported to be the same.			

Spray Drift Exposure

Drift fractions used in this assessment for liquid formulation are consistent with those used in the 2016 DWA (USEPA, 2016) and are presented in **Table 12**. Spray drift estimates reflect the most recent offsite deposition guidance (USEPA, 2013a, 2013b) and consider the 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. No spray drift is assumed for granular applications.

Table 12. Chlorpyrifos Spray Drift Estimates for Liquid Formulations for Use in PRZM5/VVWM (PWC) Model Simulations

Method	Buffer	Spray Drift Fraction (unitless) Application Method and Buffer	Calculation[1]
Ground	**25 ft**	0.008	Ground: 25 ft. distance to water body from edge of field based on labeled buffer; ASAE Fine to medium/course [$dv_{0.5}$ = 341 µm; labels specify 255-340 µm which is larger than ASAE very fine to fine ($dv_{0.5}$ = 175 µm); high boom; 90th percentile; Index Reservoir - downwind water body width 82 m (fraction applied 0.0061); Streams – 4 m (fraction applied 0.0164); Adjusted Spray drift fraction 0.0061 (spray drift fraction for the Index Reservoir) + [0.0164 (spray drift fraction for all Stream) x 0.114 (Surface areas of all streams/surface area of reservoir)] = 0.0079
Air-blast	**50 ft**	0.009	Air-blast: 50 ft. distance to water body from edge of field based on labeled buffer; droplet size not specified; sparse (young, dormant); Index Reservoir - downwind water body width 82 m (fraction applied 0.0056); Streams – 4 m (fraction applied 0.0265); Adjusted Spray drift fraction 0.0056 (spray drift fraction for the Index Reservoir) + [0.0265 (spray drift fraction for all Stream) x 0.114 (Surface areas of all streams/surface area of reservoir)] = 0.0086
Aerial	**150 ft**	0.039	Aerial: 150 ft. distance to water body from edge of field based on labeled buffer; ASAE fine to medium ($dv_{0.5}$ = 255 µm; labels specify 255-340 µm); Index Reservoir - downwind water body width 82 m (fraction applied 0.0331); Streams – 4 m (fraction applied 0.0552); Adjusted Spray drift fraction 0.0331 (spray drift fraction for the Index Reservoir) + [0.0552 (spray drift fraction for all Stream) x 0.114 (Surface areas of all streams/surface area of reservoir)] = 0.039
[1] calculation taken from 2014 DWA.			

4. Post-processing or Output Adjustments

Drinking Water Treatment Adjustment Factor

EDWCs for chlorpyrifos-oxon were derived by multiplying the EDWCs for chlorpyrifos by 0.9541 (molecular weight adjustment factor) and 100% to account for the quantitative conversion of chlorpyrifos to chlorpyrifos-oxon during water treatment as well as the stability of oxon in the persistence in residual chlorine.

Percent Cropped Area Adjustment Factors

Community water system (CWS) watersheds large enough to support a drinking water facility rarely consist of a single crop (e.g., apples) or land cover type (e.g., orchards). To account for the variability in use patterns, PCA adjustment factors are used to reflect the percentage of a watershed that is covered by a particular use or land cover type. The application of PCAs has been extensively documented, reviewed, and utilized in drinking water assessments (USEPA, 2014). Prior to 2020, PCA values were only available for seven crops (e.g., soybean) or crop groups (e.g., vegetables) along with all-agricultural and turf, and combinations thereof. For additional information on the development of the CWS PCA values and use as a refinement in DWAs, see *Development of Community Water System Drinking Water Intake Percent Cropped Area Adjustment Factors for use in Drinking Water Exposure Assessments: 2014 Update* (USEPA, 2014). PCAs are applied by multiplying the modeled estimated concentration by the PCA fraction that captures all the use sites for the pesticide under evaluation.

In this assessment, the PCAs used do not reflect all currently registered chlorpyrifos uses or those uses provided on the Master Use Summary document. Instead, the PCAs used only reflect the subset of critical or high benefit uses described in the Usage Data Section of this assessment by respective 2-digit HUC. In addition to the previously available PCAs, this assessment also uses the recently developed miscellaneous agricultural (misc-ag) PCA. The misc-ag PCA was developed as an alternative to using the all-ag PCAs when a use site does not fall within the existing crop, crop group, or combination of agricultural PCAs. For more information on the development of the misc-ag PCA see*: Integrating a Distributional Approach to Using Percent Crop Area (PCA) and Percent Crop Treated (PCT) into Drinking Water Assessment (USEPA, 2020)*. If more use sites are added (i.e., beyond those considered in this assessment), the PCA used to calculate EDWCs may need to be increased to capture the larger use pattern specific footprint. For example, if non-agricultural uses need to be considered it would be necessary to use a PCA of 1 or add in the non-agricultural PCA depending on the region where the non-agricultural uses need to be considered.

This assessment begins by calculating the maximum use patten specific 2-digit HUC PCAs for each of the respective regions under consideration. Then, if the estimated concentration using the maximum use pattern specific PCA is above the 10x DWLOC, the full distribution of PCAs for the respective region is described. These two steps are described in more detail in the subsections below.

Modeling Refinement 1: Application of Use Pattern Specific PCA

The first refinement of the new drinking water improvement methods includes the use of a use pattern PCA (USEPA, 2020). The use pattern specific PCA is the PCA value for the combination of crops or crop groups specific to the registered uses of the individual pesticide under evaluation. A use pattern specific PCA can be calculated at the national or regional level. For example, in this assessment for HUC-03 where chlorpyrifos use on cotton, citrus, peach and soybean are being considered, the PCA used is the summation of the individual PCAs for cotton, orchards (to cover citrus and peach) and soybean within each individual watershed. While in HUC-04 where chlorpyrifos use on alfalfa, apple, asparagus, cherry, peach, soybean, and sugar beet is under consideration, the PCA used is the summation of misc-ag (to cover alfalfa and sugar beet), orchard (to cover apple, cherry and peach), soybean, and vegetable (to cover asparagus) within each individual watershed. This approach allows for the more accurate EDWC that captures the area of the watershed allocated to the uses under consideration, rather than using the default all-agricultural land PCA, which could encompass more area within the watershed.

For those 2-digit HUCs with concentrations above the 10x DWLOC after consideration of the maximum use pattern, the full distribution of PCA values are then characterized (see following section).

Modeling Refinement 2: Use of the Full Distribution of Watershed PCA Values

The second refinement of the new drinking water improvement methods includes assessing the full distribution of available PCA instead of only using the maximum regional PCA value (USEPA, 2020). EDWCs are calculated for each community water system. The full distribution of PCAs used in this assessment include the majority of the 6,550 CWS drinking water intake (DWI) locations from EPA's Safe Drinking Water Information System (SDWIS) database between the years 1997 and 2004. Of the 6,550 locations, 74% (4,840) had unique, delineated watersheds where PCAs have been calculated. Two of these intakes had watersheds that extend into Canada and, therefore, are not considered in the development of PCAs. In addition to the 4,840, the distribution includes surrogate PCAs (i.e., 12 digit HUC) for a set of community water system drinking water intakes locations that watershed delineation was determined appropriate but had not been validated at the time of the 2014 publication of the percent cropped area adjustment factors for community water systems.

The critical PCA, the ratio between the unrefined EDWC and the DWLOC, is the PCA value that would generate a refined estimated drinking water concentration equal to the DWLOC, was calculated. The critical PCA permits the quick identification of the number (or percentage) of watersheds with PCAs that would results in concentrations above the DWLOC. The critical PCA is used as a benchmark to determine the need to continue to consider additional refinements.

For watersheds with a PCA higher than the critical PCA, the crop-specific footprint (county level acres harvested) overlap is assessed for crops (e.g., cherries or apples) where a crop group (e.g., orchard) PCA is used since a crop-specific PCA is not available for individual crops like cherries and apples available. For more information on the overlap analysis, see the following section. For HUCs where the use-site specific PCA is less than the critical PCA, no further refinement is necessary as the concentrations would be below the DWLOC.

Use Site Overlap Analysis of Watersheds with PCAs Larger than the Critical PCA

Also included in the new drinking water improvement methods is the overlap analysis (USEPA, 2020). PCA values for groups of crops (i.e., orchards, vegetables) are derived from generalized crop data layers based on the National Land Cover Database (NLCD) and Census of Agriculture (Ag Census). Specifically, the calculated PCA is based on the reported acreage of crops/crop groups in a county, as reported in the Ag Census, proportioned to the footprint of agricultural land covers from the NLCD. This approach has the potential to overestimate the percent of a given watershed with the noted use site (e.g., planted with a single crop). For instance, an individual CWS watershed with an orchard PCA of 20% may very well have little or no cherries or apples grown within the watershed. Spatial overlap helps further identify CWS watersheds with potential exposure concerns.

For these analyses, a visual inspection for overlap follows a spatial overlay of the 2007 USDA Census of Agriculture county-level acres harvest data with the watershed or surrogate watershed boundary for community water systems with PCAs above the critical PCA was completed using ArcMap (version 10.5). While there are more recent Census of Agriculture data (i.e., 2012 and 2017) the community water systems PCAs were developed using the 2007 census data. Therefore, for consistency in data sources the 2007 census data were used for the overlap analysis. If any part of the county with reported acres of crop under evaluation overlaps with the community water system under investigation it is considered an overlap for the purposes of this assessment.

For those watersheds with PCA higher than the critical PCA and county overlap, aggregated EDWCs are developed (see following section). Watersheds with no overlap are no longer considered for further refinement.

Development of Aggregated Estimated Drinking Water Concentrations

Another refinement included as part of the new drinking water improvement methods includes calculating EDWCs are based individual use site residue contribution. Prior to this step, EDWCs are based on the highest concentration of all uses modeled within the respective 2-digit HUCs, however, the relative contributions of each modeled use site can be determined by adding the contributing concentrations within each CWS watershed. This is the summation of the crop-specific PCA multiplied by the crop-specific model estimated concentration values for each registered crop or crop group within each watershed.

Aggregated EDWC =
(use pattern 1 individual EDWCs x crop specific PCA) + …
+ (use pattern (1+n) individual EDWCs x crop specific PCA)

Equation 1. Aggregation of Estimating Drinking Water Concentrations

There are two options for doing this aggregation (see the *Integrating a Distributional Approach to Using Percent Crop Area (PCA) and Percent Crop Treated (PCT) into Drinking Water Assessment (USEPA, 2020)* for more details. The option used in this assessment, is to aggregate individual PCA adjusted 1-in-10 year estimated concentrations for each use site in a region without regard to timing (e.g., 1-in-10 year EDWCs may come from different calendar days).

Percent Crop Treated Adjustment Factors

In this case, one of new drinking water improvement methods includes the integrating percent cropped treated (PCT) data to adjust estimated concentrations to reflect only those sites which are treated based on available survey data (USEPA, 2020). Use of a PCT further refines the fraction of the area of the respective planted crop area treated with pesticide in a watershed. PCT values are typically aggregated at the state level Chlorpyrifos usage data are summarized in the Science Information and Analysis Branch (SIAB) Use and Usage Matrix (SUUM) which is provided by BEAD. The SUUM reports PCT data based on usage that occurred for a given 5-year range (depending on the crop this spans 2012-2017 or 2014-2018) for chlorpyrifos (Paisley-Jones, 2020). Three statistics for PCT are available for each state and crop combination (where states and crops are surveyed): 5-year average, 5-year minimum and 5-

year maximum annual value. This information is provided in **ATTACHMENT 3**. For chlorpyrifos, only the 5-year maximum annual PCT are considered in this assessment.

The PCT statistics are used to calculate the number of acres treated in each state (referred to as base acres treated). Then the acres treated need to be allocated within each individual community water system watershed. In this assessment, this is done using an upper distribution approach for allocating treated acres within each watershed, described below. A post-processing tool was used to estimate the maximum PCT/upper distribution. For more information on these approaches see: *Integrating a Distributional Approach to Using Percent Crop Area (PCA) and Percent Crop Treated (PCT) into Drinking Water Assessment (USEPA, 2020)*. The files to support this work are provided in **ATTACHMENT 3**.

Upper Distribution: This approach assumes that all the treated acres for a given land cover class in a state can occur within a drinking water watershed boundary, up to the PCA adjusted acreage of the watershed including non-agricultural uses. A graphical depiction is provided in **Figure 5**. In this example, 400 acres (40 green squares) are assumed to be the potential use sites across Colorado. The PCT for Colorado is 10%. Therefore, 40 acres (4 filled green boxes) are treated within Colorado. If these acres are all placed within an individual community water system watershed 4 of the 7 green boxes (potential use sites) within the watershed (orange shape) become filled (as shown in the figure). The 4 green boxes or 40 acres are then divided by the total areas of the community water system watershed (orange shape) to generate the PCA-PCT value for the maximum PCT upper distribution.

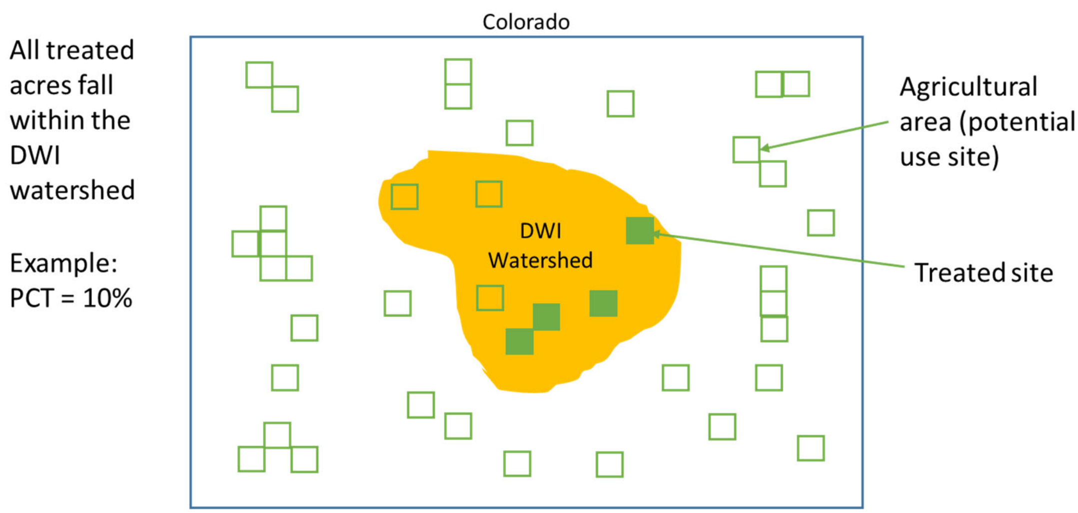

Figure 5. Conceptual Illustration of the "Upper" Distribution Method

PCT adjustments can be used to better understand exposure based on historical use, as well as provide a tool to facilitate the interpretation of model estimated exposure results compared to measured exposure concentrations. It should be noted that often watersheds are much smaller than a state. Use of the upper distribution is a conservative approach for allocating acres within a watershed providing an upper bound EDWC.

c. Monitoring Data

There are several challenges with interpreting available surface water monitoring data that may result in underestimating actual concentrations that people may be exposure as a result of consuming surface sourced drinking water. However, tools are available to help account for and describe the uncertainty in the data.

A Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), Scientific Advisory Panel (SAP) meeting was held in November of 2019 on Approaches for the Quantitative use of Surface Water Monitoring Data in Drinking Water Assessments. EPA presented the use of the USGS model, the Seasonal Wave with Streamflow Adjustment with Extended Capability (SEAWAVE-QEX), and developed sampling bias factors. Both approaches allow assessors to quantify the uncertainty in available use surface water monitoring data such that the results can be used with reasonable confidence in pesticide drinking water assessments. Additionally, EPA explored presented methods to evaluate the spatial relevancy of monitoring sites and sampling bias factors with respect to vulnerable drinking water locations using quantitative methods such as regression equations, and qualitative methods such as a weight-of-evidence approach. These approaches are detailed in a White Paper. Supporting documents included a Standard Operating Procedure for using SEAWAVE-QEX, a drinking water assessment framework document, and two drinking water assessment case studies. All of these documents, including EPA's response to the SAP comments can be accessed on the docket at EPA-HQ-OPP-2019-0417.

A thorough analysis of available monitoring data for chlorpyrifos and chlorpyrifos-oxon was completed in the 2016 DWA. Based this prior work and preliminary analyses completed as part of this assessment, it was decided that a Tier 4 monitoring data analysis would be beneficial to the assessment and could be informative if additional crops were evaluated. The current assessment focuses on updating the monitoring data analysis based on feedback from the 2019 FIFRA SAP and therefore focuses on monitoring data for chlorpyrifos only, as use of SEAWAVE-QEX on a transformation product was not recommended without further investigation.

The monitoring data considered in this update were primarily data exported from the Water Quality Portal (WQP) downloaded on January 6, 2020, which includes data from NWIS and STORET. Data from Dow Agrosciences (now Corteva Agriscience) California Monitoring Program (DACMP), Washington State Department of Agriculture (WSDA), and the National Center for Water Quality Research (NCWQR) are also considered, as well as the modified chlorpyrifos data sets from the data release files supporting SEAWAVE-QEX (Vecchia and Williams-Sether, 2018). Data from WSDA and NCWQR were obtained recently as part of the preparation for the 2019 SAP and were subject to Quality Assurance/Quality Control (QA/QC) protocols by the organizations that collected the data; these have been provided to EPA and the data are considered reliable.

All monitoring data were analyzed by program and by site-year. To be considered a site-year, there only needs to be one sample taken per year at a given site. A site-year analysis approach was employed because pesticide occurrence depends on spatially specific site conditions including pesticide usage, agronomic practices, soil properties, meteorology, as well as temporally dependent conditions, including pesticide application timing and rainfall occurrence.

These data sources are briefly summarized below with more details provided in the 2016 DWA.

1. Monitoring Program Summary

The *NAWQA* program samples for many pesticides and pesticide transformation products and is larger than any other monitoring program in terms of scope and duration. Sampling sites are distributed across the United States and include a range of site vulnerabilities and waterbody types.

NAWQA is not designed to target a specific pesticide use (i.e., sample timing, frequency, site); however, many sampling sites are in pesticide use areas including agricultural and non-agricultural sites. 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 *DACMP* included sampling at three locations on the lower reach of Orestimba Creek (California) for one year (May 1, 1996 to April 30, 1997). Daily time-proportional composite samples were collected, along with weekly grab samples. The report included chlorpyrifos use information for fields that drained into the creek or had the potential to contribute spray drift (fields within 305 m buffer on either side of the mid-streamline).

The *WSDA* monitoring programs began sampling salmon-bearing streams in two different Washington State sub-basins in 2003. The program has gradually increased monitoring to 10 different sub-basins throughout the state. Sampling sites are monitored weekly for pesticides during the pesticide use season. While the study does not specifically target pesticide applications, the sampling sites are in agricultural areas with known pesticide use.

The *NCWQR* monitoring program is historically one of the most intensive pesticide sampling programs in the country with sample frequencies ranging from daily to monthly. The most frequent sampling occurs during the spring and summer months. Monitoring sites are in agricultural areas (i.e., corn production) and were established as part of a nutrient and sediment loading monitoring program well before pesticide monitoring began.

2. Evaluation

Monitoring data evaluation included in this update builds upon past work including the monitoring data analyses completed to support the 2016 drinking water assessment (USEPA, 2016), as well as work done as part of the 2019 SAP on the quantitative use of surface water monitoring data in drinking water assessments (USEPA, 2019). Prior work indicated that when the uncertainty in having non-daily sampling data for chlorpyrifos is quantified, it is possible concentrations in surface water may occur above the drinking water level of comparisons described in this document. Therefore, consistent with the drinking water assessment framework, Tier 4 tools (SEAWAVE-QEX and pesticide-specific SBFs) are utilized in this assessment.

Several sites from these combined data sources met the criteria for evaluating chlorpyrifos concentrations quantitatively in surface water using SEAWAVE-QEX and SBFs. Both methods were presented as part of the FIRFA SAP on the quantitative use of surface water monitoring data in drinking water assessments (USEPA, 2019). Analyses reported here consider comments received from the Panel. Specifically, this work focuses on addressing the uncertainty in available monitoring data due to non-daily sampling and limited spatial coverage across the landscape by:

1. using SEAWAVE-QEX to estimate chlorpyrifos concentrations between sampling events,
2. deriving and applying SBFs to measured chlorpyrifos concentrations, and
3. employing a weight-of-evidence approach to understand the relevance of sampling sites with respect to potential chlorpyrifos use sites within the watershed.

3. *Interpretation and Extrapolation*

SEAWAVE-QEX

Background

The U.S. Geological Survey SEAWAVE-QEX (Vecchia, 2018) model, a time series regression model run in R statistical computing software (R Core Team, 2017) that interpolates sparse pesticide monitoring data using a daily covariate (e.g., streamflow) to develop daily pesticide chemographs from non-daily sampling data at a specific site, is a tool that can be used to fill in concentration data between sampling events. The model creates multiple, equally probable estimates of daily concentrations (i.e., conditional simulations or chemographs), with each chemograph constrained by the measured input data. Since SEAWAVE-QEX pairs measured concentrations with daily streamflow measurements, the model is able to estimate concentrations that are larger than the measured concentrations, addressing a concern expressed by previous SAPs regarding the consistent underestimation of pesticide concentrations occurring between sampling events (i.e., missing the peak) from other infilling methods.

In addition to multiple estimated chemographs, the model produces a file of diagnostic plots that can be used to determine if the model assumptions were verified (e.g., if the model fit the data appropriately). Refer to the White Paper and the SEAWAVE-QEX SOP for more information on diagnostic plots (USEPA, 2019).

More information on SEAWAVE-QEX and its use in drinking water exposure assessment can be found in the supporting documents for the 2019 FIFRA SAP (USEPA, 2019).

Method

Chlorpyrifos surface water monitoring data for sites in the conterminous United States from the WQP and NCWQR were screened to determine which sites had adequate samples for SEAWAVE-QEX to be used to estimate concentrations between sampling events. This was done by screening available monitoring data to identify sites that met the following criteria:

1. 12 samples per year,
2. detection frequency greater than 25%,
3. minimum of 3 years of data meeting criteria 1 and 2, and
4. daily flow or stage data for the period meeting criteria 1, 2, and 3.

Sites were considered in all 2-digit HUCs for this assessment. While use of these data likely capture labeled and possible cancelled chlorpyrifos uses, all available data were included to capture the range of possible environmental and use conditions that are possible for the uses considered in this assessment. For example, while pecans are not considered in this assessment, chlorpyrifos application to pecans and subsequent occurrence concentrations could be a reasonable surrogate for peaches or other crops grown in the same areas with similar use rates. For this analysis, it is important to have a robust number of site-years to capture the variability in weather and use across years, thus, eliminating sites based on geographical location reduced the confidence in the ability to capture the true range of potential concentrations of chlorpyrifos in source drinking water. Furthermore, environmental variabilities can vary as much within a region as it does across the country.

SEAWAVE-QEX input and output files are provided in **ATTACHMENT 4**. All SEAWAVE-QEX diagnostic plots were evaluated according to the SEAWAVE-QEX Standard Operating Procedure (SOP) and in consultation with the 2019 SAP team. If the model assumptions are not verified by the diagnostic plots, then the data are not used quantitatively. Improvements to the model fits were attempted using options within the SEAWAVE-QEX model, as needed, and may have included: using a different subset of years of data or adding a small constant (e.g., fraction of the LOD) to concentration data for the purposes of model fitting (subsequently removed). This process is detailed further in the SEAWAVE-QEX SOP. When data were available a sensitivity analysis (i.e., using more data than the minimum requirements) was completed.

Confidence in the SEAWAVE-QEX results are noted as high, medium, or low based on evaluation of the diagnostic plots. **SEAWAVE-QEX Results** section summarizes the SEAWAVE-QEX analysis results, while a detailed narrative of each SEAWAVE-QEX analysis by site is provided in **Appendix B.** The narrative includes a discussion of the evaluation of the diagnostic plots including the waveform, sample collection timing, usage data as available, and a description of the watershed and waterbody characteristics. This information is also integrated into the **Spatial** Variability and Relevance Weight-of-evidence analysis.

To use the SEAWAVE-QEX data quantitatively from accepted sites, the maximum of the 99th percentile 1- and 21-day concentrations for each site are compared to the DWLOCs. These summary statistics were derived from calculating 99th percentile 1- or 21-day concentrations of the 100 SEAWAVE-QEX chemographs for each year, then taking the maximum of those 100, 99th percentile concentrations. The maximum of the 99th percentile 1- and 21-day concentrations are chosen to represent the maximum concentration occurring in the waterbody between measurements.

Sampling Bias Factor

Background

While SEAWAVE-QEX provides a way to estimate daily pesticide concentrations from non-daily surface water monitoring data, for many sites, there are not enough monitoring data to use SEAWAVE-QEX. This is because the data are too highly censored (i.e., values below the reporting limit) or there are not enough samples per year or across years. SBFs offer an alternative approach to overcome uncertainty around chlorpyrifos concentrations in source water from non-daily pesticide surface water monitoring data that do not meet the minimum requirements of SEAWAVE-QEX or the SEAWAVE-QEX model fits are not good enough to better understand the potential range of chlorpyrifos concentrations in surface water at that site.

In simple terms, SBFs are multiplicative factors used to calculate an upper level prediction interval (e.g., 95th percentile) on the measured concentration value. By multiplying the SBF and the maximum measured value from the available monitoring data, EPA can derive an upper-bound concentration to address the uncertainty in the measured pesticide concentrations due to infrequent sampling. The development of SBFs is a multi-step process requiring a daily concentration chemograph (i.e., 365 days) and is described in the *Approaches for Quantitative Use of Surface Water Monitoring Data in Pesticide Drinking Water Assessments* (USEPA, 2019).

Use of SEAWAVE-QEX chemographs to develop SBFs for those sites that meet the criteria (minimum data quantity criteria or flow data) resulting in reasonable model fits expands the ability to develop SBFs for most pesticides, including chlorpyrifos, as daily data often does not exist or is limited.

Method

SEAWAVE-QEX results from sites accepted for quantitative use (i.e., verifying the model assumptions) as described in the **SEAWAVE-QEX Analysis** Section were used to calculate pesticide-SBFs to be applied to other monitoring sites with insufficient data to run in SEAWAVE-QEX. SBFs were developed using a python code named "short term SBF calculator updated July 2020" (included in **ATTACHMENT 4**) and summarized on a site-year basis prior to application. The subsections below describe how SBFs are developed (Process Description) and subsequently applied (Application).

Process Description

The multi-step process for developing short-term SBFs, previously presented to the SAP, which uses a daily concentration chemograph, is detailed in the SAP White Paper (USEPA, 2020) and follows these general steps:

1. The maximum average 1- and 21-day concentration is calculated from the daily pesticide concentration chemograph for each year of available data.
2. Bootstrapped samples are drawn from the daily pesticide concentration data for each year of available data from Step 1. These bootstrapped samples are generated using several sampling frequencies (13, 17, 26, and 52 samples per year using a random sampling strategy.
3. The bootstrapped[16] samples are log-linearly interpolated to generate daily pesticide concentration chemographs.
4. The maximum 1- and 21-day average concentration from the interpolated daily pesticide concentration chemograph for each year of available data is calculated. Residuals of interpolated chemographs are calculated along with root mean square error (RMSE).
5. Steps 2 through 4 are repeated 10,000 times.
6. The 10,000 maximum average concentrations and RMSE for each year are ranked.
7. The ratio of the 5th percentile concentration from the 10,000 bootstrapped samples for each year is compared to the maximum concentration for each year from the input chemograph calculated in Step 1.

When SBFs are developed from daily measured concentration data, there is only one set of SBFs developed – one for each sampling interval and duration of exposure concern. The SBF program provides an output file that contains results for each SEAWAVE-QEX realization across all years of the simulation for each sampling interval and duration of exposure concern. To obtain a single SBF for a site-year, the data must be condensed across SEAWAVE-QEX realizations. For this assessment, the median across years is calculated.

[16] Bootstrapping is any test or metric that uses random sampling with replacement and falls under the broader class of resampling methods.

Application

Sampling Sites with Greater Than or Equal to 13 Samples per Year

The range of SBFs for all sites across the conterminous United States are applied to the available surface water monitoring sites and summarized on a 2-digit HUC basis based on respective sampling number per year (n=13-16, 17-25, 26-52, 52+ samples collected per year) to generate the upper confidence bound on measured concentration. All SBFs generated across the conterminous United States are considered to increase the robustness of the analysis. Having more sites and site years increases the number of SBFs increasing the likelihood of capturing the true range of watersheds and waterbody attributes that exist across the landscape and are represented by community water system watersheds. Even though sites where SBFs were developed fall outside the regions considered in this assessment does not mean that site does not represent areas that fall within the regions (and community water system watersheds) under evaluation. This is particularly important when few acceptable sites are available for SEAWAVE-QEX analysis.

The general equation used to apply sampling bias factor is as follows:

$\hat{Y}$=X*Bias Factor
Where:

$\hat{Y}$ = Estimated chlorpyrifos concentration
X = Chlorpyrifos concentration obtained from monitoring data
Bias Factor = Measured chlorpyrifos concentration / Estimated 5th percentile pesticide concentration estimated from 10,000 simulated chemographs

The 1-day and 21-day sampling bias factor is multiplied by the maximum measured concentration based on the number of samples collected per year to provide the upper confidence bound on the measured value. 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. The SBF-adjusted 1- and 21-day upper confidence bound on the measured concentration are compared to the DWLOCs. For site-years where the upper confidence bound for the 21-day average concentration using the maximum single day measured value in the calculation is above the DWLOC, the maximum 21-day average concentration was estimated from the available monitoring data using log-linear interpolation. In the analysis for 21-day average concentrations, the data were analyzed assuming non-detections were equal to ½ limit of quantification (or minimum reporting limit) or the limit of quantification in the log-linear interpolation when less-than values are reported for a sample. This was done as a sensitivity analysis to assess the impact of using different assumptions for the limit of quantification on the calculation of the 21-day average concentration. The 21-day sampling bias factor is then applied to the maximum 21-day average concentration for each site-year.

For any site-year with an SBF-adjusted concentration above the respective DWLOCs, additional analyses are conducted to confirm the appropriateness of the application of the SBFs. These include evaluating sample collection timing and frequency, usage data when available, and a description of the watershed and waterbody characteristics. This information is integrated into a weight-of-evidence analysis (see **Spatial Variability and Relevance Weight-of-evidence**).

Sampling Sites with Less Than 13 Samples Collected per Year

There is a lot of uncertainty in the ability to estimate pesticide concentrations at sites where there are less than 13 samples collected per year. For further characterization, maximum concentrations on a site-year basis are multiplied by the sampling bias factor for sample number 13-16. A count of the number of site-years where SBF-adjusted concentrations are above the DWLOC is reported on a HUC basis. No additional analysis of these sites is provided.

Spatial Variability and Relevance Weight-of-evidence

Background

Monitoring data used in a drinking water assessment should be relevant (i.e., hydrologically connected) to the drinking water intake in pesticide use areas. Evaluating an overlay of the monitoring sites using Geographic Information Systems (GIS) with potential use sites (e.g., cropland data) can provide confidence that the sites are relevant to pesticide use.

Conversely, monitoring sites that are located outside of potential use areas and are not hydrologically connected to these use sites probably will not provide useful information on pesticide concentrations, unless an alternative transport mechanism (i.e., spray drift) can be ascertained. If pesticide usage data are available indicating that the pesticide was applied when monitoring occurred, this adds confidence to the site's spatial relevance.

A lack of monitoring data in a CWS watershed, or the presence of monitoring data in a CWS watershed that is not co-located with potential pesticide use sites, suggest the need for monitoring data in this area or reliance on modeled estimated concentrations. However, additional spatial analysis can be performed to determine if surrogate monitoring sites could be used in lieu of additional monitoring data. If a site has similar or more vulnerable characteristics, such as soil and weather conditions, potential pesticide use patterns and pesticide usage, as areas in the same or another drinking water watershed, then the monitoring data for the site may be of potential use as a surrogate for those areas with missing monitoring data.

Method

GIS was used to determine how relevant monitoring sites are to a CWS intake, as well as determine how similar the SBF watersheds are to CWS watersheds. The weight-of-evidence approach integrates multiple lines of evidence including, chlorpyrifos usage, crop footprints, location of monitoring sites in relation to drinking water intake watersheds, and time of travel to the drinking water intakes, as described below.

Potential Use Sites

Potential use sites are defined in this assessment as alfalfa, apple, asparagus, cherry, citrus, cotton, peach, soybean, sugar beet, wheat, and strawberry in specific 2-digit HUC regions. 2007 USDA Census of Agriculture county-level acres of harvest data are overlaid with monitoring sites to determine if the sites, and the monitoring data, are representative of the uses.

Watershed and Waterbody Properties

Proximity of the site relative to the community water system drinking water intake is determined. Use of lines of evidence, such as hydrologic connectivity and the presence of nearby potential use sites, can add confidence, as the site is connected to the CWS intake and represents an area where the pesticide could be used.

Additionally, how far away the site is from the drinking water intake, how fast the flow of the stream is (i.e., time of travel), and the persistence of the pesticide is also considered. This information provides an approximation of how long the pesticide would take to reach the intake and, along with the pesticide persistence, gives an indication if the pesticide would be expected to persist long enough to reach the intake. If the monitoring site is at the top of the community water system watershed, the monitoring data might not reflect the potential dissipation that could occur before the pulse of flow (i.e., during time of travel) reaches the drinking water intake. This dissipation maybe the results of transformation or dilution, for example. If the monitoring site is near a community water system intake, then there is confidence that it is representative of the community water system.

Use of other lines of evidence, such as the presence of nearby potential use sites, can add confidence, as the monitoring site may represents an area where the pesticide could be used. If a site occurs downstream of a drinking water intake, it should be carefully evaluated, to determine if there are potential sources of pesticide load or dilution between the intake and the monitoring site, there may be uncertainty as to the source of the pesticide and its contribution to drinking water. The closer the monitoring site is to the intake the more confidence the concentrations represent concentrations in source water used for drinking water.

Contributing-area characteristics, such as soil properties, geology, slope, etc., and climatic factors, such as rainfall history and intensity, can provide information on the potential for the pesticide to be in runoff from a treated field. Soil and geology data, obtained from the Soil Survey Geographic Database (SSURGO), as well as the slope, obtained from topographic maps, of the potential pesticide use areas near the monitoring or SBF site can be used to see if the area is conducive to runoff. Likewise, the use of weather data, particularly average daily precipitation data, can be indicative of whether the site is in a wet or dry region and whether the short, intense rain events can generate flashy pesticide peaks. If the potential for runoff and the weather data for the site are like those observed at the potential use sites in the CWS, then there is confidence that the monitoring data may be representative of the CWS. More information on these types of factors can be found in ILSI, 1999.

d. Weight of Evidence

As available, all factors mentioned above are used to determine confidence in the model EDWCs and monitoring data and the representation of the concentrations and impact on drinking water. While analysis of monitoring data inherently considers all uses, this assessment focuses on the relevance of the available data to the uses considered in this assessment. This weighs heavily in the weight of evidence.

Results

a. Modeling

1. *Pesticide Water Calculator*

Application of Use Pattern Specific PCA

As mentioned in the **Post-processing or Output Adjustments** section, the first refinement considered in this assessment is the application of the use pattern specific PCA. Use pattern specific PCA were calculated for each of the 2-digit HUCs considered in this assessment and are specific to the uses considered in this assessment.

Results from PWC are presented in **Table 13** for both chlorpyrifos and chlorpyrifos-oxon resulting from upper bound average rate provided by BEAD after looking at the full distribution of survey results. A description is provided by crop in the supporting document provided by BEAD in **ATTACHMENT 1**. Application of use pattern specific PCAs indicate that the 1-in-10 year 21-day average chlorpyrifos-oxon concentration may be greater than the 21-day 10x DWLOC in four 2-digit HUCs (HUC-04, -07, -09, and -17) for upper bound applications rates. None of the 1-in-10 year 1-day or 21-day average chlorpyrifos-oxon concentrations are higher than the 1x DWLOC. In addition, none of the 1-in-10 year 1-day average chlorpyrifos concentration are greater than the 1-day 10x DWLOC.

Table 13. PCA Adjusted EDWCs for Upper Bound Application Rates of Chlorpyrifos

2-digit HUC	Use Site	2-digit HUC Maximum Use Pattern Specific PCA	Batch Run ID[a]	1-day Model EDWC (cpy)	21-day Model EDWC (cpy)	1-day Model EDWC (cpyo)	21-day Model EDWC (cpyo)	Adj 1-day EDWC (cpy)	Adj 21-day EDWC (cpy)	Adj 1-day EDWC (cpyo)	Adj 21-day (cpyo)
				µg/L							
02	Apple	0.07	127_4_PAappleSTD	10.8	7.6	10.3	7.3	0.8	0.5	0.7	0.5
	Peach			16.2*	11.4*	15.5	10.9	1.1	0.8	1.1	0.8
03	Citrus	0.27	136_4_FL-1421189-7026-72	6.5	3.8	6.2	3.6	1.8	1.0	1.7	1.0
	Peach[b]		216_4_GAPeachesSTD	11.6	6.9	11.0	6.6	3.2	1.8	3.0	1.8
	Cotton		196_4_GA-325617-11261-2	4.9	2.9	4.7	2.8	1.3	0.8	1.3	0.7
	Soybean		221_4_GA-325947-11736-5	11.9	6.8	11.4	6.5	3.2	1.8	3.1	1.8
04	Alfalfa	0.92[d]	2_4_MI-186800-22356-36	2.8	2.1	2.7	2.0	2.6	1.9	2.5	1.8
	Sugar beet		362_4_MI-186667-22116-41	7.2	4.8	6.9	4.6	6.6	4.4	6.3	**4.2**
	Apple[c]		128_4_MIcherrySTD	17.3	14.9	16.5	14.2	15.9	13.7	15.2	**13.1**
	Cherry		134_4_MIcherrySTD								
	Peach			26.0*	22.4*	24.8	21.4	23.9	20.6	22.8	**19.6**
	Soybean		245_4_MI-186667-22116-41	3.9	2.1	3.7	2.0	3.6	2.0	3.4	1.9
	Asparagus		133_4_MIasparagusSTD	3.7	2.1	3.5	2.0	3.4	2.0	3.3	1.9
05	Apples	0.58	129_4_PAappleSTD	9.6	7.2	9.2	6.9	5.6	4.2	5.3	4.0

2-digit HUC	Use Site	2-digit HUC Maximum Use Pattern Specific PCA	Batch Run ID[a]	1-day Model EDWC (cpy)	21-day Model EDWC (cpy)	1-day Model EDWC (cpyo)	21-day Model EDWC (cpyo)	Adj 1-day EDWC (cpy)	Adj 21-day EDWC (cpy)	Adj 1-day EDWC (cpyo)	Adj 21-day (cpyo)
				µg/L							
	Soybean		254_4_OH-198271-18810-5	5.4	3.3	5.2	3.1	3.1	1.9	3.0	1.8
06	Apples	0.02	130_4_NCappleSTD	20.8	13.0	19.8	12.4	0.4	0.3	0.4	0.2
07	Alfalfa	0.90	11_4_MO-2528577-19014-37	7.7	4.5	7.3	4.3	7.0	4.0	6.7	3.8
	Sugar beet		371_4_MN-2423043-23487-41	11.5	8.3	11.0	7.9	10.4	7.5	9.9	**7.2**
	Soybean		263_4_MN-2877271-22781-5	5.6	3.4	5.3	3.2	5.0	3.1	4.8	2.9
09	Alfalfa	0.95[e]	20_4_SD-416559-24423-36	2.0	1.5	1.9	1.4	1.8	1.4	1.7	1.3
	Sugar beet		437_4_ND-2642948-27020-41	9.7	6.5	9.3	6.2	8.7	5.8	8.3	**5.6**
	Soybean		281_4_ND-2571399-26297-5	3.6	2.3	3.4	2.2	3.3	2.1	3.1	2.0
	Spring wheat		473_4_ND-2585363-27001-23	2.9	1.8	2.8	1.7	2.6	1.6	2.5	1.6
	Winter wheat		527_4_ND-341303-27230-24	5.8	3.9	5.5	3.7	5.2	3.5	5.0	3.3
10	Alfalfa	1.0[e]	29_4_IA-404845-19717-37	5.5	3.4	5.2	3.2	5.5	3.4	5.2	3.3
	Soybean		299_4_NE-427060-20409-5	6.0	3.7	5.7	3.5	6.0	3.7	5.7	3.6
	Spring wheat		512_4_ND-339036-26757-22	5.1	3.3	4.9	3.1	5.1	3.3	4.9	3.2
	Winter wheat		536_4_CO-95043-18735-24	3.0	1.8	2.9	1.7	3.0	1.8	2.9	1.7
11	Alfalfa	0.79[e]	65_4_CO-2808264-16377-37	4.1	2.6	3.9	2.5	3.2	2.0	3.1	2.0
	Soybean		335_4_AR-565399-14294-5	3.8	2.3	3.6	2.2	3.0	1.8	2.9	1.7
	Winter wheat		572_4_TX-367160-13558-24	5.2	3.0	5.0	2.9	4.1	2.4	3.9	2.3
12	Citrus[h]	0.18	163_4_TX-367665-6012-72	6.3	3.9	6.1	3.6	1.2	0.7	1.1	0.7
	Peach		163_4_TX-367665-6012-72	5.4	3.3	5.2	3.1	1.0	0.6	0.9	0.6
	Winter wheat		590_4_TX-372533-12603-24	3.9	2.3	3.7	2.2	0.7	0.4	0.7	0.4
17	Alfalfa	0.53	110_4_WA-71453-24575-36	2.4	1.6	2.3	1.5	1.3	0.9	1.2	0.8
	Sugar beet		389_4_ID-79974-21766-41	7.0	4.9	6.7	4.7	3.7	2.6	3.5	2.5
	Apple[c]		131_4_ORappleSTD	9.6	6.2	9.2	5.9	5.1	3.3	4.9	3.1
	Strawberry		353_4_ID-80309-21523-12	16.8	12.1	16.0	11.5	8.9	6.4	8.5	**6.1**

a. Batch run name is truncated (DWA_2020 was removed for reporting purposes).
b. Model run was completed for 2.0 lb a.i./A; however, upper bound rate for peach on a national level is 3 lb a.i./a. Results were multiplied by 3/2.
c. Model run was completed for 2.0 lb a.i./A (maximum rate observed is noted as 3.0 lb a.i./A)
d. Use pattern specific PCA is slightly higher (0.93) than all-ag PCA (0.92). Use pattern specific PCA is capped at all-ag value.
e. Use pattern specific PCA is higher (>1) than all-ag PCA (0.95). Use pattern specific PCA is capped at all-ag value.
f. Use pattern specific PCA is slightly higher (>1) than all-ag PCA (1.0) Use pattern specific PCA is capped at all-ag value.
g. Use pattern specific PCA is slightly higher (0.96) than all-ag PCA (0.79). Use pattern specific PCA is capped at all-ag value.
h. Model run was completed for 3.0 lb a.i./A and should have been 3.5 lb a.i./A for the upper bound rate. Results were multiple by 3.5/3 to adjust the concentrations.

*Upper bound rate modeled for apples and cherries is 2 lb a.i./a. The upper bound rate for peach on a national level is 3 lb a.i./a. Results were multiplied by 3/2 to estimated concentrations for peach.
Green shading indicates concentrations below the 10xDWLOC.
Reg shading and bold font indications concentrations above the 10x DWLOC.
Chlorpyrifos (cpy)
Chlorpyrifos-oxon (cpyo)

Subsequent refinements focus on four (i.e., HUC-04, -07, -09, and -17) of the 11 HUC-02 regions considered in this assessment and focus on the 21-day average concentration assuming retention (i.e., 10x) of the FQPA safety factor.

Results for average application rates are provided in **APPENDIX B**.

Use of the Full Distribution of Watershed PCA Values, Critical PCAs, and Percent of Watersheds with PCA Values Larger than the Critical PCAs

Examination of the full distribution of PCAs for HUC-04, -07, -09 and -17 (i.e., those 2-digit HUCs with upper bound application rates resulting in EDWCs above the 21-day 10x DWLOC for chlorpyrifos-oxon) indicate that 232 community water system watersheds may have chlorpyrifos-oxon concentrations above the 21-day 10x DWLOC for upper bound application rates as shown in **Table 14**. This was determined by counting the number of community water systems with PCAs above the critical PCA for each respective region. In addition, **Table 14** provides a count of the total number of community water systems watersheds within each HUC so that the percentage of watershed with concentrations above the DWLOC can also be determined.

Table 14. Full Distribution of Watershed Specific PCA-Adjusted EDWCs for Upper Bound Applications of Chlorpyrifos-oxon

2-digit HUC	Total Community Water System Watersheds	Max[1] 1-in-10 year 21-day Concentration µg/L	Critical 21-day Percent Cropped Area	Number of Community Water Systems with Concentrations Above the 10x 21-day DWLOC	Percent of Community Water Systems with Concentrations Above the 21-day 10x DWLOC	Overlap Counties Crop Acres Community Water System Watersheds (number)
04	196	21.4	0.19	139	71	Yes (several)
07	158	7.9[2]	0.51	79	50	Yes (1)
09	16	5.2	0.67	12	75	Yes (several)
17	343	11.5	0.35	2	<1	-

[1] This column provides the maximum concentration associated with use of the maximum regional use pattern specific PCA. Concentrations would be lower for other community water systems within the 2-digit HUC.
[2] Use pattern specific PCA is higher (>1) than all-ag PCA (0.95). Use pattern specific PCA is capped at the all-ag value in the prior refinement step; however, when aggregating the individual contributions, the concentration (max=6.1 µg/L) exceeds the prior estimate (max=5.6 µg/L). Therefore, since the model output value is higher for the misc-Ag use site the soybean contribution is low (3%) and a low estimated concentration and wheat falls in the middle, soybean contribution was made zero, and the wheat contribution (PCA) was adjusted down to be the difference in the all-ag and misc-ag. This approach is expected to be conservative yet accounts for the double cropping that is likely occurring in the watershed.
- refinement not considered

There are several community water systems with EDWCs above the 21-day 10x DWLOC in HUC-04, -07, and -09. Only two community water systems in HUC-17 had concentrations above the 10x 21-day DWLOC.[17] Therefore, HUC-17 was not considered for overlap refinements.

The same analysis is provided for average application rates and the results are provided in **APPENDIX B**. The excel file supporting this analysis is provided in **ATTACHMENT 3** (PCA_Analysis subfolder cpy pca_analysis.xlsx).

Overlap analysis of Watersheds with PCAs Larger than the Critical PCA with Use Site Footprint

As described in the **Post-processing or Output Adjustments** section of this document, one of the new refinement methods is to examine the overlap of community water system watersheds with estimated concentrations above the DWLOC with use pattern specific county level acres data. This is done because the PCA values are often calculated for crop groups (e.g., orchards) which contain multiple crops (e.g., citrus, apples, peaches, pecans (USEPA, 2020). Overlap analysis was completed for the community water systems with EDWCs above the critical PCA in HUC-04, HUC-07, and HUC-09. The results are discussed in the subsections below for each of the 2-digit HUCs suspected to have concentrations above the 21-day 10x DWLOC.

HUC-04 (Great Lakes)

Examination of county boundaries with reported acres associated with uses under consideration in HUC-04 suggests overlap with community water systems with PCAs higher than the critical PCA. In this region, chlorpyrifos use on orchard crops (apple, cherry, and peach) result in estimated concentrations above

[17] Concurrent examination of individual community water system watershed PCAs (i.e., aggregation) indicate the concentrations in these two community system watersheds should not be above the 21-day 10 DWLOC. See **ATTACHMENT 3** PCA analysis.

the 21-day 10xDWLOC for chlorpyrifos-oxon. The other uses considered (alfalfa, asparagus, and soybean) have estimated concentrations less than the DWLOC. Further spatial analysis of HUC-04 indicates there are several community water system watershed with use pattern specific PCAs greater than the critical PCA (0.19) for counties reporting acres of either apple, cherry, or peach in 2007 (**Figure 6**). Because there are several watersheds with overlap a count of the number of community water systems with overlap was not done. Instead, this region is considered for additional refinements.

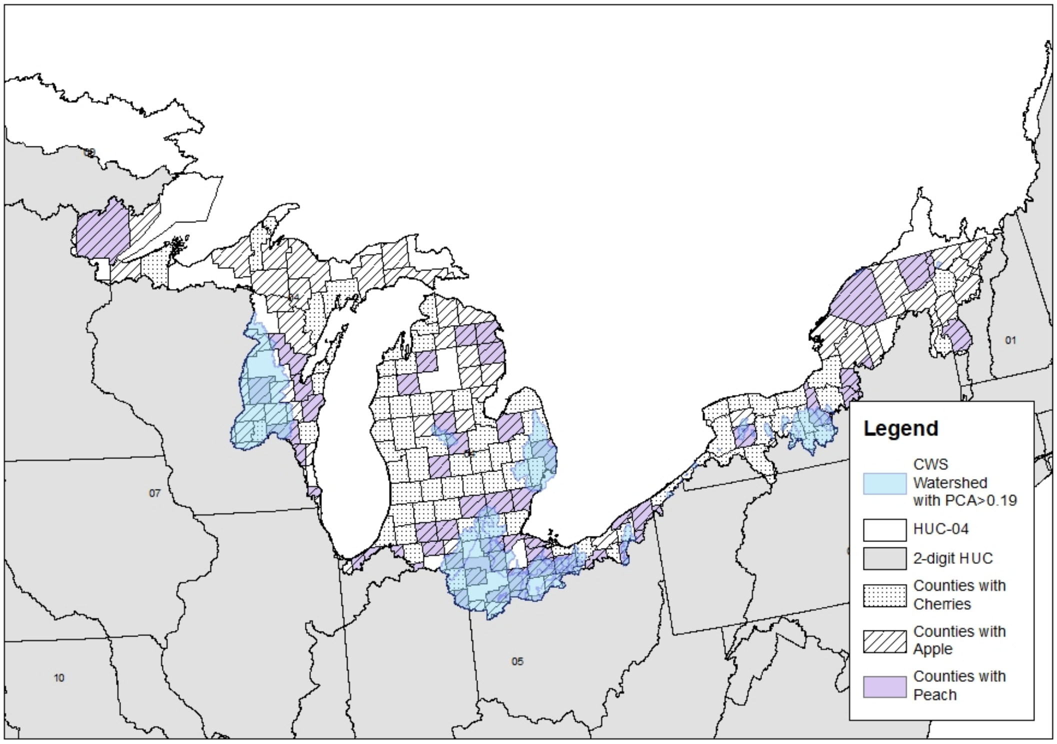

Figure 6. HUC-04 Crop Land Overlap Analysis with Community Water Systems with PCAs Greater than the Critical PCA (0.19)

HUC-07

Examination of county boundaries with reported acres associated with uses under consideration suggests overlap with community water systems with PCAs higher than the critical PCAs. In this region, chlorpyrifos use on sugar beet is the only use considered in this assessment with estimated concentrations above the 10x DWLOC. The other uses considered (alfalfa and soybean) have estimated concentrations less than for use on sugar beet and the 10x DWLOC. Further spatial analysis of HUC-07 indicates there is only one community water system with a use pattern specific PCA greater than the critical PCA for counties reporting acres of sugar beet in 2007 (**Figure 7**). This watershed (object ID 2703) has a use-site specific PCA of 0.69 (misc-ag PCA of 0.42 + soybean PCA of 0.27). Since there is spatial overlap with at least one community water system in HUC-07 this region is considered for additional refinement.

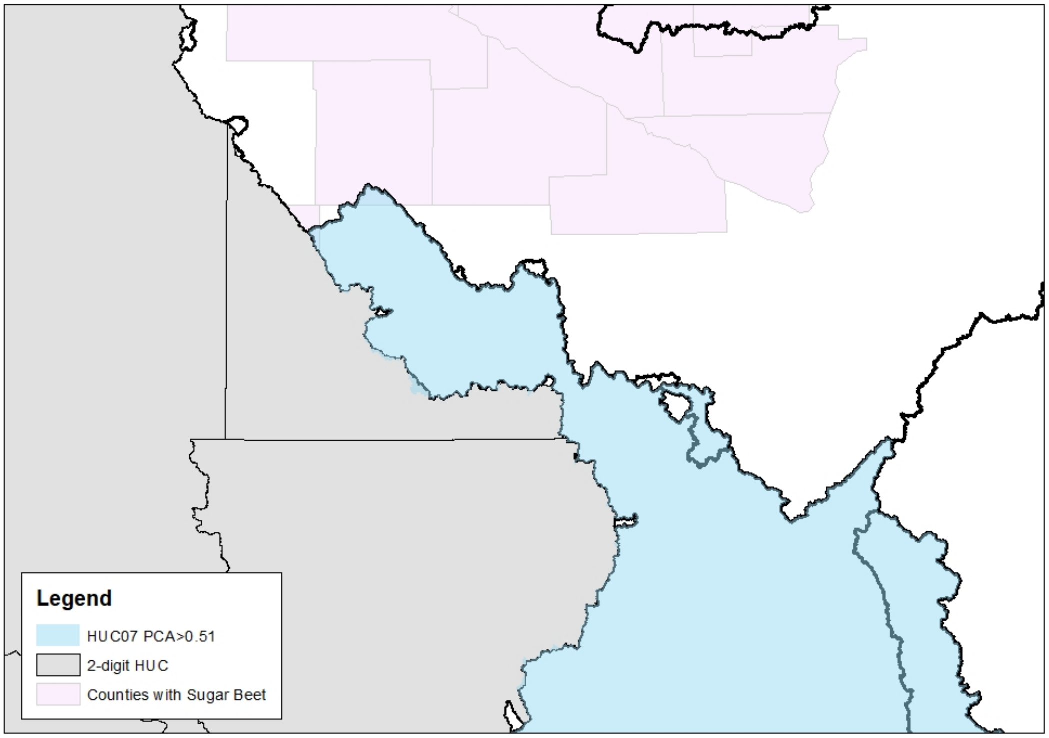

Figure 7. HUC-07 Sugar Beet Overlap Analysis with Community Water Systems with PCAs Greater than the Critical PCA (0.51)

HUC-09

The same spatial analysis was completed for HUC-09. It showed several community water system with use pattern specific PCAs greater than the critical PCA for counties reporting acres of sugar beet in 2007 (**Figure 8**). Again, chlorpyrifos use on sugar beets results in the highest model output for this region and is the only use with estimated concentrations above the 21-day 10x DWLOC. Since there is spatial overlap between county with acres of sugar beet HUC-09 is considered for additional refinement.

Because there are several watersheds with overlap a count of the community water systems with overlap was not done.

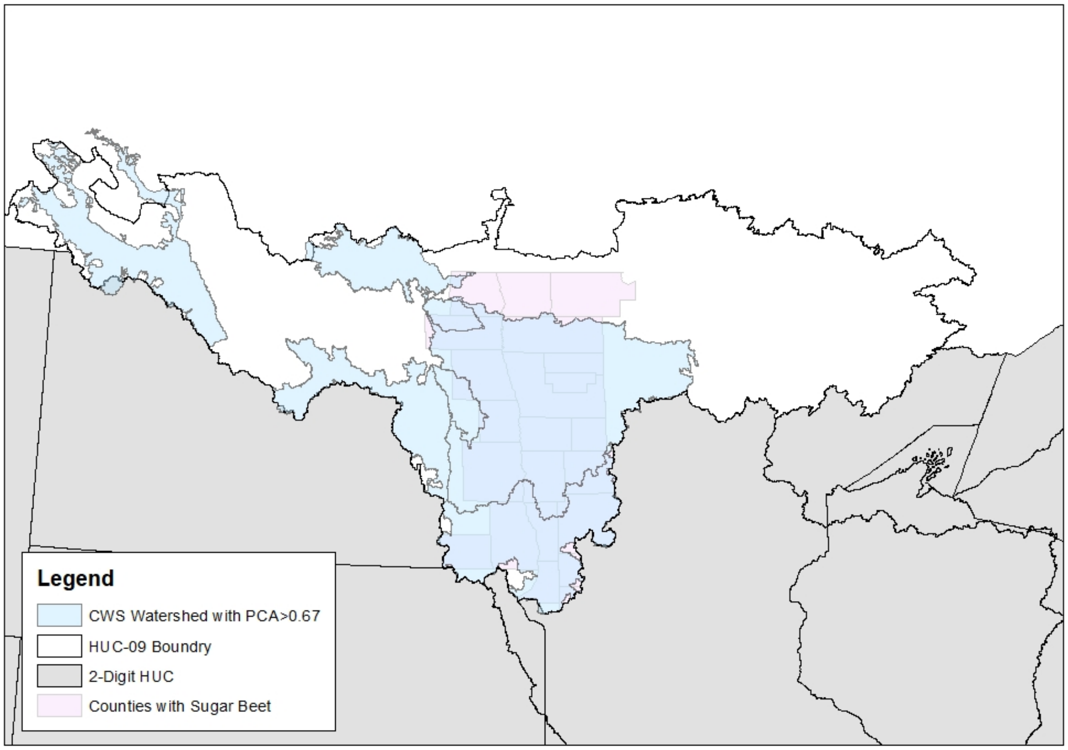

Figure 8. HUC-09 Sugar Beet Overlap Analysis with Community Water Systems with PCAs Greater than the Critical PCA (0.67)

HUC-17

Examination of county boundaries with reported acres associated with strawberry (2007) in HUC-17 suggests there is no overlap with community water systems with PCAs higher than the critical PCA (**Figure 9**). This region was no longer considered for refinement.

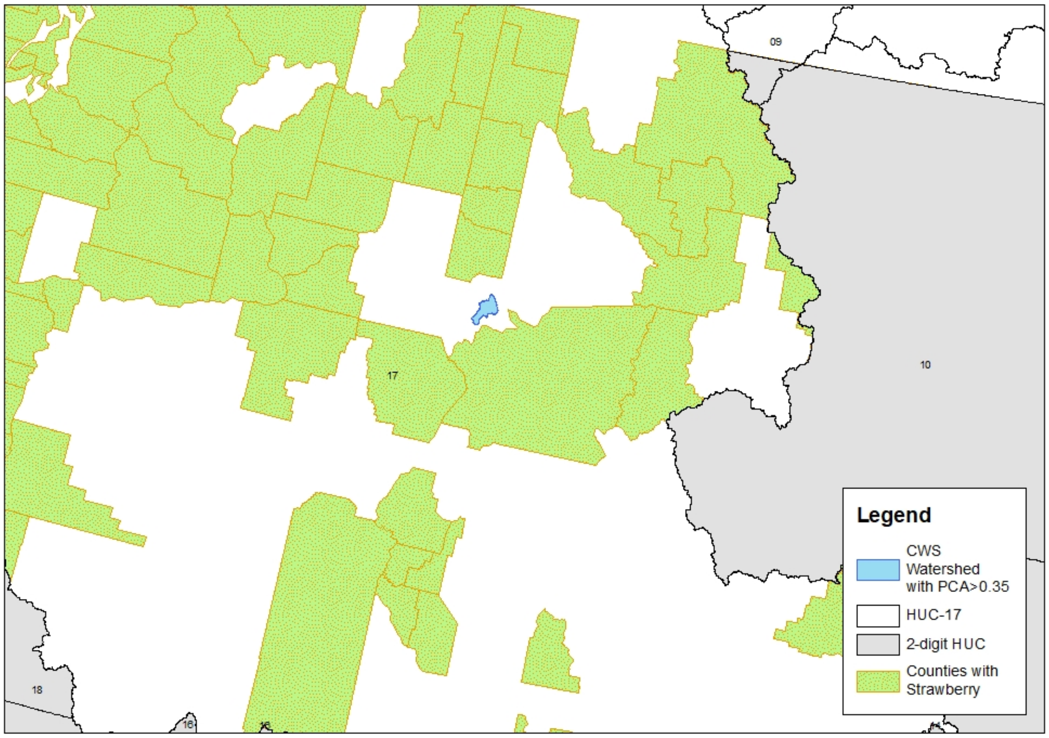

Figure 9. HUC-17 Crop Land Overlap Analysis with Community Water Systems with PCAs Greater than the Critical PCA (0.35)

Development of Aggregated Estimated Drinking Water Concentrations

As described in the **Post-processing or Output Adjustments** section of this document, one of the new refinement methods includes calculating EDWCs based individual use site residue contribution. Prior to this step, EDWCs are based on the highest concentration of all uses modeled within the respective 2-digit HUCs, however, the relative contributions of each modeled use site can be determined by adding (or aggregating) the contributing concentrations within each CWS watershed. This refinement step in this assessment focuses on aggregating 1-in-10 year aggregation.

The aggregated EDWCs reported in this section only represent the uses considered in this assessment and in the regions assessed. If additional uses patterns need to be considered the aggregated concentrations need to be updated to account for the additional exposure resulting from the contribution of additional uses to the overall EDWCs. The results are reported in the subsection below.

1-in-10 year Aggregation

Aggregation of the 1-in-10-year concentrations for community water systems with chlorpyrifos-oxon concentrations estimated to be above the 10x DWLOC indicate that community water systems in HUC-07 and HUC-09 continue to need to be refined as concentration are still estimated to be above the 10x DWLOC for upper bound application rates. Results are presented in **Table 15**. The aggregated concentrations only reflect the uses considered in this assessment and do not account for the temporal contribution of each use.

Table 15. Aggregation of 1-in-10 year PCA-Adjusted 21-day Average EDWCs for Upper Bound Application Rates of Chlorpyrifos

2-digit HUC	Total CWS	Aggregated 1-in-10 year 21-day Average Concentration (cpyo) µg/L	No. of CWS above 21-day DWLOC	Percent of CWS above 21-day DWLOC
04	196	3.4	-	-
07	158	**4.2**[1]	1	<1%
09	16	**6.1**	9	56%

Bold font indicates concentrations above the 10xDWLOC (21-day = 4.0 µg/L)
[1] The watershed (object ID 2703) identified as having overlap with the sugar beet has an aggregated 1-in-10 21-day average concentration of 4.2 ug/L. This value is above the 21-day 10x DWLOC.
- no calculation needed as the concentration is below the 21-day 10x DWLOC.

The watershed in HUC-07 previously identified to have overlap with HUC-09 is a region where the use-site specific PCA is greater than the all-ag, and in the prior step, the use site-specific PCA was capped at the all-ag value as the sum of the individual crop PCA should not exceed the PCA for all cropped land. However, when aggregating concentrations, the individual contributions are adjusted based on the individual crop contributions even if, when combined, the PCAs are greater than the all-ag value. Nevertheless, the maximum aggregated chlorpyrifos-oxon concentration is lower than that calculated concentration reported in the prior step; however, still not below the 21-day 10x DWLOC.

Based on this analysis, one community water system in HUC-07 and 9 in HUC-09 are expected to have concentrations above the 21-day 10x DWLOC. Aggregation of the 1-in-10 year 21-day average concentration does not account for the temporal contribution of residue concentrations in the EDWCs; however, due to the time and tools necessary to aggregate time series data the next refinement considered is percent crop treated.

The same analysis is provided for average application rates. Results are provided in **APPENDIX B**. The excel file supporting this analysis is provided in **ATTACHMENT 3** (PCA_Analysis subfolder cpy pca_analysis.xlsx).

Percent Crop Treated Adjustment Factors

The final new refinement method considered in this assessment includes the calculation of the aggregation EDWCs using percent crop treated data. The maximum PCT is calculated by state for HUC-07 and HUC-09. This information was provided by BEAD. These data were applied using the upper distribution approach for allocating treated acres within each watershed to calculate EDWCs for each individual community water system within the HUC with concentrations above the 10x DWLOC in the prior refinement step. The results for the four approaches are presented in **Table 16**. These results suggest that based on the upper bound application rates all concentrations are expected to be below the 21-day 10x DWLOC; therefore, no additional refinements were considered. The excel file supporting this analysis is provided in **ATTACHMENT 3** subfolder PCA_PCT_Aggregation_Analysis.

Table 16. Full Distribution of Watershed Specific PCA and PCT (all usage)-Adjusted EDWCs for Upper Bound Applications of Chlorpyrifos-oxon

2-digit HUC	Total CWS	Maximum 1-in-10 year 21-day chlorpyrifos-oxon µg/L
		PCA/PCT (max upper)
07	158	0[1]
09	16	3.3[2]

[1] The watershed (object ID 2703) identified as having overlap with the sugar beet was the only watershed in this region considered in this refinement step.
[2] Considers all watershed with use pattern specific PCAs above the critical PCA and not the subset of watersheds with use pattern overlap. This is because the PCT analysis and the overlap analysis were being conducted concurrently. Had a concentration been estimated above the DWLOC the overlap analysis could have been used to refine the estimated concentrations further.

2. Discussion and Conclusions

Using the upper bound application rates provided by BEAD for the high benefit uses identified by Corteva Agriscience and critical uses identified by BEAD, all use site-2-digit HUC region combinations resulted in concentrations below the 10x DWLOC with refinements. The refinements used in this assessment are briefly summarized along with the results below.

Recall, the first refinement considered was <u>application of a use pattern specific PCA</u> to reflect only specific crops within each 2-digit HUC. This refinement identified 4 of the 11 2-digit HUCs as potentially having concentrations above the 21-day 10x DWLOC based on the maximum use pattern specific PCA in each region. However, none of the regions were determined to have concentrations above the 1- or 21-day 1x DWLOC or the 1-day 10x DWLOC.

The second refinement included the use of the full distribution of watershed PCA values and calculation of critical PCAs and percent of watersheds with PCA values larger than the critical PCAs. Examination of the full distribution of community water system watersheds in the regions identified as potentially having concentrations above the 21-day 10x DWLOC indicate that in 3 of the 4 regions there are number of community water systems where chlorpyrifos-oxon concentrations may be above the 21-day 10x DWLOC. The number of community water systems with use-site specific PCAs greater than the critical PCA were reported (**Table 14)**.

Overlap analysis of watersheds with PCAs larger than the critical PCA with use site footprint for uses (e.g., sugar beet, cherries or apples) where a crop group (e.g., misc-ag or orchard) PCA was used to determine overlap with community water systems watersheds. This refinement was useful in HUC-07 and HUC-17. In HUC-07, overlap analysis was used to ruling out all most all the community water systems with PCAs above the critical PCAs. In HUC-17, overlap analysis was not used to rule out community watersheds with PCAs above the critical PCAs because were several counties with acres reported for use sites considered in this assessment that overlapped with community water systems with PCAs greater than the critical PCAs.

Up until this point, concentration estimates relied on use of the single highest modeled estimated across uses within in the 2-digit HUC. Therefore, the development of aggregated EDWCs for each community water system exceeding the 10x DWLOC was done. This was done to allocate individual crop contributions to the EDWCs and develop a refined EDWC.

Percent crop treated adjustment factors were integrated into the exposure estimates for the 1-in-10 year 21-day average concentrations. This analysis indicated that when assuming the maximum percent crop treated over 5-years and allocating the associated acres within each individual community water system the concentrations expected would be below the 21-day 10x DWLOC.

Consistent with previous work, this update suggests the concentrations vary across the landscape and depend on the uses under consideration. The model estimated concentrations are consistent with previous assessments for average and upper bound rates. The impact of using the new scenarios does not substantially change the exposure estimates for chlorpyrifos.

The primary reason why estimated concentrations are below the DWLOC in this assessment is the number of uses considered in the respective regions. Because so many uses are currently registered, past assessments relied on a PCA of 1 because chlorpyrifos is registered for uses that can occur anywhere within a community water system watershed. This assessment, however, focuses only on high benefit and critical uses in specific regions of the country. Importantly, the results of this work do not reflect potential exposure from all currently registered uses. If additional uses were to be considered, this analysis would need to be updated. It is expected that as the number of uses assessed increases, and if application rates are higher than those considered in this assessment, the estimated concentrations will likely be higher than those presented and further refinements would need to be considered.

b. Monitoring

1. *General Data Observations*

Generally, detections of chlorpyrifos are sporadic with low concentrations. This is expected based on the environmental fate and transport properties (i.e., high sorption), usage data (i.e., applied in response to pest pressure), and low sample frequency. Much of the higher frequency sampled chlorpyrifos data comes from monitoring programs that are older and thus may not represent current use conditions. While these data may not reflect current use scenarios, the data suggest that chlorpyrifos does move to surface water and can be present in concentrations within the range of PWC estimated concentrations, even before adjustment for infrequent sampling. A summary of data accessed through the Water Quality Portal on 01/06/2020 is provided **Table 17**.

Table 17. Summary of Chlorpyrifos Data Accessed via the Water Quality Portal

Source	Number of Samples	Number of Non-detections	Minimum Reported Concentration µg/L	Maximum Reported Concentration µg/L
NWIS	66,345	60,504	0.0009	5.62
STORET	33,975	20,477	2E-07	14.7
Data accessed 1/6/2020				

These data indicate a low over all detection frequency; however, detected concentrations occur at up to 14.7 µg/L.

Surface water monitoring programs typically collect samples on a weekly or biweekly basis, even in programs with a relatively high sampling frequency such as USGS National Water Quality

Assessment (NAWQA) or Washington State Department of Agriculture (WSDA). For example, **Figure 10** shows the range of the number of samples collected per site per year (gray circles) along with the number of sites sampled per year (red dash) for chlorpyrifos (Water Quality Portal accessed 01/06/2020). The gray circles were formatted with transparency so that the darker the circle appears, the larger the number of sites with the same number of samples collected per year.

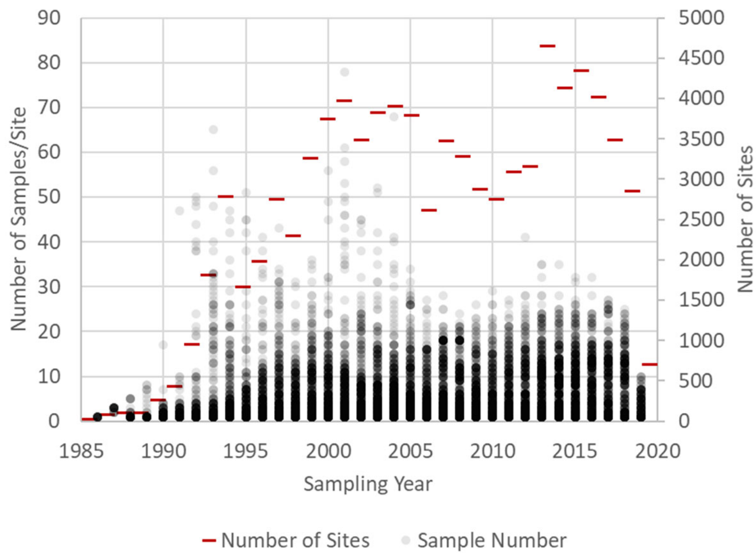

Figure 10. Sampling Quantity Characteristics for Chlorpyrifos Data from the Water Quality Portal

The sample number varies substantially across sites and the number of sites sampled varies by year. **Figure 10** also illustrates a downward trend in the number of sites as well as the number of samples collected at each site in recent years. Most sites have low sample numbers. The most samples collected at a site within a calendar year occurred in 2001 when 78 samples were collected at a monitoring location in San Joaquin River near Vernalis, California (USGS-11303500) with 53 of those samples occurring on different days. Closer analysis of this site shows that 45 samples were collected in the months of January and February. Many of the samples occurred on the same days in January and February.

Sample frequency at other sites and in other years is generally much lower, with the lowest being one sample per year for years that are sampled. **Figure 11** is a histogram showing the number of samples collected in 2016 for chlorpyrifos. Most sites do not have enough samples collected to meet the minimum data requirements for the applications of SBFs (≥ 13 samples/year) or for SEAWAVE-QEX analysis (≥ 12 samples/year with 25% detection frequency for 3 years).

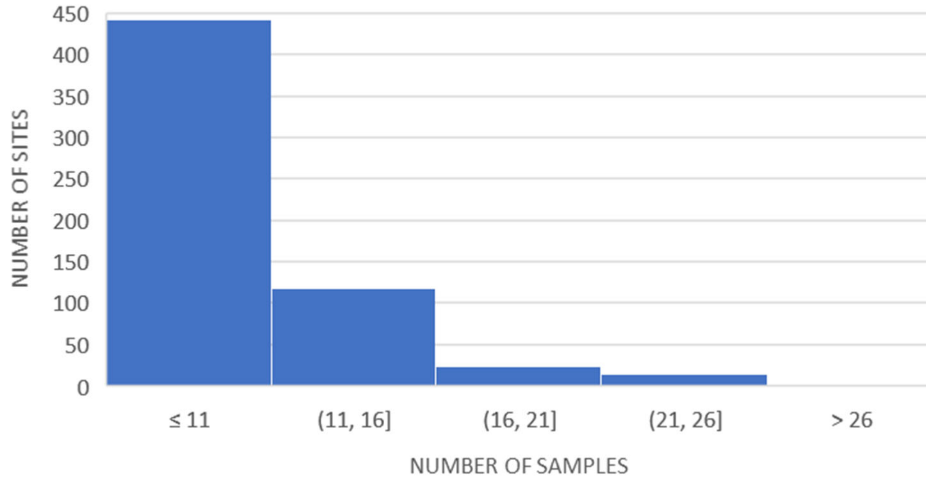

Figure 11. Histogram for Samples in 2016 for Chlorpyrifos (USGS) Across the United States

Further analysis of all years of data reveal that the number of days between sampling events ranged from 1 to 360 days across all years and sites with the average number of days between samples of 1 to 336 days across all site-years.

Analysis of data collected from programs with more frequent sampling suggest that as sample collection increases, the detection frequency also increases. For example, daily composite sampling on Orestimba Creek had detection frequencies between 42-52% for chlorpyrifos.

Sampling frequency should be considered in the context of use information, as an increase in the number of samples collected at an individual location where use is infrequent or absent, or during times of the year when applications or runoff events are not expected to occur, may reduce detection frequencies, as well as reduce the likelihood of measuring peak concentrations.

Most of the data in the Water Quality Portal come from grab samples. A grab sample is defined as an individual aliquot or volume of water collected over a short period of time (<15 minutes). For example, scooping up water in a cup, bottle or bucket. In contrast, a composite sample consist of a collection of several individual discrete samples taken at regular intervals over a period, usually 24-hours.

While differences in surface water concentrations can result from differences in the sampling design, frequency, and/or sample number with respect to the peak concentration on a daily time step, potential variation in concentrations may also occur over the course of a day for chlorpyrifos **Figure 12** shows measured chlorpyrifos concentrations from the Rock Creek sampling site from NCWQR. it is possible that daily grab samples can miss measuring peak concentrations on days which the sampling occurs. Grab samples are currently the most common sampling method within the available data sources.

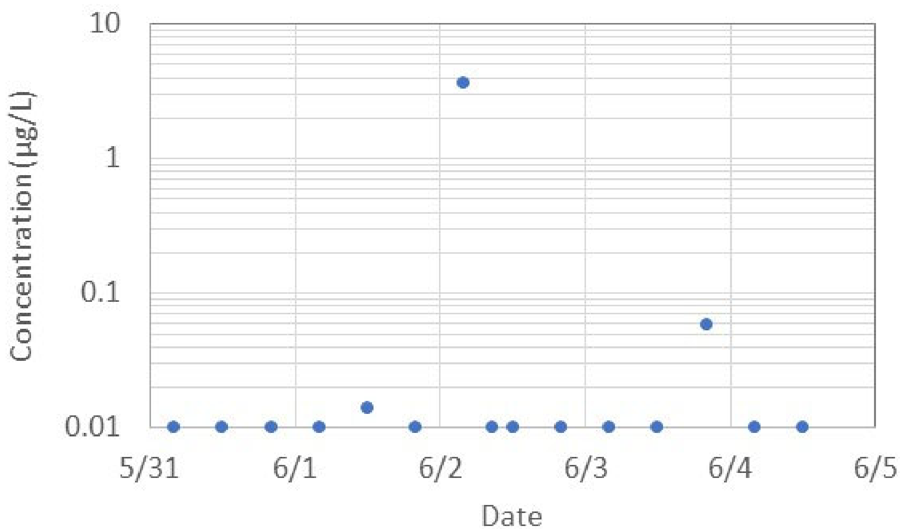

Figure 12. Pesticide Concentration Variation Over a Daily Time Step for Rock Creek (NCWQR)

Therefore, data need to be evaluated on a site-specific basis as the sampling frequency may impact the interpretation of the data. In many cases, there is not enough data either on an annual, multi-year, or multi-site basis to reliably estimate pesticide concentrations for short-term exposure estimates.

Several tables summarizing available surface water monitoring data, including more regionally-specific and site-specific summaries are provided in **APPENDIX C** and **Attachment 4**.

2. Data Interpretation and Extrapolation

SEAWAVE-QEX Results

Of the many sites with chlorpyrifos samples in the WQP datasets, 13 sites were determined to satisfy the model assumptions (see White Paper Chapter 3 and the SEAWAVE-QEX SOP for more information on satisfying model assumptions). However, upon further evaluation, two sites were excluded from quantitative analysis due to indications in the flow data that suggest the sites may not have year-round flow; however, the analysis of these sites is also included in **APPENDIX C**. A map of the sites considered for SEAWAVE-QEX analysis is presented in **Figure 13**. This map illustrates the need to consider all SEAWAVE-QEX sites across the contiguous states to capture as much of the range chlorpyrifos use conditions. For example, there are no SEAWAVE-QEX sites in HUC-10 or -11 and in most others HUCs there is only one SEAWAVE-QEX site.

Figure 13. Monitoring Sites Meeting the SEAWAVE-QEX Data Quantity Criteria

Figure 14 describes the sampling quantity characteristics for the final 11 SEAWAVE-QEX sites, showing both the number of samples at each site (y-axis) and the number of sites sampled each year (z-axis). However, data used in SEAWAVE-QEX spans from 1987-2012 as other years may not have met the minimum SEAWAVE-QEX criteria. These years may represent use patterns that are no longer registered as well as uses not considered in this assessment. Of the sites flagged for use in SEAWAVE-QEX based on the minimum criteria, recent years (e.g., after 2012) generally have less monitoring and/or lower detection frequencies. The reduced detection frequency could be the result of reduced sampling frequency in more recent years, changes in use in the early 2000s, and/or timing of sampling.

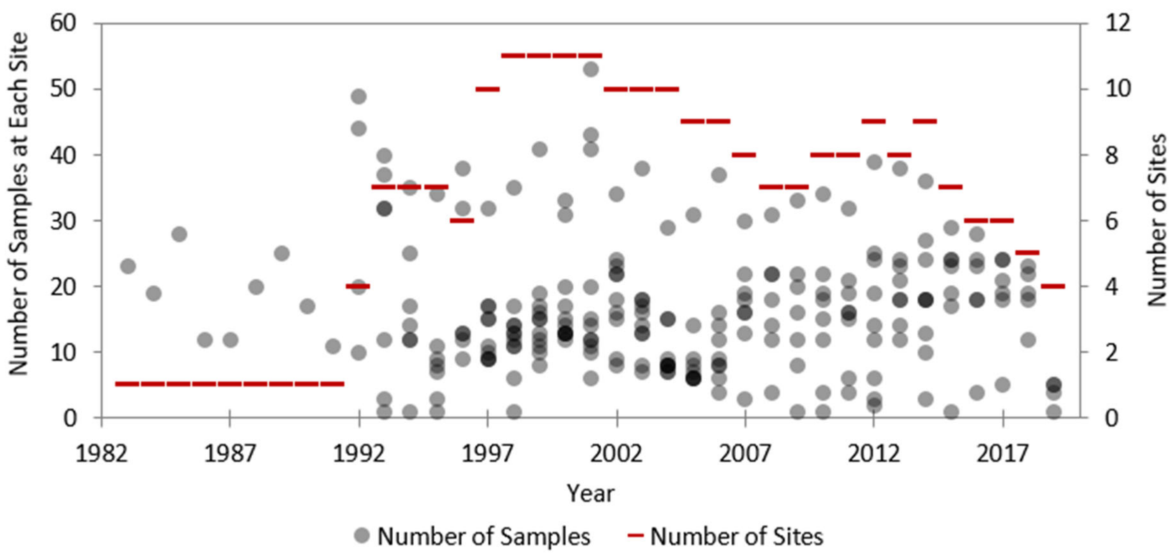

Figure 14. Sampling Quantity Characteristics for Chlorpyrifos Data for Sites Meeting the SEAWAVE-QEX Data Quantity Criteria

As observed in **Table 18** for several sites, the maximum measured concentration is lower than the reported censoring limit during other sampling events. For example, for USGS-01654000, the maximum measured concentration was 0.041 µg/L in 1994, but the reporting limit ranged from 0.0037 µg/L up to 0.0586 µg/L (i.e., greater than 0.041 µg/L) from 1994 to 2014. Reporting limits often vary between sampling events and descriptions included in the WQP are not always clear. For chlorpyrifos, which has relatively low measured concentrations that are of importance, these database issues create more uncertainty in the monitoring data. Additionally, a high censoring limit relative to measured concentrations may adversely affect the SEAWAVE-QEX output, which takes the censoring limit into account. This is because SEAWAVE-QEX randomly assigning values below the censoring limit. Therefore, a randomly high value may be selected that does not correspond with a flow event. However, not all high censoring limits occurred in years that were included in the SEAWAVE-QEX analysis.

Table 18. Summary of Monitoring Sites with Acceptable SEAWAVE-QEX Models

USGS Site No.	2-digit HUC (State)	Max Measured Conc. µg/L (Year)	Max Censoring Limit µg/L (Year)	Years Used in SEAWAVE-QEX	Final Simulation Filename (Confidence[1])	SEAWAVE-QEX Est. 1-day Conc. (µg/L)[2]	SEAWAVE-QEX Est. Est. 21-day Conc. (µg/L)[2]
01654000	02 (VA)	0.041 (1994)	0.0586 (2014)	1994-2000	cpy_1 (m)	0.026-0.060	0.011-0.036
02174250	03 (SC)	0.338 (2005)	0.02 (1999)	1996-2008	cpy_7 (m)	0.088-0.50	0.055-0.25
02335870	03 (GA)	0.034 (1993)	0.5 (2001)	1993-2000	cpy_2 (l)	0.022-0.085	0.013-0.041
03353637	05 (IN)	0.11 (1996)	0.3 (1993)	1992-1996	cpy_1 (m)	0.13-0.24	0.046-0.11
04193500	04 (OH)	0.0299 (1996)	0.21 (1998)	1996-2007	cpy_4 (l)	0.077-2.1	0.049-1.4
08057200	12 (TX)	0.0549 (2000)	0.025 (2016, 2017)	1998-2002	cpy_6 (h)	0.022-0.058	0.010-0.027
11274538	18 (CA)	0.3 (1992)	0.025 (2016)	1992-2010	cpy_4[3] (l)	0.48-2.1	0.20-1.1
11303500	18 (CA)	0.079 (1993)	0.025 (2016)	1994-2012	cpy_2 (h)	0.024-*0.073*	0.016-0.043
14211720	17 (OR)	0.0137 (2007)	0.013 (2006)	1997-2007	cpy_1 (m)	0.015-0.029	0.011-0.019
04208000	04 (OH)	0.5 (1988)	0.12 (2012-2014)	1987-1991	cpy_2 (m)	2.9-12.7	1.3-4.7
11447360	18 (CA)	0.0445 (1997)	0.02 (1998, 2002, 2005)	1997-2008	cpy_3 (n/a[4])	n/a	n/a
14201300	17 (OR)	0.401 (1995)	0.02 (2004)	1993-2018	cpy_1 (n/a[4])	n/a	n/a
03612500	05 (IL)	0.01 (2005, 2008-2010, 2013)	0.038 (1992)	1992-2000	cpy_6 (l)	0.031-0.35	0.021-0.23

[1] Confidence categories are: h=highest, m=medium, l=lowest
[2] Range of the yearly maximum of the 99th percentile concentration
[3] Additional data from Dow (now Corteva Agriscience) for 1996-1997 was included with the USGS site data for Orestimba Creek.
[4] Site excluded based on seasonal streamflow variation (i.e., intermittently flowing).
Italic font notes concentration measured is higher than summary statistic pulled from the SEAWAVE-QEX simulation.

Confidence in the SEAWAVE-QEX results are noted as high (h), medium (m), or low (l) (see **Table 18**). Reasoning based on goodness of fit of the diagnostic plots for these qualifiers are detailed in **APPENDIX C** on a site-by-site basis. For all sites except USGS-11303500, the highest 1-day estimated concentration was greater than the maximum measured concentration. For USGS-11303500, the SEAWAVE-QEX estimate was up to 0.073 µg/L while the maximum measured concentration was 0.079 µg/L. More than half of the sites have a single broad seasonal wave, likely because of either uses occurring year-round, applications occurring at different times across multiple years, and sporadic detections or a combination. Use of SEAWAVE-QEX may not be suitable for some pesticides with sporadic occurrence and low seasonality (e.g., not consistent use patterns at certain times of the year) as observed at these sites. To date, EPA's evaluation of SEAWAVE-QEX has focused on pesticides with strong seasonality (i.e., atrazine, metolachlor) and was limited geographically as the data used in the evaluation was from the NCWQR for sites in Ohio (tile drained). Even chlorpyrifos sites that had more seasonality in the data have shallow seasonal waves, suggesting that the monitoring analysis is not likely underestimating concentrations due to low seasonality.

Figure 15. Summary of Site Landcover Characteristics for Final SEAWAVE-QEX Sites summarizes several properties from the landcover data of the final 11 sites used quantitatively from SEAWAVE-QEX (National Land Cover Database reported in StreamCat). The graphed landcover data shown in **Figure 16** may not add up to 100% due to other contribution of other landcovers not presented. To determine the relevance of these monitoring sites to chlorpyrifos uses, landcover characteristics were examined. The 11 sites represent a mixture of urban environments with high percentages of impervious surfaces and agriculturally relevant sites, such as cropland and hay.

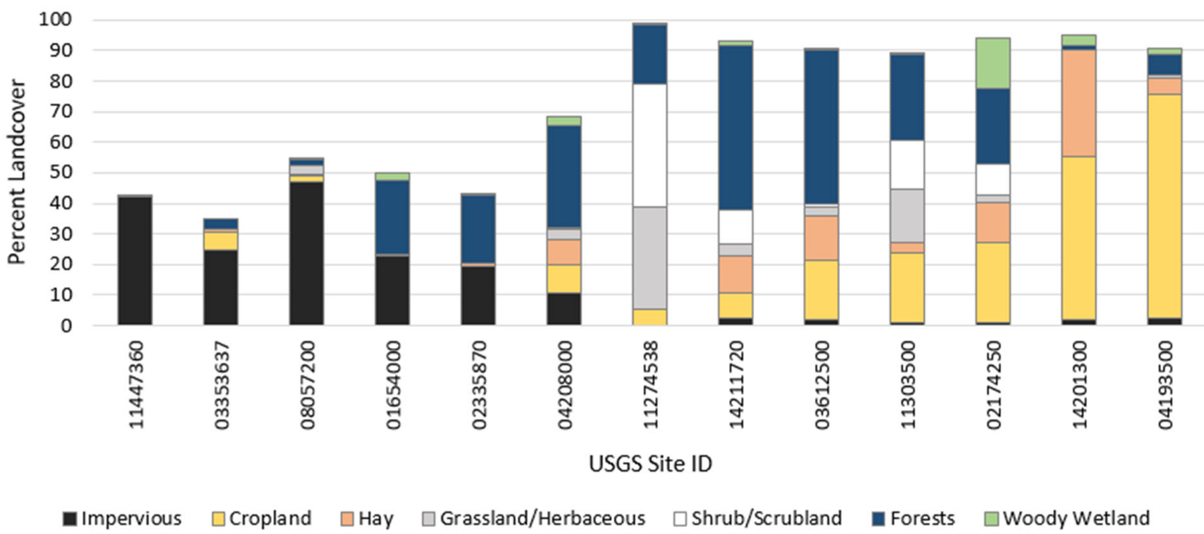

Figure 15. Summary of Site Landcover Characteristics for Final SEAWAVE-QEX Sites

Figure 16 and **Figure 17** below provide a summary of the 1- and 21-day estimated concentrations derived for each site-year from SEAWAVE-QEX. Note that one site (USGS-04208000) has the highest estimates of any other, from 1987-1991. These are also the oldest sampling data included and may represent uses that are no longer registered. Based on the StreamCat landcover data (Hill et al., 2016) (**Figure 15.** Summary of Site Landcover Characteristics for Final SEAWAVE-QEX Sites), the site is not substantially different from other sites with similar amounts of impervious surfaces and cropland; however, the gage station for the site is shared with the NCWQR Cuyahoga sampling site, and it is known that these are influenced by tile drainage. This is also true of USGS-04193500 (Maumee River), which includes higher concentrations than most other sites from 1996-2007. USGS-11274538 (Orestimba Creek) also stands out as having higher concentrations than most sites from 1992-2010.

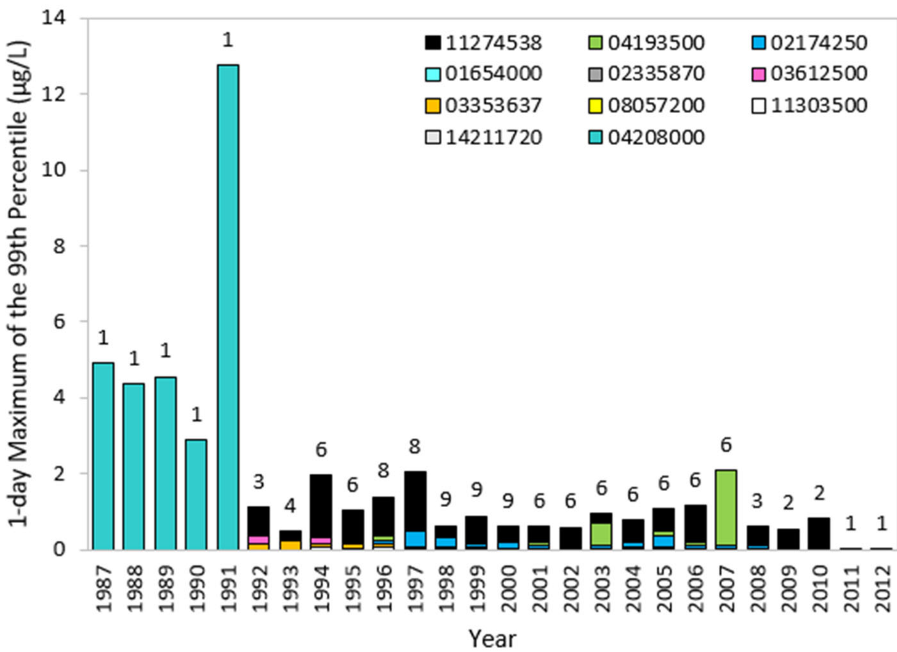

Figure 16. Summary of SEAWAVE-QEX 1-day Maximum of the 99th Percentile Chlorpyrifos Concentrations for Each Site (data labels are number of sites per year)

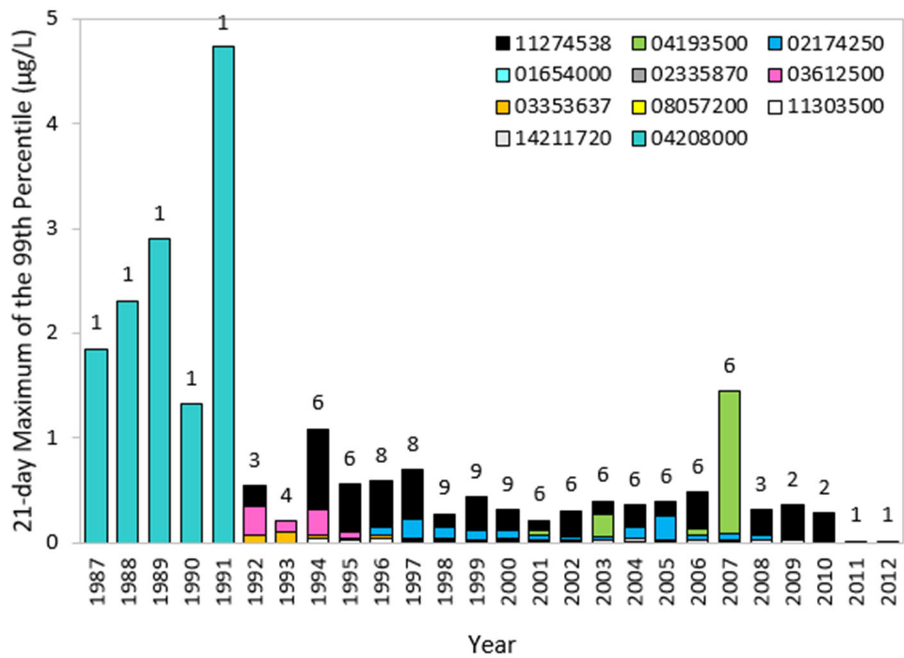

Figure 17. Summary of SEAWAVE-QEX 21-day Maximum of the 99th Percentile Chlorpyrifos Concentrations for Each Site (data labels are number of sites per year)

Sampling Bias Factors Development

SBFs were developed for 110-site years (11 sites) for estimating the upper bound confidence intervals on the 1- and 21-day average concentrations. The results are shown in **Figure 18** and **Figure 19**, respectively. The entire distribution of SBFs within each sampling frequency (e.g., 13-16 samples/year) was used to assess the potential concentrations across time and across the landscape. The maximum SBFs for 52, 26, 17, and 13 samples per year are 11, 23, 29, and 55, respectively, for estimating the 1-day average concentration and 4, 6, 8, and 12, respectively, for estimating the 21-day average concentration. These SBFs are much lower than SBFs developed for chlorpyrifos presented to the FIFRA SAP in November 2019. This is because only a subset of the SEAWAVE-QEX simulations were determined to be adequate for the development of SBFs based on feedback from the SAP panel.

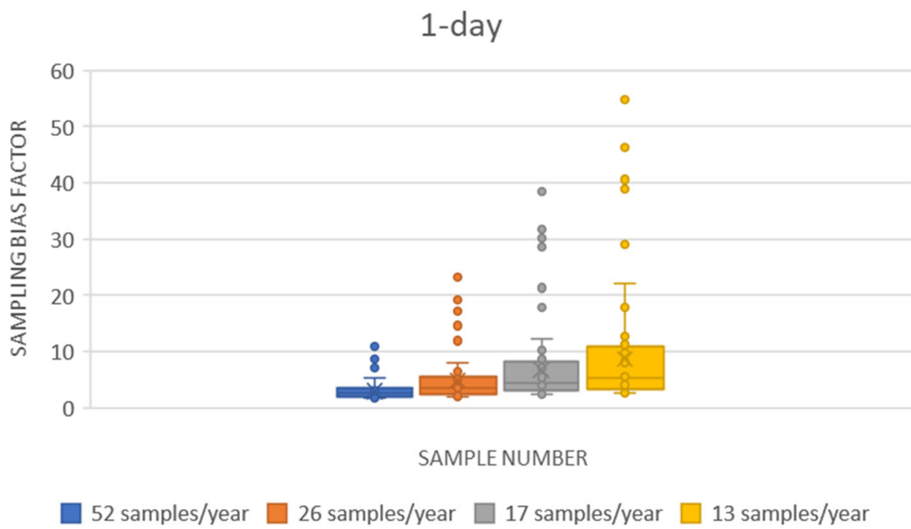

Figure 18. Chlorpyrifos Sampling Bias Factors for Estimating the Upper Bound Confidence Interval on the 1-day Concentration Across All Sites

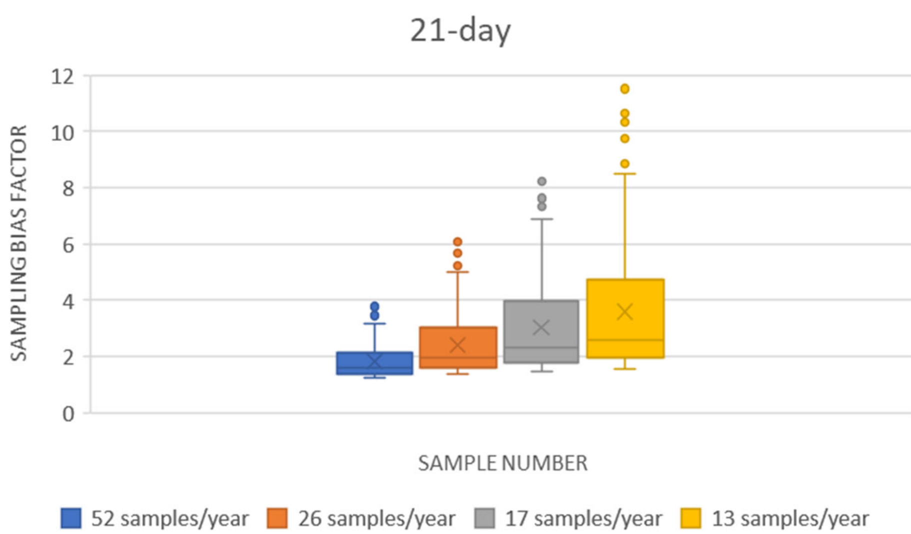

Figure 19. Chlorpyrifos Sampling Bias Factors for Estimating the Upper Bound Confidence Interval on the 21-day Concentration Across All Sites

Additional analysis of the developed SBFs revealed that SBFs varied more across sites than across years for most sites. **Figure 20** and **Figure 21** show the variability in the SBFs for 1- and 21-day across sites, respectively. However, there are a few sites where the SBFs notably varied across years. These sites include USGS-02174250 (Cow Castle Creek near Bowman, SC), USGS-0420800 (Cuyahoga River at Independence, OH), and USGS-11274538 (Orestimba Creek near Crows Landing, CA).

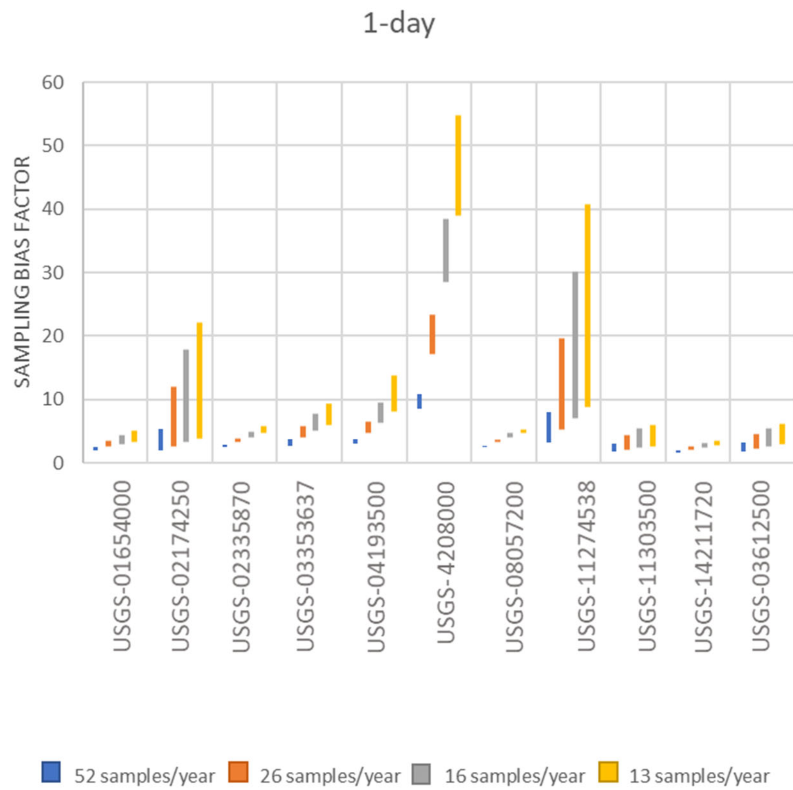

Figure 20. Chlorpyrifos Sampling Bias Factors for Estimating the Upper Bound Confidence Interval on the 1-day Concentration by Site

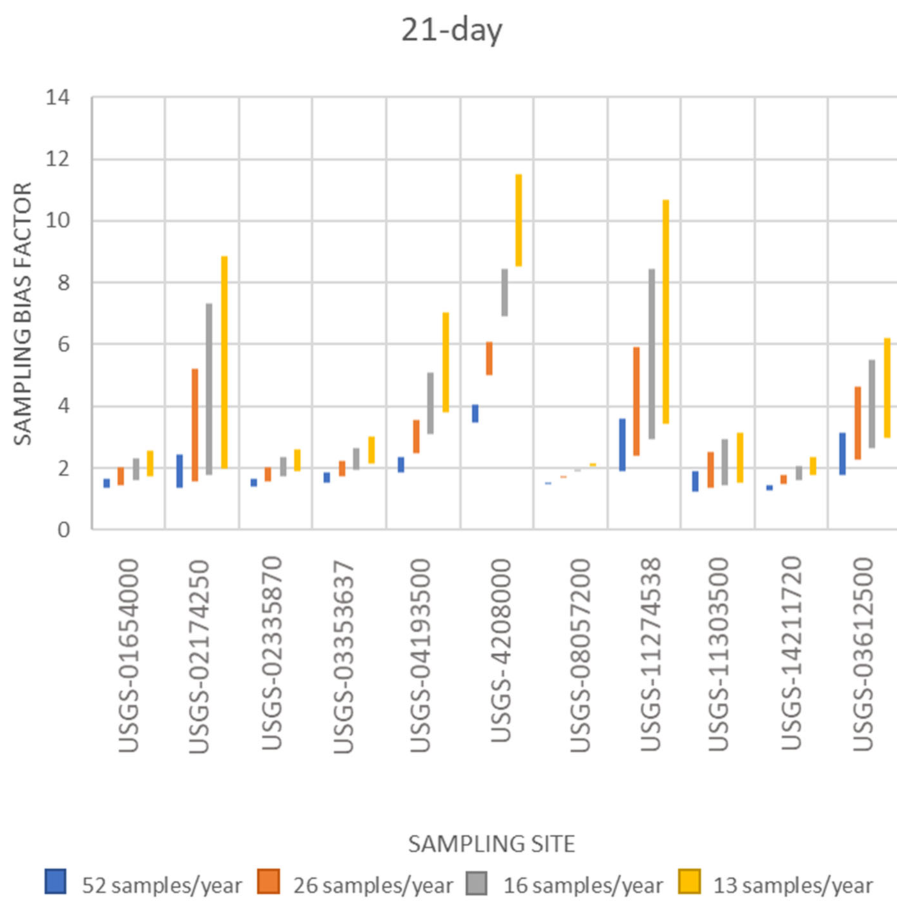

Figure 21. Chlorpyrifos Sampling Bias Factors for Estimating the Upper Bound Confidence Interval on the 21-day Concentration by Site

Further analysis of the sites indicates that:

For USGS-02174250, the large range and higher SBFs are due to a measured concentration in 2005 that resulted in much higher SBFs for 2005 than calculated for other years and sites. SBFs ranged from 2.0 to 2.9 for 52+ samples per year, 2.6 to 3.9 for 26-51 samples/year, 3.3 to 4.9 for 17-25 samples/year and 3.8 to 6.0 for 13-16 samples/year for estimating the upper bound concentration on the 1-day average for all years excluding 2005. In comparison, SBFs for 2005 are 5.3, 11.9, 17.8, and 22.2, for the corresponding sampling number.

For USGS-04208000, the large range and higher SBFs are observed for years 1987 through 1991. The SBFs are consistently high ranging from 9 to 11 for 52+ samples per year, 17 to 23 for 26-51 samples/year, 29 to 38 for 17-25 samples/year and 39 to 55 for 13-16 samples/year for estimating the upper bound concentration on the 1-day average concentration and 4 to almost 12 for 52+ samples per year and 13-16 samples/year, respectively, for 21-day average concentration.

For USGS-11274538, the larger range and higher SBFs are observed for 1996 and 1997. Again, the higher SBFs observed for this site are driven by a measured concentration. In addition, 1996 and 1997 had the most sampling data (i.e., daily) across years at this site and across sites.

This analysis, for USGS-11274538, suggests that for other years or other sites where peak occurrence concentration may have gone unmeasured, the SBFs may not capture the true range of potential chlorpyrifos concentrations. This is likely due to the sporadic application of chlorpyrifos and wide potential application window. In addition, chlorpyrifos is not observed to be persistent at a given point (e.g., sampling site) in a waterbody due to stream flow. Chlorpyrifos concentrations are driven by pulse inputs due to application or high runoff events. As discussed in the SEAWAVE-QEX section, the use patterns of chlorpyrifos and pulse inputs cause broad, shallow seasonal waves in SEAWAVE-QEX and fewer estimates of the pulse (peak) concentrations.

Figure 22 and **Figure 23** show the variability in the SBFs for 1- and 21-day across time, respectively. The number and specific sites where SBFs are calculated each year is different. The difference in sites is expected to be the primary contributor to the differences in magnitude of SBFs calculated across years.

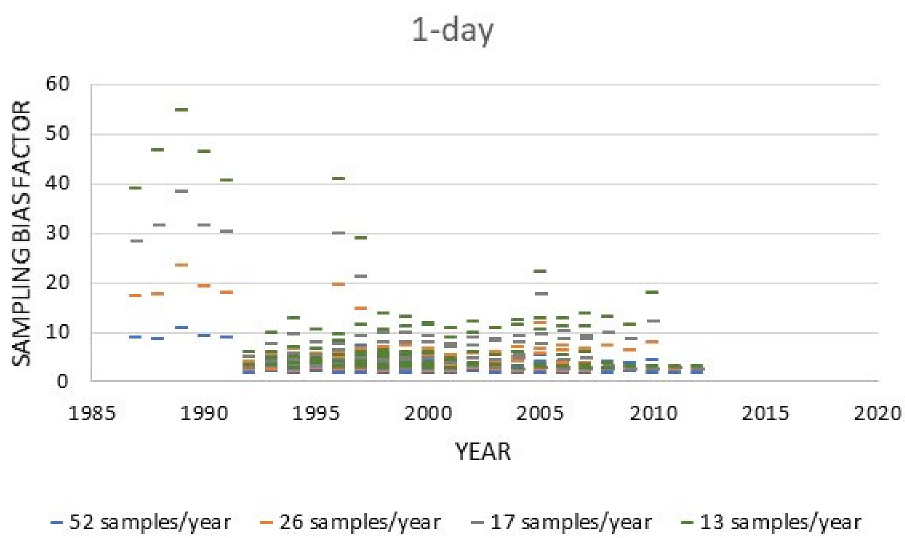

Figure 22. Chlorpyrifos Sampling Bias Factors for Estimating the Upper Bound Confidence Interval on the 1-day Concentration Across Years

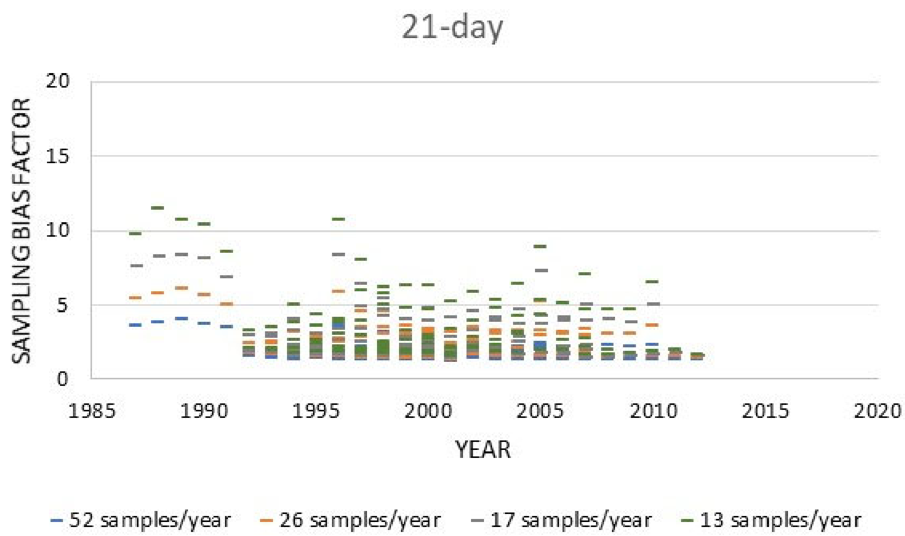

Figure 23. Chlorpyrifos Sampling Bias Factors for Estimating the Upper Bound Confidence Interval on the 21-day Concentration Across Years

Given that the use profile for chlorpyrifos changed in the early 2000s (see Use Characterization page 17 for more information), SBFs developed for 2005-2012 (post-registration review label changes) are presented in **Figure 24** and **Figure 25** for estimating the upper bound confidence interval on the 1- and 21-day average concentration.

The maximum SBFs for 52, 26, 17, and 13 samples per year are 5, 12, 18, and 22, respectively, for estimating the 1-day average concentration and 2, 5, 7, and 9 for estimating the 21-day average concentration, respectively. While these SBFs were developed based on data that likely better reflect current use, the data only represent 23-site years (5 sites) as compared to 110 site-years (11-sites) considering all available SBFs. Therefore, the abbreviated time span is not expected to represent a robust number of site-years to capture the range of potential chlorpyrifos concentrations in surface water. The 2012 FIFRA SAP suggested that 100 site years of data would be enough to capture a range of weather and site conditions.

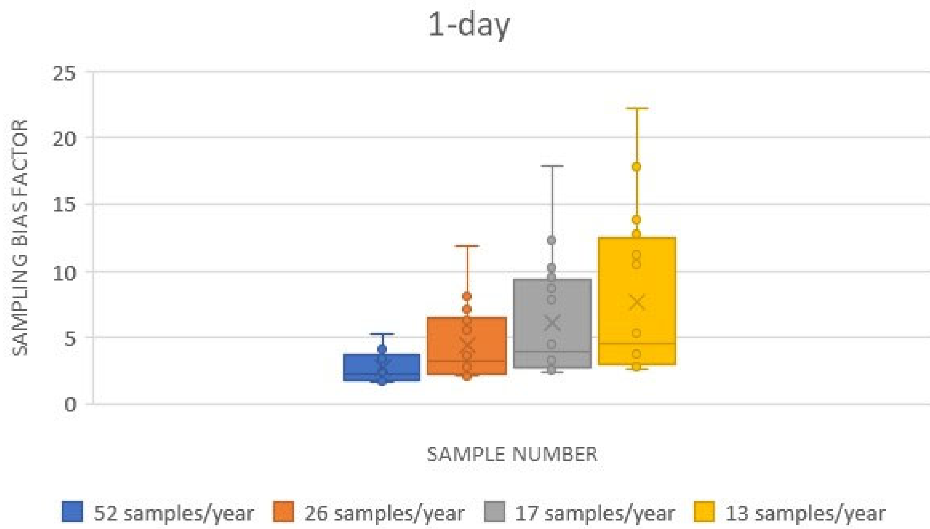

Figure 24. Chlorpyrifos Sampling Bias Factors for Estimating the Upper Bound Confidence Interval on the 1-day Concentration Across All Sites (2005-2012)

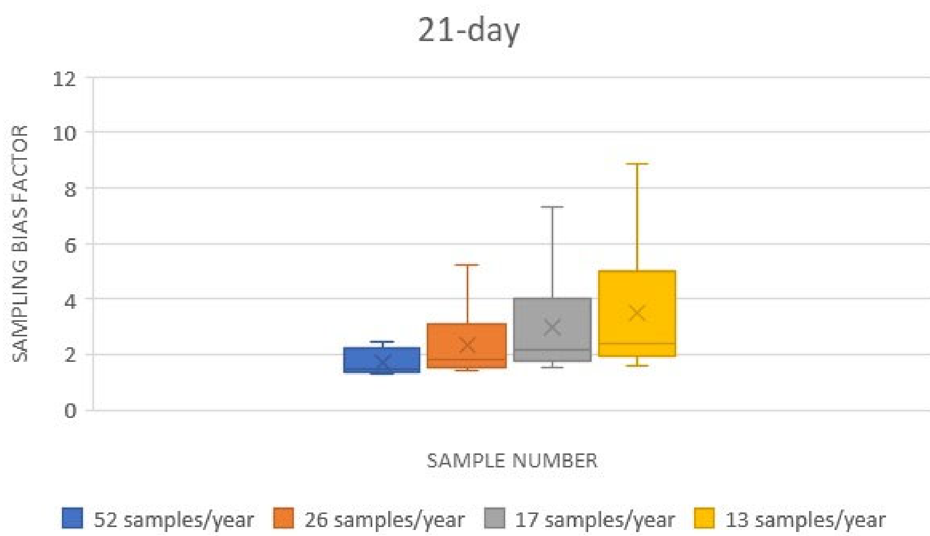

Figure 25. Chlorpyrifos Sampling Bias Factors for Estimating the Upper Bound Confidence Interval on the 21-day Concentration Across All Sites (2005-2012)

Sampling Bias Factors Application

Sampling Sites with Greater Than or Equal to 13 Samples per Year

SBFs for 1987-2012 (all years) and 2005-2012 (post-registration review label changes) are presented in **Table 19**. While there is a 2x difference in the 1-day SBFs for the two different periods of time the difference in 21-day SBFs is not that different especially when considering the 12-16 per year sampling category. Most chlorpyrifos data fall within the 12-16 per year sampling category or in the less than 13 sampling category. Therefore, to capture the most variability across time and space all SBFs years were considered and applied based on the number of samples per year for all site-years of data from the Water Quality Portal with greater than or equal to 13 samples per year (**Table 19**). A sensitivity analysis using the SBFs for the abbreviated time period was also completed. The results for the sensitivity analysis were not notably different.

Table 19. Maximum Sampling Bias Factors

Sample Number	Maximum 1987-2012 Sampling Bias Factor	Maximum 2005-2012 Sampling Bias Factor	Maximum 1987-2012 Sampling Bias Factor	Maximum 2005-2012 Sampling Bias Factor
	1-day		21-day	
52+	10.9	5.3	4.0	2.4
26-51	23.3	11.9	6.1	5.2
17-25	38.5	17.8	8.4	7.3
13-16	54.8	22.2	11.5	8.9

SBFs adjusted concentrations (i.e., the upper confidence bound) that are above the 10x DWLOC for 1-day or 21-day average concentration based on the maximum SBFs are shown in **Table 20** and **Table 21**, respectively. There are 7-site-years (4 sites in HUC-17) where concentrations may be above the 10x DWLOCs (1-day) using the maximum SBFs across all years. Considering only bias factors developed for years 2005-2012 (i.e., post label modifications) results in 4-site years (3-sites) where concentrations may be above the 10x DWLOC. There are 8-site-years (5 sites in HUC-17) with concentrations above the 10x DWLOCs (21-day) using the maximum SBFs across all years. Considering only SBFs developed for years 2005-2012 results in 5-site years (3-sites) where concentrations may be above the 10x DWLOC. The sites where concentrations may be above the DWLOC are consistent across the exposure duration of concern. The site-years of data resulting in potential concentration above the 10x DWLOC were collected in the mid-2000s to as recent as 2018, post label changes. Therefore, these sites would be expected to represent uses currently permitted on chlorpyrifos labels. For site OREGONDEQ-34235-ORDEQ, the highest concentration is for a censored value; however, this assumption has not been confirmed.

Table 20. Summary of Monitoring Sites with Sampling Bias Factor Adjusted Chlorpyrifos Concentrations Above the 1-day 10x DWLOC (24 µg/L)[1]

Monitoring Site	Year	Number of Samples	Detection Range (µg/L)	Range of Detection Limits (µg/L)	Maximum 1-day Sampling Bias Factor Adjusted Maximum 1-day Chlorpyrifos Concentration (µg/L)	Maximum 1-day Sampling Bias Factor Adjusted Maximum 1-day Chlorpyrifos-oxon Concentration (µg/L)
OREGONDEQ-32010-ORDEQ	2005	15	0.033-0.49	0.023-0.026	26.9	**25.7**
	2009	14	0.0618 - 0.6494	0.038-0.079	35.6	**34.0**
OREGONDEQ-32068-ORDEQ	2007	14	0.026 - 2.4	0.024-0.03	131.5	**125.5**
	2015	15	0.125 - 1.77	0.021 - 0.0865	97.0	**92.5**
	2016	13	0.039 - 0.722	0.0214 - 0.023	39.6	**37.8**
OREGONDEQ-32069-ORDEQ	2007	13	0.04 - 1.3	0.025 - 0.03	71.2	**67.9**
OREGONDEQ-34235-ORDEQ	2018	13	0.0591	0.0213-2.72[2]	74.5	**71.1**

Bold font Indicates concentration above the 10x DWLOC.
[1] The source water concentration of chlorpyrifos necessary to result in the chlorpyrifos-oxon concentration in drinking water following conversion during treatment was back calculated from the DWLOC for chlorpyrifos-oxon using a molecular weight adjustment factor (DWLOC/0.9541) (23 µg/L/0.9541) = 24 µg/L
[2] value is a censored concentration.

Table 21. Summary of Monitoring Sites with Sampling Bias Factor Adjusted Concentrations Above the 21-day 10x DWLOC (4.2 µg/L)[1]

Monitoring Site	Year	Number of Samples	Detection Range (µg/L)	Range of Detection Limits (µg/L)	Maximum 21-day Sampling Bias Factor Adjusted Maximum 1-day Concentration (µg/L)[2]	21-day Interpolated Concentration (µg/L)[2]	Maximum 21-day Sampling Bias Factor Adjusted Maximum Estimated 21-day Concentration (µg/L)
					1987-2012		1987-2012
OREGONDEQ-32010-ORDEQ	2005	15	0.033-0.49	0.023-0.026	**5.6**	0.14 (0.14)	1.6 (1.6)
	2009	14	0.0618 - 0.6494	0.038-0.079	**7.5**	0.14 (0.02)	1.6 (0.2)
OREGONDEQ-32068-ORDEQ	2007	14	0.026 - 2.4	0.024-0.03	**27.6**	1.7 (2.7)	**19.3 (19.3)**
	2015	15	0.125 - 1.77	0.021 - 0.0865	**20.4**	0.66 (0.63)	**7.6 (7.3)**
	2016	13	0.039 - 0.722	0.0214 - 0.023	**8.3**	0.57 (0.57)	**6.5 (6.5)**
OREGONDEQ-32069-ORDEQ	2007	13	0.04 - 1.3	0.025 - 0.03	**15.0**	0.42 (0.41)	**4.8 (4.7)**
OREGONDEQ-34235-ORDEQ	2018	13	0.0591	0.0213-2.72[3]	**15.6**	1.4 (0.7)	**16.4 (8.2)**
OREGONDEQ-37639-ORDEQ	2014	14	0.0274-0.395	0.0212 – 0.0862	**4.5**	0.22 (0.20)	2.5 (2.3)

[1] The source water concentration of chlorpyrifos necessary to result in the chlorpyrifos-oxon concentration in drinking water following conversion during treatment was back calculated from the DWLOC for chlorpyrifos-oxon using a molecular weight adjustment factor (DWLOC/0.9541) (4 µg/L/0.9541) = 4.2 µg/L
[2] The 1-day max concentration multiplied by the 21-day sampling bias as a surrogate from to estimate the upper bound 21-day average concentrations.
[3] 21-day average concentration was estimated using log-linear interpolation. Interpolated 21-day concentration using the detection limit was calculated using the detection limit, bracketed values include use of ½ the detection limit.
value is a censored concentration (i.e., below the minimum reporting limit)
Bold font Indicates concentration above the 10x DWLOC.

Watershed characteristics for these sampling sites are provided in **Figure 26**. All the sampling sites are in HUC-17 with sampling data collected by the Oregon Department of Environmental Quality. An overlap of the sampling site locations with counties associated with cropped acres for the use sites considered in this assessment is provided in **Figure 27**. Only three blue dots are visible on the map due to scaling as there are multiple sampling sites in proximity to one another (OREGONDEQ-32068-ORDEQ is near OREGONDEQ-32069-ORDEQ and OREGONDEQ-34235-ORDEQ is near OREGONDEQ-37639-ORDEQ).

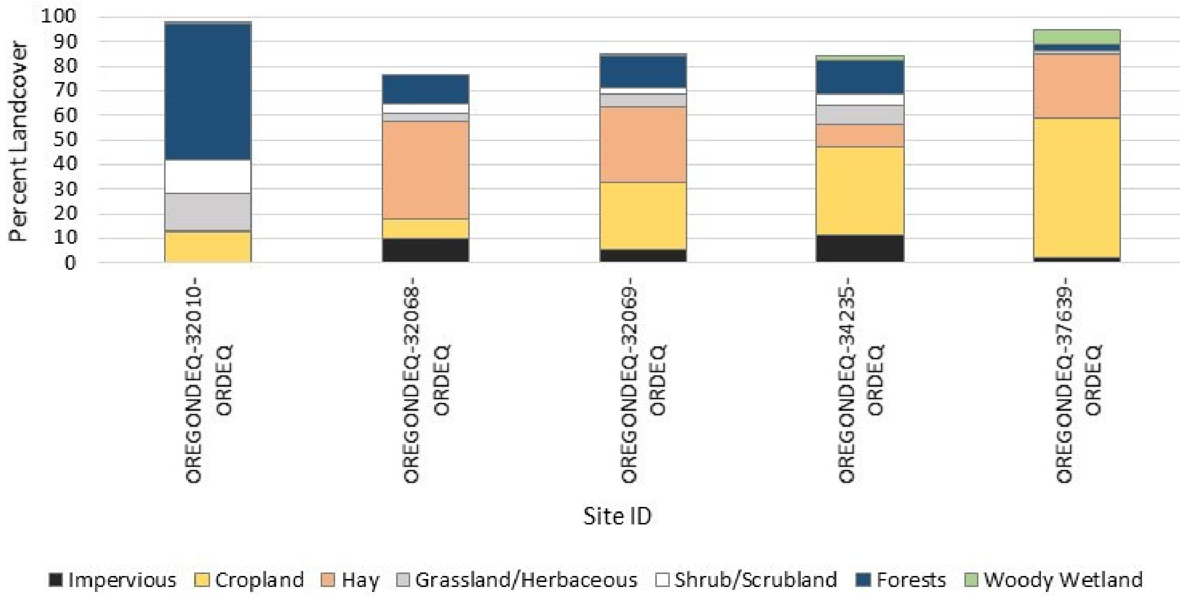

Figure 26. Summary of Site Landcover Characteristics for Sampling Sites with Sampling Bias Factor Adjusted Concentrations above 10x DWLOCs

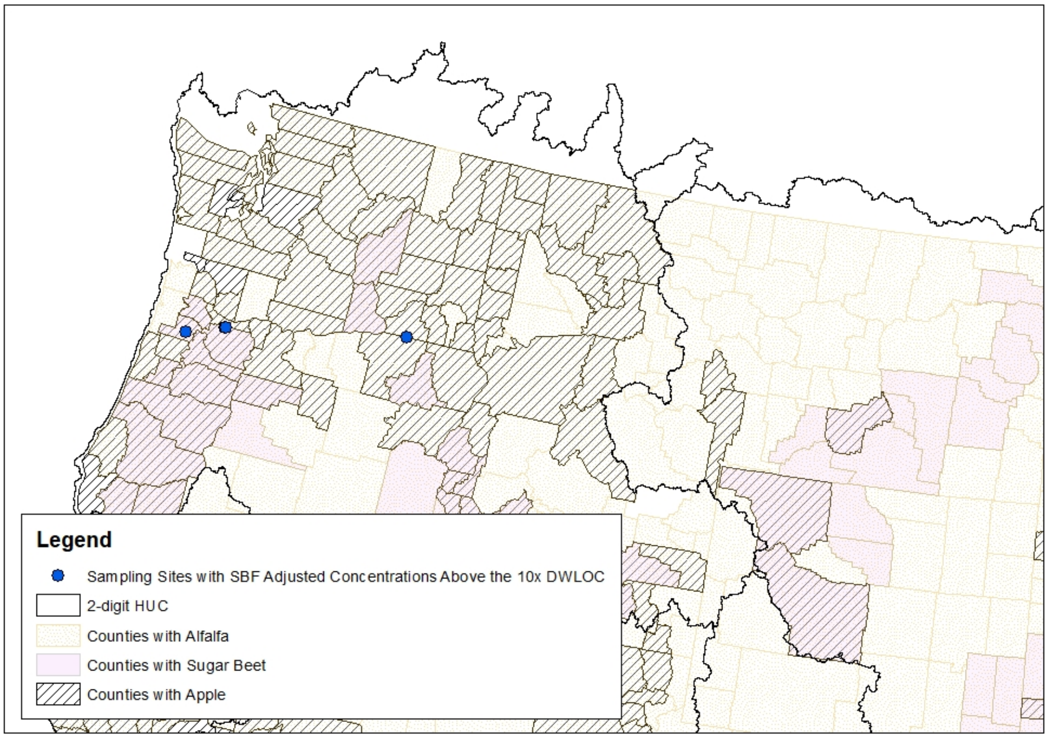

Figure 27. Summary of Site Landcover Characteristics for Sampling Sites with Sampling Bias Factor Adjusted Concentrations above 10x DWLOCs

Four of the sites have overlap with counties with all four uses (alfalfa, apple, strawberry and sugar beet) considered in this assessment in HUC-17 (**Figure 27**). These sites are in western Oregon. The occurrence timing is sporadic April through October. This suggest that there are likely multiple chlorpyrifos uses leading to occurrence in surface water within and across years. The other site OREGONDEQ-32010-ORDEQ is in eastern Oregon. This site overlaps with counties with three (alfalfa, apple, and strawberry) of the four uses considered in this assessment. For this site, chlorpyrifos is detected in surface water in March and April suggesting an early season dormant application such as to a tree fruits including apple, a use considered in this assessment. However, it cannot be determined if other uses are contributing.

Additional characterization of these sites is provided in **APPENDIX C.**

<u>Sampling Sites with Less Than 13 Samples per Year</u>

Sites with greater than 13 samples per year are appropriate for consideration quantitatively in DWAs, however, there is the potential that pesticide concentrations, from monitoring sites not meeting the criteria, could be higher and could lead to an underestimation of exposure in drinking water. Therefore, sampling data from sites where less than 13 samples per year are examined. Concentration data for these sites indicates there are several sites in several HUCs that may have concentrations above the 1-day and 21-day 10xDWLOC and a few sites that may have concentrations above the 1- and 21-day 1x DWLOC. There is overlap with the regions considered in this assessment (i.e., HUCs 03, 04, 06, 07, 08, 10, 12, 15, and 17.

Table 22 highlights the regions where concentrations may occur above the various DWLOCs. In addition, **Table 22** provides the total number of samples that suggest concentrations are above the respective DWLOCs. Additional characterization of these sites is provided in **APPENDIX C**.

Table 22. 2-digit HUC Summary of the Number of Sites with Potential Concentrations Above the DWLOCs

2-digit HUC	Max Measured Value	Site-Years			
		>1-day 10xDWLOC[1]	>21-day 10xDWLOC[2]	>1-day 1xDWLOC[3]	>21-day 1xDWLOC[4]
01	1.3	1	1		
02	0.2				
03	1.5	16 (1)	33 (4)		
04	0.8	3	3		
05	0.2				
06	1.5	6	10 (1)		
07	1.1	4 (1)	6 (1)		
08	1.7	1	1		
09	0.2				
10	14.7	1	2	1	1
11	0.2				
12	2.2	2	2		
13	0.2				
14	0.2				
15	0.6	1	1		
16	0.02				
17	3.3	4	6		
18	8.9	37 (13)	47 (18)	2	3
19	-				
20	0.9	1	1		
21	0.04				
Total Sites		76	113	3	4
Total Site-Years		119	165	3	4

1. 1-day chlorpyrifos-oxon 10x DWLOC = 23 µg/L; 1-day SBF = 54.8; reference concentrations >0.42 µg/L
2. 21-day chlorpyrifos-oxon 10x DWLOC = 4.0 µg/L; 21-day SBF = 11.5; reference concentrations >0.35 µg/L
3. 1-day chlorpyrifos-oxon 1x DWLOC = 230 µg/L; 1-day SBF = 54.8; reference concentrations >4.2 µg/L
4. 21-day chlorpyrifos-oxon 1x DWLOC = 43 µg/L; 21-day SBF= 11.5; reference concentration >3.7 µg/L

Bracketed values indicate the number of sites with multiple years where concentrations may be above the respective DWLOCs.
Gray shading indicates HUCs considered in the modeling analysis of this assessment.
SBF based on 13 samples per year was used although the same number may be much lower.

c. Weight of Evidence

Model estimated concentrations as well as measured concentrations of chlorpyrifos were evaluated to determine whether monitoring data suggested a potential DWLOC exceedance for either chlorpyrifos or chlorpyrifos-oxon (following drinking water treatment), with the lines of evidence described in **Table 23**.

Model estimated concentrations indicate that for the subset of assessed uses concentrations of chlorpyrifos and chlorpyrifos-oxon are not expected to be above the DWLOCs with or without the retention of the FQPA safety factor.

However, monitoring data suggest that in some areas of the country concentrations may exceed the DWLOC with and without the FQPA safety factor when all uses currently registered are considered since available monitoring data represent usage of chlorpyrifos. When considering the data with more than 13 samples per year, five sites all in HUC-17 indicated a potential for DWLOC exceedances. This is based on the application of sampling bias factors.

When considering the data with fewer than 13 samples per year, several sites indicated a potential for concentrations to be above the DWLOC. In one region, concentrations may exceed the 1x 1- and 21-day DWLOCs. Further analysis of sites with concentrations that could be higher than the DWLOCs could not definitively determine that the measured concentration was the results of a use or combination of uses considered in this assessment (i.e., the 11 critical or high benefit uses). It is possible that if more frequent monitoring data were available these conclusions could change.

Table 23. Lines of Evidence Used to Quantify and Characterize Potential Exposure to Chlorpyrifos and Chlorpyrifos-oxon

Lines of Evidence	
Modeling	
PWC Modeling	All uses and regions assessed are below DWLOCs. Some regions required a high-level of refinement. • **HUC-02 (apple and peach):** concentrations below DWLOCs based on upper bound application rates • **HUC-03 (cotton, citrus, peach, and soybean):** concentrations below DWLOCs based on upper bound application rates • **HUC-04 (alfalfa, sugar beet, apple, cherry, peach, soybean, and asparagus):** PCA aggregated concentrations below DWLOCs based on upper bound application rates • **HUC-05 (apple and soybean):** concentrations below DWLOCs based on upper bound application rates • **HUC-06 (apple):** concentrations below DWLOCs based on upper bound application rates • **HUC-07 (alfalfa, sugar beet, and soybean):** PCA-PCT aggregated concentrations below DWLOCs based on upper bound application rates • **HUC-09 (alfalfa, sugar beet, soybean, spring wheat, and winter wheat):** PCA-PCT aggregated concentrations below DWLOCs based on upper bound application rates • **HUC-10 (alfalfa, soybean, spring wheat, and winter wheat):** concentrations below DWLOCs based on upper bound application rates • **HUC-11 (alfalfa, soybean, and winter wheat):** concentrations below DWLOCs based on upper bound application rates • **HUC-12 (citrus, peach, and winter wheat):** concentrations below DWLOCs based on upper bound application rates • **HUC-17 (alfalfa, sugar beet, apple, and strawberry):** PCA aggregated concentrations below DWLOCs based on upper bound application rates

Monitoring	
SEAWAVE-QEX	Concentrations are not expected to exceed the DWLOC for 11 sites dispersed across the country.
Sampling Bias Factors	Monitoring data in HUC-17 indicate that concentrations could be above 10x DWLOC. These monitoring sites are in areas where the crops considered in this assessment are grown. However, there is also expected to be other crops where chlorpyrifos is applied and the contribution of these uses to the measured concentrations cannot be precluded.
Sites <13 Samples/year	This dataset had the highest detected concentration (14.7 µg/L) across the sample number categories and is predicted to have the lowest probability of capturing upper-bound concentrations. Nevertheless, there are several sites across the country that indicate concentrations may exceed the 1x and 10x DWLOCs including in regions assessed in this assessment. This suggests that current usage of chlorpyrifos could lead to concentrations above the DWLOCs.
Monitoring in Major Usage Area	There is limited data (i.e., low sample frequency and a low number of sites) in many areas of the locations and across years.
Uncertainty	The major uncertainty in understanding the monitoring results is an understanding of the usage data in relation to where and when monitoring occurred and how those relate to the uses under consideration in this assessment.

1. *HUC-02 (apple and peach)*

Upper bound use rates used in this assessment were from national level data supplied by BEAD several years ago. Modeling suggest concentrations for chlorpyrifos and chlorpyrifos-oxon are below the DWLOCs for chlorpyrifos use on apple and peach in HUC-02.

Monitoring data where the uncertainty could be quantified were limited. There was only 1 SEAWAVE-QEX site in HUC-02, which indicated concentrations were below the DWLOCs. Application of SBFs also indicated concentrations are likely below the DWLOCs in this region; however, sample frequency is generally low thus higher occurrence concentration likely occurred.

2. *HUC-03 (cotton, citrus, peach, and soybean)*

Upper bound use rates used in this assessment were from national level data for peach supplied by BEAD several years ago while usage data for cotton, citrus, and soybean were provide at a state-level and are based on more recent data. Modeling suggest concentrations for chlorpyrifos and chlorpyrifos-oxon are below the DWLOCs for chlorpyrifos use on cotton, citrus, peach, and soybean in HUC-02.

Monitoring data where the uncertainty could be quantified were limited. There were only 2 SEAWAVE-QEX sites in HUC-03, which indicated concentrations were below the DWLOCs. These sites are in the northern portion of the region and does not capture the citrus growing area within the region. Application of SBFs suggested that concentrations maybe above the 10x DWLOCs in this region. Cotton, peach, and soybean are grown through the region and likely overlap with some of the sites where potential exceedance are possible. Generally, sample frequency is low in this region limiting the ability to confidently estimate concentration in the region from available monitoring data.

3. HUC-04 (alfalfa, sugar beet, apple, cherry, peach, soybean, and asparagus)

Upper bound use rates used in this assessment were from national level data for apple, cherry and peach supplied by BEAD several years ago while usage data for alfalfa, sugar beet, soybean and asparagus were provide at a state-level and are based on more recent data. Modeling suggest concentrations for chlorpyrifos and chlorpyrifos-oxon are below the DWLOCs following aggregation using available PCAs. This is primarily driven by the low overlap of orchard acres with community water system watersheds.

Monitoring data where the uncertainty could be quantified were limited. There were only 2 SEAWAVE-QEX sites in HUC-04, which indicated concentrations were below the DWLOCs. These sites are in northern Ohio. The monitoring sites fall in areas where alfalfa, apple, peach, and soybean. The SEAWAVE-QEX sites are not in areas where sugar beet, cherry, or asparagus are grown. Application of SBFs suggested that concentrations maybe above the 10x DWLOCs in this region. This region has high frequency monitoring data includes those supported by NCWQR. Again, these high frequency sampling sites do not coincide with sugar beet, cherry, or asparagus growing areas.

4. HUC-05 apple and soybean

Upper bound use rates used in this assessment were from national level data for apple supplied by BEAD several years ago while usage data for soybean was provide at a state-level and are based on more recent data. Modeling suggest concentrations for chlorpyrifos and chlorpyrifos-oxon are below the DWLOCs.

Monitoring data where the uncertainty could be quantified were limited. There was only 1 SEAWAVE-QEX site in HUC-05, which indicated concentrations were below the DWLOCs. This site falls withing a country with reported acres of soybean; however, there is no reported acreage of apples in the county where the sampling site falls. Application of sampling bias factor suggested that concentrations do not exceed the DWLOCs in this region. However, this region generally has low frequency monitoring data.

5. HUC-06 apple

Upper bound use rates used in this assessment were from national level data for apple supplied by BEAD several years ago. Modeling suggest concentrations for chlorpyrifos and chlorpyrifos-oxon are below the DWLOCs.

Monitoring data where the uncertainty could be quantified were not available for this region. Application of SBFs suggest there are sites that could exceed the 10x DWLOC. These sites overlap with counties reporting acres of apples. This region generally has low frequency monitoring data.

6. HUC-07 alfalfa, sugar beet, and soybean

Upper bound use rates used in this assessment were from usage data for alfalfa, sugar beet, and soybean provide at a state-level. Modeling suggest concentrations for chlorpyrifos and chlorpyrifos-oxon are below the DWLOCs based on PCA-PCT aggregation, the highest level of model refinement used in this assessment.

Monitoring data where the uncertainty could be quantified were not available for this region. Application of SBFs suggest there are sites that could exceed the 10x DWLOC. These sites overlap with counties reporting acres of apples. This region generally has low frequency monitoring data.

7. HUC-09 Alfalfa, Sugar beet, Soybean, Spring Wheat, and Winter Wheat

Upper bound use rates used in this assessment were from usage data for alfalfa, sugar beet, soybean spring wheat, and winter wheat were provided at a state-level. Modeling suggest concentrations for chlorpyrifos and chlorpyrifos-oxon are below the DWLOCs based on PCA-PCT aggregation, the highest level of model refinement used in this assessment.

Monitoring data where the uncertainty could be quantified were not available for this region. Application of SBFs did not lead to the identification of sites that could have concentrations above the DWLOCs. However, generally this region has a low frequency monitoring data.

8. HUC-10 Alfalfa, Soybean, Spring Wheat, and Winter Wheat

Upper bound use rates used in this assessment for alfalfa, soybean, spring wheat and winter wheat were provided at a state-level and are based on more recent data. Modeling suggest concentrations for chlorpyrifos and chlorpyrifos-oxon are below the DWLOCs.

Monitoring data where the uncertainty could be quantified were not available for this region. This region has the highest single measured concentration of chlorpyrifos (14.7 µg/L). Application of SBFs indicate that this region could have sites that exceed the 10x DWLOC and 1x DWLOC. This is primarily driven by the one high detection. Generally, this region has a low frequency monitoring data.

9. HUC-11 Alfalfa, Soybean, and Winter Wheat

Upper bound use rates used in this assessment for alfalfa, soybean, and winter wheat were provided at a state-level and are based on more recent data. Modeling suggest concentrations for chlorpyrifos and chlorpyrifos-oxon are below the DWLOCs.

Monitoring data where the uncertainty could be quantified were not available for this region. This region has the highest single measured concentration of chlorpyrifos (14.7 µg/L). Application of SBFs indicate that this region could have sites that exceed the 10x DWLOC and 1x DWLOC. This is primarily driven by the one high detection. Generally, this region has a low frequency monitoring data.

10. HUC-12 Citrus, Peach, and Winter Wheat

Upper bound use rates used in this assessment for citrus, peach, and winter wheat were provided at a state-level and are based on more recent data. Modeling suggests concentrations for chlorpyrifos and chlorpyrifos-oxon are below the DWLOCs. Recall, that at the time of this assessment a new model scenario was not available for deciduous orchards. Therefore, the evergreen orchard scenario was used. The impact on estimated concentrations is not known.

Monitoring data where the uncertainty could be quantified were not available for this region. There was only 1 SEAWAVE-QEX site in HUC-12, which indicated concentrations were below the DWLOCs. This site falls withing a county with reported acres of peach and wheat. However, this site does not cover areas where citrus is grown. Application of SBFs indicate that this region could have sites that exceed the 10x DWLOC.

11. HUC-12 Alfalfa, Sugar beet, Apple, and Strawberry

Upper bound use rates used in this assessment for alfalfa, sugar beet was provided at a state-level and are based on more recent data. Modeling suggest concentrations for chlorpyrifos and chlorpyrifos-oxon are below the DWLOCs following aggregation using available PCAs. Application of SBFs indicate that this region could have sites that exceed the 10x DWLOC.

Monitoring data where the uncertainty could be quantified were not available for this region. There was only 1 SEAWAVE-QEX site in HUC-17, which indicated concentrations were below the DWLOCs. There are five sites in Oregon with enough sampling to have confidence in the prediction intervals to have confidence in the SBF-adjusted concentrations. In some cases, concentrations above the 10x DWLOC were estimated to occur over multiple years. Furthermore, these estimates were all estimated to occur after the labels for chlorpyrifos were updated in the mid-2000s. These sites were determined to be relevant to community water systems as all the sites were upstream with a short travel time to the often less than a day. These sites were in areas where may different chlorpyrifos uses could be occurring includes those considered in this assessment for HUC-17.

12. Other Considerations

One major uncertainty in understanding the monitoring results is the uncertainty in the usage data, which is only available at the state level for a limited number of use patterns. Additionally, how the monitoring relates to the usage in time and space is not readily available. This makes it extremely difficult to determine if any of the reported exceedance may have been the result of one of the uses considered in this assessment. Therefore, the results of this assessment indicate that it is important to consider all potential use sites when estimating potential exposure in drinking water.

Another major uncertainty is that in general sampling frequency for chlorpyrifos has tapered off over the last decade as well as detection frequency. It is unknow if the lack of sampling is contributing to the reduced detection frequency or if detection frequencies are decreased. Likely both are contributing factors. Often reduced testing lead to reduced detection frequency unless sampling is specifically started to use.

Higher SBFs were driven by measured concentrations value input into SEAWAVE-QEX. This generally resulted in tighter confidence bounds around the measured concentration; however, the ability of SEAWAVE-QEX to capture the peak occurrence concentration for a sporadically used pesticide is questionable. Furthermore, when more frequent data were input into SEAWAVE-QEX higher concentrations were estimated. Therefore, when infrequently sampling data are input into SEAWAVE-QEX it is possible that concentrations as well as SBFs developed from the resulting chemographs underestimate the potential range of concentrations occurring in the environment. It is possible that SBFs are underestimated for chlorpyrifos in this assessment and the exposure potential underestimated. More frequency data would help address this concern.

Chlorpyrifos-oxon concentrations in drinking water are primarily driven by chlorpyrifos concentrations in source water. In source water chlorpyrifos is stable compared to chlorpyrifos-oxon. Once formed during drinking water treatment chlorpyrifos-oxon has increased stability (t ½= 12 days) under drinking water conditions compared to environmental conditions. This suggests that chlorpyrifos -oxon is stable during the expected range of distribution times which can be a few hours to several days.

Conclusions

This assessment focuses on a subset of currently registered chlorpyrifos uses – alfalfa, apple, asparagus, cherry, citrus, cotton, peach, soybean, sugar beet, strawberry, and wheat in specific areas of the country. This subset of uses was identified as being the most important of all the currently registered uses of chlorpyrifos. This assessment utilized new surface water model scenarios (i.e., soil, weather, and crop data), integrates the entire distribution of community water system percent cropped area adjustment factors and integrates state-level percent crop treated data, and considers the quantitative use of available surface water monitoring data.

Concentrations of chlorpyrifos and chlorpyrifos-oxon in drinking water are not likely to exceed the drinking water level of comparison (DWLOC) with or without the retention of the FQPA safety factor for the subset of uses considered. This conclusion is based on upper bound application rates for the subset of assessed uses. Furthermore, a thorough analysis of monitoring data was completed and indicates that there are several monitoring sites across the United States that could have concentrations higher than the DWLOCs (with and without the retention of the FQPA safety factor). However, the contribution of other currently registered uses of chlorpyrifos (i.e., uses not considered in this assessment) could not be ruled out, nor could a definitive conclusion be made that the measured concentration data correlated to one of the specific uses evaluated in this assessment.

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APPENDIX A. Summary of Uses Considered

Critical Uses

Alfalfa

Use of chlorpyrifos to treat alfalfa weevil was identified as one of the most critical uses by Corteva Agriscience. Analysis completed by BEAD indicates that chlorpyrifos is only used on alfalfa in HUC-04, -07, -09, -10, -11, -13, -14, -15, -16, and -17. Application rates for alfalfa weevil larvae and adults are permitted between 0.47-0.94 lb a.i./A (Lorsban Advance Reg. No. 62719-591). This falls within the reported use range for chlorpyrifos use on alfalfa. Usage data across all regions with reported use, suggest that only one of the four permitted applications occurs per year in alfalfa. Most applications are applied by ground equipment; however, in some regions, such as HUC-14, almost half of the applications are made by aerial equipment. Generally, applications to treat alfalfa weevil occur mid-April through early June depending on the 2-digit HUC region.

Citrus – Oranges, Lemons, and Grapefruit

Since the introduction of the Asian citrus psyllid (ACP) to the continental U.S. in 1998, chlorpyrifos has become one of several insecticides used to control this pest, which transmits the incurable citrus greening disease, or Huanglongbing. Use of chlorpyrifos to treat scale insects[18] was identified as one of the most critical uses by Corteva Agriscience. While growers report the use of chlorpyrifos against scale insects over the largest area in HUC-12, usage of chlorpyrifos in HUC-03 against scale is over a much smaller area compared to ACP and citrus rust mites. Application timing and information focused on the most significant use. An analysis completed by BEAD indicates that (outside California) chlorpyrifos is only used on citrus in HUC-03 and HUC-12. Usage data suggest only one chlorpyrifos application occurs per year on average, and that most applications occur via ground equipment. The average application rate is 2.7 lb/A, while the upper bound application rate is 3.5 lb/A. Applications to treat ACP and citrus rust mite occur in early May in HUC-12, while applications targeting ACP, citrus rust mite and scales occur in early June in HUC-03.

Cotton

Chlorpyrifos is used against cotton aphid, silverleaf whitefly, and stinkbugs (various species) (**ATTACHMENT 2**). Analysis recently completed by BEAD indicates that chlorpyrifos is only used on cotton in HUC-03. Label rates for cotton are permitted at up to 1.0 lb/A three times per year. The average rate of chlorpyrifos made to cotton is 0.21 lb/A, with an upper bound application rate of 0.50 lb/A, with 99% of all application occurring via foliar ground spray. Usage data suggest that two applications of chlorpyrifos occur per year in cotton. Using the state of Georgia to represent use of chlorpyrifos on cotton in HUC-03, BEAD suggests the first application of chlorpyrifos occurs on May 20 with the second application occurring on June 30.

Soybean

Use of chlorpyrifos to treat two-spotted spider mites was identified as one of the most critical uses by Corteva Agriscience. An analysis completed by BEAD indicates that chlorpyrifos is only used on soybean

[18] Exclude California red scale (California and Arizona). California recently cancelled almost all chlorpyrifos use.

in HUC-03, -04, -05, -07, -09, -10, and -11. Application rates for two-spotted spider mites are permitted between 0.23-0.47 lb/A (Lorsban Advance Reg. No. 62719-591). This falls within the reported average use range for chlorpyrifos use on soybean. Usage data across all regions with reported use suggest only one application of chlorpyrifos occurs per year on soybean. Most applications are made by ground equipment, except in HUC-10, where about half of the applications are made by air. Generally, applications that are made to treat two-spotted spider mites occur in early to mid-July, depending on the region.

Sugar beet

Use of chlorpyrifos to treat sugar beet root maggot was identified as one of the most critical uses by Corteva Agriscience. Analysis completed by BEAD indicates that chlorpyrifos is only used on sugar beet in HUC-04, -07, -09, and -17. Applications rates for sugar beet root maggot larvae and adults are permitted between 0.23-0.94 lb/A (Lorsban Advance Reg. No. 62719-591) and 2.0 lb/A (Lorsban 15G). Average application rates range from 0.5 to 1.16 lb a.i./A with upper-bound rates ranging between 1.25-1.5 lb a.i./A. Usage data across all regions with reported use, suggest only one application occurs per year in sugar beet. Both at-plant and foliar applications are reported. Most applications are applied by ground equipment. The highest percent of application applied by air is 20% for HUC-17. Generally, applications to treat sugar beet root maggot occur in June for foliar applications. Soil applications are noted to occur earlier in the season – roughly 1.5 months.

Wheat

Use of chlorpyrifos to treat Russian wheat aphid was identified as one of the most critical uses by Corteva Agriscience. However, there are multiple species of aphids present in wheat (wheat aphid complex), and Russian wheat aphid is not necessarily the most targeted species in all states. Russian wheat aphid and other species in the wheat aphid complex can affect both spring and winter wheat. An analysis completed by BEAD indicates that chlorpyrifos is only used on spring wheat in HUC-09 and -10 and on winter wheat in HUC-09, -10, -11, and -12. Applications rates for all aphids are permitted between 0.23-0.47 lb a.i./A (Lorsban Advance Reg. No. 62719-591). Average application rates range from 0.21 to 0.44 lb a.i./A for winter wheat with upper-bound rates ranging between 0.5 to 0.75 lb a.i./A. Usage rates are similar for spring wheat. Usage data across all regions with reported use, suggest only one application occurs per year in wheat. Most applications are applied by ground equipment. The highest percent applied by air is 41% for HUC-10. Applications begin as early as April and extend through June depending on the region.

High Benefit Uses

Apple

The use of chlorpyrifos on apples is a high benefit in HUC-02, -04, -05, -06, and -17 for the control of scale insects. Chlorpyrifos applications up to 3 lb a.i./A are permitted on apples with no more than 2 lb a.i./A permitted as a dormant/delayed dormant application (no in season applications are allowed). The majority (95%) of applications are applied by ground equipment. The average application rate is 1.5 lb/A (USEPA, 2013). The maximum rate observed is 2.8 lb/A with the 90th percentile at 2.0 lb/A. Average number of applications is 1.2. This usage information is based on data provided by BEAD in 2012 and covers usage between 2006-2010 (USEPA, 2012).

Asparagus

A high benefit use of chlorpyrifos identified by BEAD is managing cutworms in asparagus in HUC-04. All applications are expected to occur via ground equipment. Application rates are permitted up to 1.5 lb a.i./A for granular applications and up to 1.0 lb a.i./A for liquid applications. Based on usage data, only one application is expected to occur each year, either once in the spring or once in the fall. Spring applications are soil directed while fall applications are foliar. The average application rate is 0.96 lb a.i./A with the maximum observed application rate of 1.0 lb a.i./A. Only about 7% of applications are made at a lower rate of 0.5 lb a.i./A.

Cherry

The use of chlorpyrifos to control borers that damage tart cherry in HUC-04 is considered a high benefit use. Single application rates on cherries are permitted at up to 4.0 lb a.i./A, with maximum annual rates of 4.5 lb a.i./A for sweet cherries and 14.5 lb a.i./A for tart cherries. The majority (98%) of applications are applied by ground equipment. The average application rate is 1.5 lb/A (USEPA, 2013). The maximum rate observed is 3.0 lb/A with the 90th percentile at 2.0 lb/A. Average number of applications is 1.1. This usage information is based on data provided by BEAD in 2012 and covers usage between 2006-2010 (USEPA, 2012).

Peach

The use of chlorpyrifos to control borers that damage peach trunks is a high benefit in the southeastern United States (HUC-02, 03, 04, and 12). Chlorpyrifos applications up to 3 lb a.i./A are permitted on peaches with no more than 2 lb a.i./A permitted as a dormant/delayed dormant application. The majority (95%) of applications are applied by ground equipment. The average application rate is 1.3 lb/A (USEPA, 2013). The maximum rate observed is 3.0 lb a.i./A with the 90th percentile at 2.0 lb/A. Average number of applications is approximately one per year. This usage information is based on data provided by BEAD in 2012 and covers usage between 2006-2010 (USEPA, 2012).

Strawberry

A critical use of chlorpyrifos identified by BEAD is to treat garden symphylans and strawberry crown moth[19] in strawberry in HUC-17, specifically in Oregon. A single application at up to 2.0 lb a.i./A is permitted with a maximum annual rate of 4.0 lb a.i./A. All applications are expected to occur via ground equipment to the soil. Only one application is expected to occur each year. The average application rate is 1.24 lb a.i./A with the maximum observed application rate of 2.0 lb a.i./A. Usage data are based on data from 2011 to 2015. Insecticide usage has not been surveyed in Oregon since 2015.

[19] http://storage.dow.com.edgesuite.net/dowagro/chlorpyrifos/Who_needs_chlorpyrifos_and_why_(by_crop).pdf accessed June 23, 2020.

APPENDIX B. Results for Average Application Rates

Results from PWC are presented in

Table 24 for both chlorpyrifos and chlorpyrifos oxon for average application rates. This table only presents results for the four 2-digit HUCs (HUC-04, -07, -09 and -17) where the upper bound EDWCs are above the 10x DWLOC. Application of PCAs indicates that only the 1-in-10 year 21-day average chlorpyrifos-oxon concentration may be greater than the 10x DWLOC in two 2-digit HUC regions (HUC-04 and -07) for average applications rates. It should be noted in using this approach, there are four regions where crop specific PCAs are greater than the all-agricultural PCA. This is due to how the misc-Ag value is calculated to account for the potential double cropping. In these situations, the use pattern specific PCAs are capped at the all-Ag PCA.

Table 24. PCA Adjusted EDWCs for Average Application Rates of Chlorpyrifos

2-digit HUC	Use Site	2-Digit HUC Maximum Use Pattern Specific PCA	Batch Run ID[a]	1-day Model EEC (cpy)	21-day Model EEC (cpy)	1-day Model EEC (cpyo)	21-day Model EEC (cpyo)	Adj 1-day EDWC (cpy)	Adj 21-day EDWC (cpy)	Adj 1-day EDWC (cpyo)	Adj 21-day (cpyo)
				µg/L							
04	Alfalfa	0.92[b]	608_4_MI-186800-22356-36	1.3	1.0	1.2	1.0	1.2	0.9	1.2	0.9
	Sugar beet		1016_4_MI-186667-22116-41	2.8	1.9	2.7	1.8	2.6	1.7	2.5	1.7
	Apple		734_4_MIcherrySTD	13.0	11.2	12.4	10.7	11.9	10.3	11.4	**9.8**
	Cherry		740_4_MIcherrySTD	13.0	11.2	12.4	10.7	11.9	10.3	11.4	**9.8**
	Peach		740_4_MIcherrySTD	9.5*	8.28*	9.1	7.9	8.8	7.5	8.3	**7.2**
	Soybean		851_4_MI-188235-22121-5	2.1	1.2	2.0	1.1	2.0	1.1	1.9	1.0
	Asparagus		739_4_MIasparagusSTD	3.6	2.1	3.4	2.0	3.3	1.9	3.1	1.8
07	Alfalfa	0.90	617_4_MO-2528577-19014-37	4.1	2.3	3.9	2.2	3.7	2.1	3.5	2.0
	Sugar beet		989_4_MN-2423043-23487-41	8.9	6.4	8.5	6.1	8.0	5.8	7.7	**5.5**
	Soybean		869_4_MN-2877271-22781-5	2.2	1.4	2.1	1.3	2.0	1.2	1.9	1.2
09	Alfalfa	0.95[c]	626_4_SD-416559-24423-36	1.1	0.9	1.0	0.9	1.1	0.8	1.0	0.8
	Sugar beet		1043_4_ND-2642948-27020-41	5.4	3.6	5.2	3.4	5.1	3.4	4.9	3.2
	Soybean		887_4_ND-2571399-26297-5	1.6	1.0	1.5	1.0	1.5	1.0	1.4	0.9
	Spring wheat		1079_4_ND-2585363-27001-23	1.4	0.9	1.3	0.9	1.3	0.8	1.3	0.8
	Winter wheat		1133_4_ND-341303-27230-24	3.4	2.3	3.2	2.2	3.2	2.1	3.1	2.0
17	Alfalfa	0.53	717_4_WA-71453-24575-36	1.3	0.9	1.2	0.9	0.7	0.5	0.6	0.4
	Sugar beet		1007_4_ID-79974-21766-41	3.7	2.5	3.5	2.4	1.9	1.3	1.8	1.3
	Apple		737_4_ORappleSTD	7.2	4.7	6.9	4.5	3.8	2.5	3.7	2.4
	Strawberry		966_4_ID-80309-21523-12	10.4	7.5	9.9	7.2	5.5	4.0	5.3	3.8

a. Batch run name is truncated (DWA_2020 was removed for reporting purposes).
b. Use pattern specific PCA is slightly higher (0.93) than all-ag PCA (0.92). Use pattern specific PCA is capped at all-ag value.
c. Use pattern specific PCA is higher (>1) than all-ag PCA (0.95). Use pattern specific PCA is capped at all-ag value.

*Average rate modeled for apples and cherries is 1.5 lb a.i./a. The upper bound rate for peach on a national level is 1.1 lb/a. Results were multiplied by 1.1/1.5 to estimated concentrations for peach.
Green shading indicates concentrations below the 10xDWLOC.
Reg shading and bold font indications concentrations above the 10x DWLOC.
Chlorpyrifos (cpy)
Chlorpyrifos-oxon (cpyo)

Examination of the full distribution of PCAs for HUC-04 and -07 (i.e., those 2-digit HUCs with average application rates resulting in EDWCs above the 10x DWLOC) indicate that there are 138 CWS watersheds where chlorpyrifos-oxon concentrations could be above the 10x DWLOC (**Table 14**).

Table 25. Full Distribution of Watershed Specific PCA-Adjusted EDWCs for Average Applications of Chlorpyrifos-oxon

2-digit HUC	Total CWS	Max 1-in-10 year 21-day (cpyo) µg/L	Critical 21-day PCA (cpyo)	No. of CWS above 21-day DWLOC (percent)
		Average Application Rates		
04	196	10.7	0.37	79 (40)
07	158	6.1	0.66	49 (31)

The prior analysis for the average application rates indicates there could be concentrations above the 10x DWLOC for HUC-04 and HUC-07. However, aggregation of the 1-in-10 year concentrations indicates that concentrations in HUC-04 are not expected to be above the 21-day 10x DWLOC. Therefore, aggregation of concentrations in only HUC-07 was completed for the average application rates.

Aggregation of the 1-in-10-year concentrations for watersheds in HUC-07 indicate that two CWS watersheds could have concentrations above the 10x DWLOC for average application rates. Results are presented in **Table 26**.

Table 26. Aggregation of 1-in-10 year PCA adjusted 21-day Average EDWCs for Average Application Rates of Chlorpyrifos-oxon

2-digit HUC	Aggregated 21-day (cpyo) µg/L	No. of CWS above 21-day DWLOC	Total CWS	Percent of CWS above 21-day DWLOC
07	4.1	2	158	1

Appendix C. Monitoring Data Analysis Technical Chapter

a. Introduction

This technical chapter is intended to supplement the drinking water assessment by providing the technical details of the analysis and interpretation of the available monitoring data considered quantitively and summarized in the drinking water assessment. Each subsequent subsection is dedicated to an individual sampling site. Depending on what analysis was done for the site each section may include: 1) site characterization based on size and landcover percentages of the National Land Cover Database for 2006 as reported in StreamCat 2) SEAWAVE-QEX analysis, 3) sampling bias factor development and 4) sampling bias factor application. For example, a summary of the available monitoring data for each site, procedures for fitting SEAWAVE-QEX, and description of the diagnostic plots from the final fit are provided for each site. In addition, developed SBFs are presented and described.

SEAWAVE-QEX Analysis

For SEAWAVE-QEX analysis, surface water monitoring sites were screened for potential use in SEAWAVE-QEX based on the minimum requirements of the model. A Microsoft Access query was used to determine which sites might be able to run in SEAWAVE-QEX (Access file is provided in **ATTACHMENT 3**). The tool searched for sites that met the minimum criteria (at least 3 years with 12 or more samples with a 25% detection frequency), which included comparing the results column with the detection limit column, as often data in the WQP are not properly identified as being detected or below the detection limit. The sites that remained were evaluated for use in SEAWAVE-QEX.

Sites that could not be successfully used in SEAWAVE-QEX are summarized in **Table 27** One site did not have accompanying flow data and two sites could not be confidently simulated by the model as model assumptions were not verified. Two additional sites were successfully run in SEAWAVE-QEX but a surface-level analysis of the streamflow data and how it is used in SEAWAVE-QEX for these sites indicated that the sites may not be appropriate to use quantitatively. Monitoring data from the 11 remaining sampling sites run in SEAWAVE-QEX were deemed acceptable for quantitative use based on goodness-of-fit criteria described in the model's Standard Operating Procedure (SOP; USEPA, 2019). The model fit was optimized for each site as needed by changing the years included in the analysis or adding a small constant to the concentration values within SEAWAVE-QEX. These sites are detailed in the following section along with the 11 sites selected for quantitative analysis.

Table 27. Summary Table of Sites Not Included in SEAWAVE-QEX Analysis

USGS Site ID	Site Name	No or limited flow data	Model assumptions not verified	Site not applicable	Comment
06800000	Maple Creek near Nickerson, NE		**X**		Estimated maximum concentration above blue boxes, large 2x SSD. Tight residuals. CTS maxed out and correlogram is too low (overestimating).
08364000	Rio Grande at El Paso, TX		**X**		Flow data not available at USGS but found data from the International Boundary and Water Commission.

USGS Site ID	Site Name	No or limited flow data	Model assumptions not verified	Site not applicable	Comment
					However, correlogram often missing from diagnostic plot at lower sampling times (e.g., 5-day).
11273500	Merced R A River Road Bridge near Newman, CA	**X**			No flow data found.
11447360	Arcade Creek near Del Paso Heights, California			**X**	Intermittently flowing site (see description below)
14201300	Zollner Creek near Mt. Angel, OR			**X**	Intermittently flowing site (see description below)
SSD standard deviation					

Sampling Bias Factor Development

Using the chemographs from the SEAWAVE-QEX analysis, short-term pesticide-specific SBFs were developed for chlorpyrifos for application to monitoring data that did not meet the SEAWAVE-QEX criteria. This was done using Python code (ncg_merg.py), a Python integrated development environment (IDE) (Spyder 3.7), and the methods described in Chapter 4 of the White Paper for the 2019 FIFRA SAP. Short-term SBFs are developed for all sites where model assumptions were satisfied for SEAWAVE-QEX (i.e., 11 sites) as data are only available to calculate SBFs for a limited number of sites.

Sampling Bias Factor Application

SBFs for 1987-2012 (all years) and 2005-2012 (post-registration review label changes) were applied based on the number of samples per year for all site-years of data from the Water Quality Portal with greater than or equal to 13 sampled per year (**Table 28**).

Table 28. Maximum Sampling Bias Factors

Sample Number	Maximum 1987-2012 Sampling Bias Factor	Maximum 2005-2012 Sampling Bias Fact	Maximum 1987-2012 Sampling Bias Factor	Maximum 2005-2012 Sampling Bias Factor
	1-day		21-day	
52+	10.9	5.3	4.0	2.4
26-51	23.3	11.9	6.1	5.2
17-25	38.5	17.8	8.4	7.3
13-16	54.8	22.2	11.5	8.9

b. Detailed Site Analysis

1. *USGS-11303500*

Site and Sampling Characterization

USGS site 11303500 (San Joaquin River near Vernalis, California) has a 13,844 mi^2 (35,855 km^2) watershed in HUC 18. The watershed for the collection site has 22% cropland along with a high percentage of natural areas (e.g., grasslands, forests, shrubs), as shown in **Figure 28.** Watershed Landcover Characteristics of Sampling Site USGS-11303500 . This sampling site is upstream of several community water systems drinking water intakes with a time of travel of less than a day to each intake, implying that the site is relevant to community water systems in the area. Additionally, the site may be representative of other agricultural areas that affect CWS, as it is downstream of many other intakes with travel times ranging from 2 to 8 days.

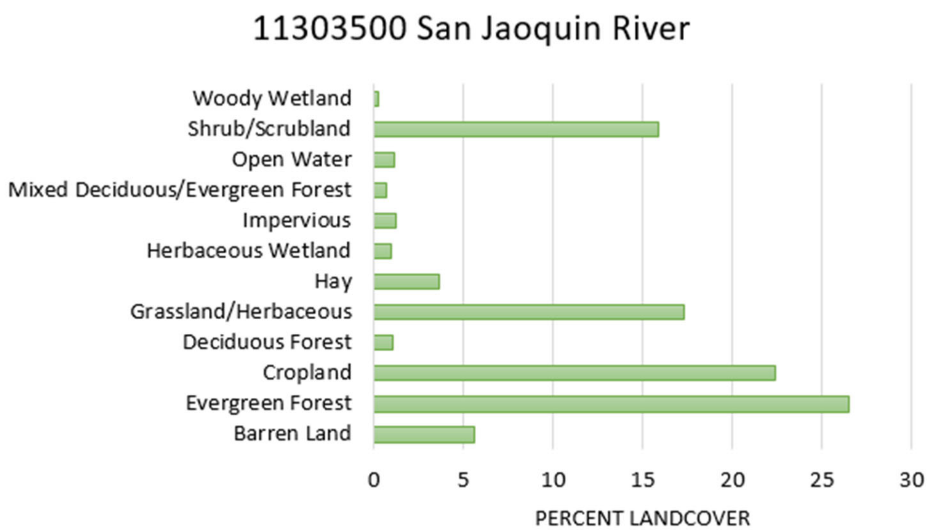

Figure 28. Watershed Landcover Characteristics of Sampling Site USGS-11303500

This site had a total of 190 chlorpyrifos detections out of 528 samples over 27 years between 1992 and 2019. Only 12 years of data have at least 12 or more samples and a detection frequency greater than 25%, as shown in **Table 29**. **Table 29** also includes information on the years simulated in SEAWAVE-QEX as well as the years SBFs were developed. SEAWAVE-QEX analysis and the developed SBFs are described in the subsections below.

Table 29. Data Summary for USGS-11303500

Year	Number of Samples Collected	Number of Detections	Detection Frequency	Years Simulated in SEAWAVE-QEX	Number of Samples Excluded by SEAWAVE-QEX[1]	Years Sampling Bias Factors Developed
1992	20	16	80%			
1993	37	23	62%			
1994	17	12	71%	✓	4	✓
1995	9	4	44%	✓	1	✓
1996	0	—	—	✓	—	✓
1997	11	6	55%	✓	0	✓
1998	12	3	25%	✓	0	✓
1999	12	1	8%	✓	0	✓
2000	31	23	74%	✓	10	✓
2001	53	31	58%	✓	14	✓
2002	22	9	41%	✓	2	✓
2003	17	7	41%	✓	0	✓
2004	8	5	63%	✓	0	✓
2005	6	1	17%	✓	0	✓
2006	8	3	38%	✓	0	✓
2007	22	9	41%	✓	0	✓
2008	22	14	64%	✓	0	✓
2009	22	0	0%	✓	0	✓
2010	22	4	18%	✓	0	✓
2011	21	7	33%	✓	0	✓
2012	25	9	36%	✓	1	✓
2013	21	0	0%			
2014	18	1	6%			
2015	23	0	0%			
2016	28	1	4%			
2017	21	0	0%			
2018	19	1	5%			
2019	1	0	0%			

Gray shading highlights sites with at least 12 samples per year and a detection frequency of 25%
[1] Samples may be excluded by SEAWAVE-QEX when samples are spaced <3 days apart (see SEAWAVE-QEX SOP).

SEAWAVE-QEX Analysis

Data for 1994-2012 were used as SEAWAVE-QEX inputs. Expanding the years to include 1992 and 1993 was explored, however, the best fit was determined to be for the period from 1994 to 2012 with default SEAWAVE-QEX parameters.

The 80% confidence bounds on the estimated maximum for each year are below 0.1 µg/L and the confidence bounds span much less than an order of magnitude. Only two years (1995 and 2004) have 80% confidence bounds that overlap with the highest measured concentration from 1994-2012 (0.05 µg/L), occurring in 2004. One other higher concentration was measured in 1993, 0.079 µg/L, a year that was not included in the final run. When running 1992-2012, there is less confidence in the normality of the residuals than when running from 1994-2012. Additionally, the high concentration in 1993 is not used by SEAWAVE-QEX due to the automatic sample spacing and higher frequency sampling occurring immediately before. The model gives a single shallow seasonal wave with a season spanning from early January to early October and few concentrations outside of the 2SSD bounds, which span less than an order of magnitude. Adjusted concentrations do not have much trend over time and have a significant (α=0.05) negative correlation with MTFA and significant positive correlation with STFA. The normalized residuals are centered on zero with one residual skewing very positive in 2004, likely corresponding with the large measured concentration in that year. The empirical correlogram 95% confidence limits overlap with the fitted exponential correlation function with a CTS of 9 days.

Table 30 summarizes the 1- and 21-day estimated concentrations from SEAWAVE-QEX for each year based on the maximum of the 99th percentile concentrations.

Table 30. Maximum of the 99th Percentile 1- and 21-day Concentrations of Chlorpyrifos at USGS-11303500

Year	1-day Conc. (µg/L)	21-day Conc. (µg/L)
1994	0.073	0.043
1995	0.047	0.030
1996	0.054	0.035
1997	0.050	0.029
1998	0.031	0.016
1999	0.031	0.018
2000	0.042	0.023
2001	0.041	0.021
2002	0.043	0.028
2003	0.037	0.022
2004	0.065	0.042
2005	0.051	0.031
2006	0.026	0.017
2007	0.041	0.021
2008	0.034	0.021
2009	0.033	0.018
2010	0.031	0.017
2011	0.025	0.016
2012	0.024	0.017

Sampling Bias Factor Development

SBFs developed for estimating the 1-day and 21-day average concentrations are shown in **Figure 29** and **Figure 30**, respectively. All the 1-day and 21-day SBFs figures have the same x- and y-axis scales to permit evaluation of the differences in magnitude of the values across sites and years. These figures show the variation in SBFs derived across the years where data are available to develop SBFs based on the number of samples collected (13-16 samples/year, 17-25 samples/year, 26-51 samples/year and 52+ samples per year). Recall, the median SBF is calculated across the 100 SEAWAVE-QEX chemographs. All SBFs associated data files are provide in **ATTACHMENT 4**.

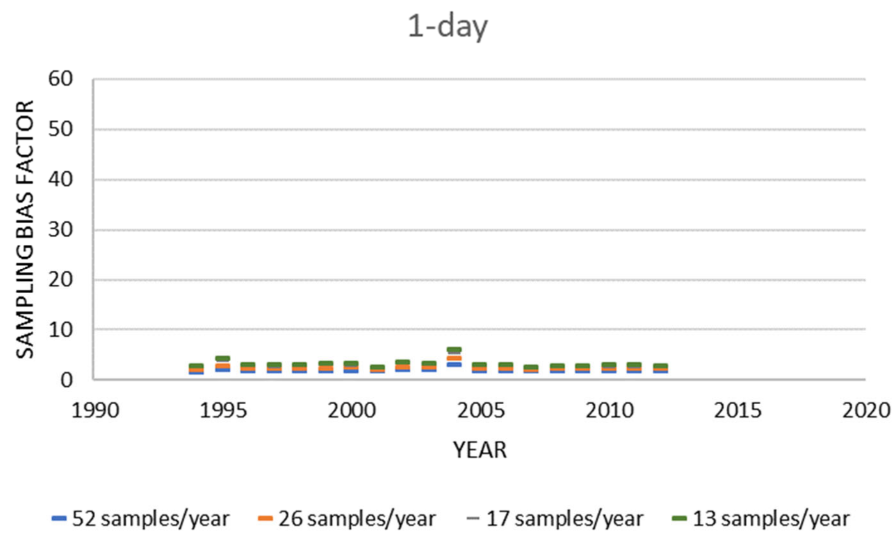

Figure 29. USGS Site 11303500: Sampling Bias Factors for Estimating the Upper Confidence Interval on the 1-day Average Concentration

Generally, the SBFs are consistent across all years for USGS-11303500 for estimating the upper confidence interval on the 1-day average concentration except for two years, 1995 and 2004. SBFs for all sample number categories are below 4 for the upper confidence interval on the 1-day average concentration. The SBFs for 1995 and 2004 are noticeably higher than other years, SBFs are roughly 6 or below for all sample categories.

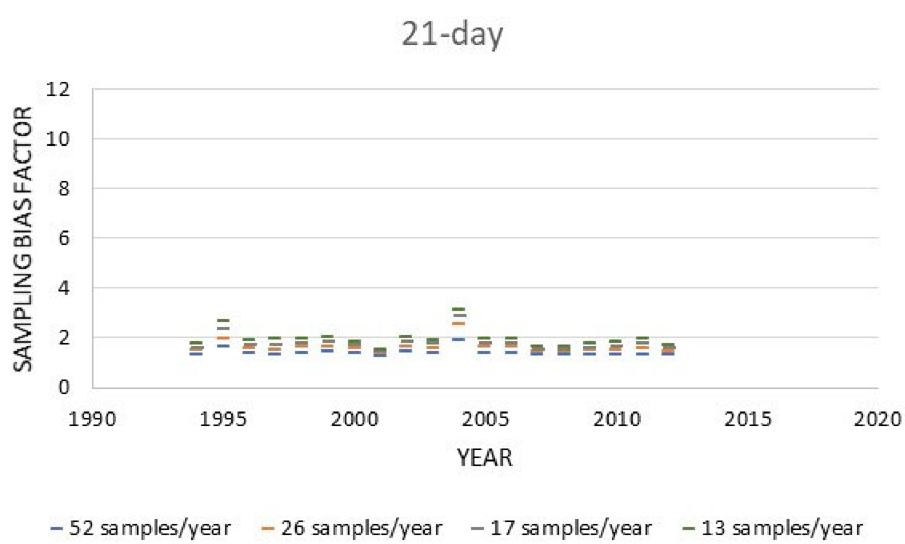

Figure 30. USGS Site 11303500: Sampling Bias Factors for Estimating the Upper Confidence Interval on the 21-day Average Concentration

A similar, consistent trend is observed for the SBFs for estimating the upper confidence interval on the 21-day average. SBFs for all sample number categories are below 2 for all years except 1995 and 2004. For these years, the maximum SBFs is below 4.

2. USGS-08057200

Site and Sampling Characterization

USGS site 08057200 (White Rk Ck at Greenville Ave, Dallas, TX) is in a 73.5 mi^2 (190 km^2) urban watershed in Hydrologic Unit Code (HUC) 12. The watershed landcover is 47% impervious surfaces and only 2% cropland (**Figure 31. Watershed Landcover Characteristics of Sampling Site USGS-08057200**). A spatial overview shows the sampling location is next to a golf course and recreational facility. The sampling location is upstream of two drinking water intakes with a 9 to 11 day time of travel from the sampling site to the intakes.

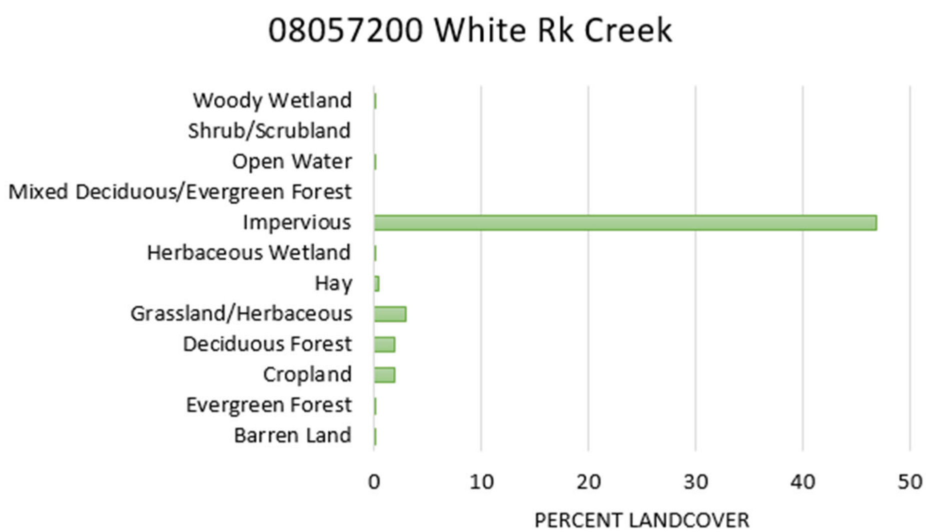

Figure 31. Watershed Landcover Characteristics of Sampling Site USGS-08057200

This site has a total of 63 chlorpyrifos detections out of 351 samples over 22 years between 1995 and 2019 (**Table 31**). Only 4 years of data (1998-2001) have at least 12 samples and a detection frequency greater than 25%, which were used as SEAWAVE-QEX inputs. **Table 31** also includes information on the years simulated in SEAWAVE-QEX as well as the years SBFs were developed. SEAWAVE-QEX analysis and the developed SBFs are described in the subsections below.

Table 31. USGS-08057200 Data Summary

Year	Number of Samples Collected	Number of Detections	Detection Frequency	Years Simulated in SEAWAVE-QEX	Number of Samples Excluded by SEAWAVE-QEX[1]	Years Sampling Bias Factors Developed
1995	7	7	100%			
1996	0	—	—			
1997	9	8	89%			
1998	17	12	71%	✓	0	✓
1999	17	9	53%	✓	1	
2000	15	12	80%	✓	6	
2001	12	4	33%	✓	0	✓
2002	24	3	13%	✓	3	
2003	18	1	6%			
2004	9	2	22%			
2005	6	1	17%			
2006	8	0	0%			
2007	16	2	13%			
2008	4	0	0%			
2009	16	0	0%			
2010	4	0	0%			
2011	16	1	6%			
2012	6	0	0%			
2013	23	0	0%			
2014	24	0	0%			
2015	24	1	4%			
2016	24	0	0%			
2017	24	0	0%			
2018	23	0	0%			
2019	5	0	0%			

Gray shading highlights sites with at least 12 samples per year and a detection frequency of 25%

[1] Samples may be excluded by SEAWAVE-QEX when samples are spaced <3 days apart (see SEAWAVE-QEX SOP).

SEAWAVE-QEX Analysis

The site has an incomplete flow record through the years that meet the minimum requirements for use in SEAWAVE-QEX (1998-2001). The discharge data for these years is shown in black in **Figure 32**, which has short gaps in the flow, particularly in the year 2000. There was a drought in the summer of 2000 which may influence the amount of sampling done. The impact of missing days of flow results from the MTFA in SEAWAVE-QEX. For a given time step, the MTFA is calculated using covariate data from the preceding 30 days, so that a day of missing flow can result in many days of missing MTFA calculations and therefore no concentration output. The days for which there is no SEAWAVE-QEX output is shown in orange in **Figure 32**.

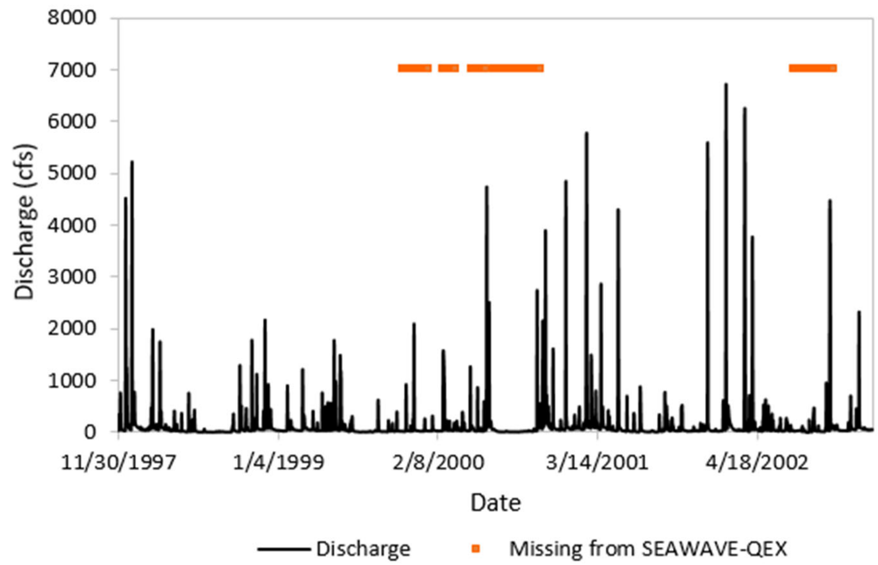

Figure 32. Discharge and Gage Height (unadjusted) Data for USGS-08057200 from 1998-2002

Using SEAWAVE-QEX on only the years 1998-2001 resulted in a poor empirical correlogram at short sampling intervals (i.e., the 5-day bar is absent from the diagnostic plot). An additional run was attempted by including the year 2002 with 13% detection. Although it does not meet the detection frequency criteria, the addition of the year 2002 resulted in a better model fit and allowed for the site to be included. The best fit was determined to be from 1998 to 2002 without modification of the default SEAWAVE-QEX parameters. The highest measured concentration at this site was 0.0549 µg/L in 2000.

The resulting diagnostic plots show 80% confidence bounds on the estimated maximum for each year well below 0.1 µg/L spanning less than an order of magnitude (**Figure 33**). There is a single a shallow wave with a season late September to late June with a short "off-season" of lower measured concentrations. All but one measured concentration fall within the 2x seasonal standard deviations (2SSD) bounds on the model (i.e., the data fall between the dashed lines on **Figure 34**), which span much less than an order of magnitude in size. There is a significant (α=0.05), slightly negative correlation of adjusted concentration with MTFA and a weakly positive correlation with STFA. The adjusted concentrations trend slightly downward over time and the normalized residuals center around zero. The empirical correlogram 95% confidence limits overlap with the fitted exponential correlation function with a CTS of 4.2 days. All other model assumptions are satisfied (all diagnostic plots are provided in **ATTACHMENT 4**).

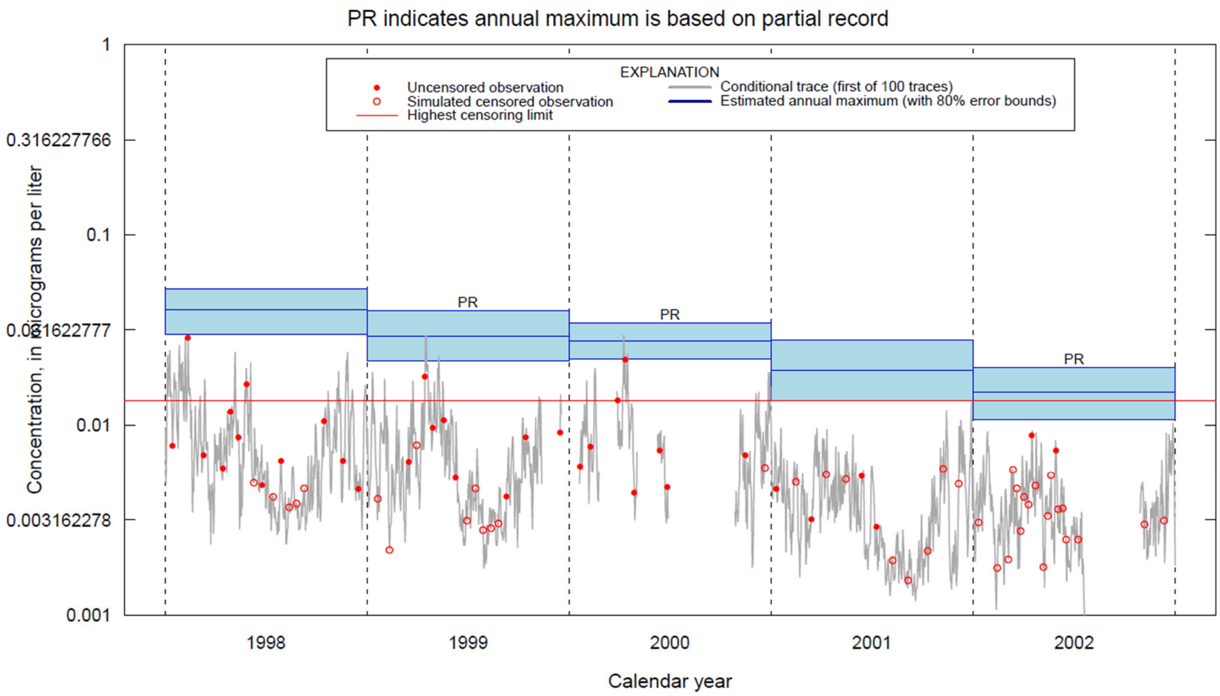

Figure 33. SEAWAVE-QEX Run Summary Diagnostic Plot for USGS-08057200

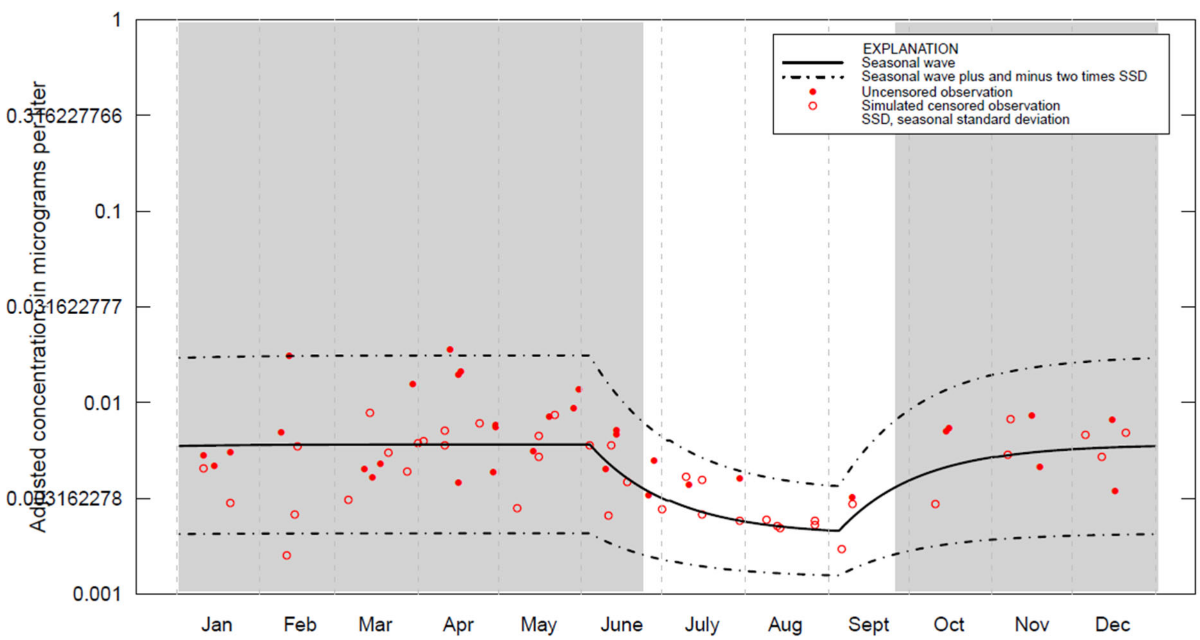

Figure 34. SEAWAVE-QEX Seasonal Wave Model for USGS-08057200 (Diagnostic Plot 2)

The resulting chemographs from this model were used to describe the estimated concentrations at site 08057200 by calculating the maximum of the 99th percentile 1- and 21-day concentrations. **Table 32** summarizes the 1- and 21-day estimated concentrations from SEAWAVE-QEX for each year based on the maximum of the 99th percentile concentrations.

Table 32. Maximum of the 99th Percentile 1- and 21-day Concentrations of Chlorpyrifos at USGS-08057200

Year	1-day Conc. (µg/L)	21-day Conc. (µg/L)
1998	0.06	0.03
1999	0.03	0.02
2000	0.03	0.03
2001	0.03	0.02
2002	0.02	0.01

Sampling Bias Factor Development

SBFs developed for estimating the 1-day and 21-day average concentrations are shown in **Figure 35** and **Figure 36**, respectively. Again, these figures show median SBFs across SEAWAVE-QEX chemographs for each site year and sample number category. Only two years of the SEAWAVE-QEX output could be used for calculating SBFs due to periods of missing flow. Years with a partial flow record cannot produce daily concentration estimates for periods of the year when the flow is missing. More than two years were simulated in SEAWAVE-QEX; however, due to missing flow in the data (-9 reported in output files for those days with missing flow) the additional years were excluded from the SBF development.

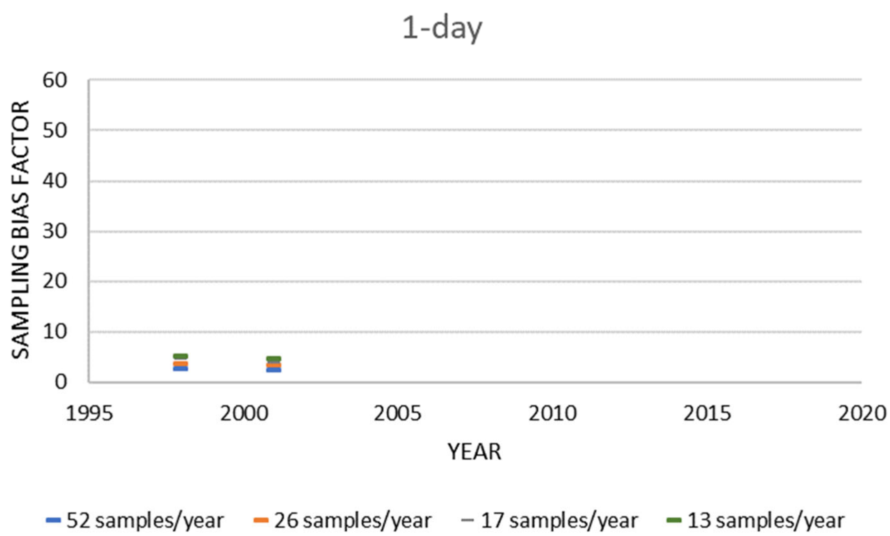

Figure 35. USGS Site 08057200: Sampling Bias Factors for Estimating the Upper Confidence Interval on the 1-day Average Concentration

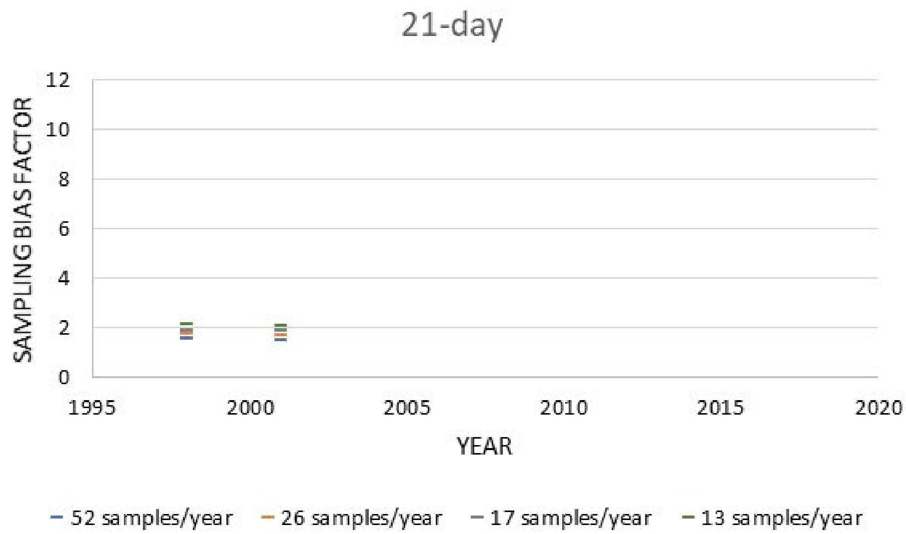

Figure 36. USGS Site 08057200: Sampling Bias Factors for Estimating the Upper Confidence Interval on the 21-day Average Concentration

The SBFs are roughly equal for the two years where SBFs could be developed. SBFs for all sample number category are below 6 for estimating the upper confidence interval on the 1-day average and are roughly 2 or below for estimating the upper confidence interval on the 21-day average.

3. USGS-01654000

Site and Sampling Characterization

USGS site 01654000 (Accotink Creek near Annandale, VA) falls within a 24 mi^2 (62.3 km^2) urban watershed in HUC 02 with land use acreage comprising of <1% cropland, 23% impervious surfaces, and 23% deciduous forest (**Figure 37.** Watershed Landcover Characteristics of Sampling Site USGS-01654000). Although this watershed does not supply source drinking water, it is possible that this site is representative of other areas relevant to drinking water intakes that have similar watershed characteristics and chlorpyrifos use.

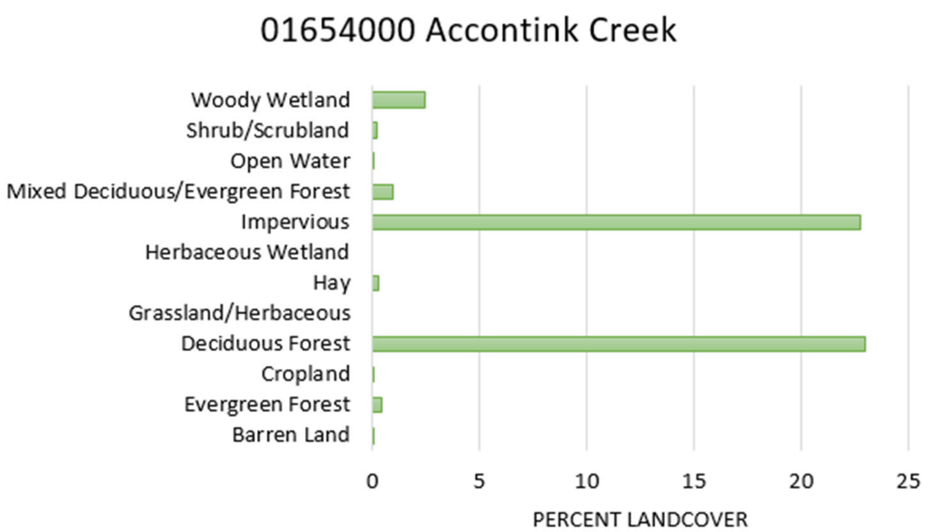

Figure 37. Watershed Landcover Characteristics of Sampling Site USGS-01654000

The site has a total of 37 chlorpyrifos detections out of 99 samples over 7 years between 1994 and 2014 (**Table 33**). Only 4 years of data have 12 or more samples and a detection frequency greater than 25%. **Table 33** also includes information on the years simulated in SEAWAVE-QEX as well as the years SBFs were developed. SEAWAVE-QEX analysis and the developed SBFs are described in the subsections below.

Table 33. USGS-01654000 Data Summary

Year	Number of Samples Collected	Number of Detections	Detection Frequency	Years Simulated in SEAWAVE-QEX	Number of Samples Excluded by SEAWAVE-QEX[1]	Years Sampling Bias Factors Developed
1994	25	12	48%	✓	2	✓
1995	0	—	—	✓		✓
1996	0	—	—	✓		✓
1997	15	9	60%	✓	0	✓
1998	11	5	45%	✓	0	✓
1999	19	6	32%	✓	0	✓
2000	13	5	38%	✓	0	✓
2001	6	0	0%			
2014[2]	10	0	0%			

Gray shading highlights sites with at least 12 samples per year and a detection frequency of 25%
[1] Samples may be excluded by SEAWAVE-QEX when samples are spaced <3 days apart (see SEAWAVE-QEX SOP).
[2] Years 2002-2013 without monitoring data excluded for brevity.

SEAWAVE-QEX Analysis

Several iterations of SEAWAVE-QEX were attempted to find the best fit to the data, such as including only the years 1997-2000 or 1994-1999. Ultimately, the best fit was determined to be for the period

from 1994 to 2000 without modification of the default SEAWAVE-QEX parameters (e.g., no constant added). The maximum measured concentration at this site is 0.041 µg/L in 1994.
The 80% confidence bounds on the estimated maximum for each year (blue boxes on first diagnostic plot) are below 0.1 µg/L and the confidence bounds span much less than an order of magnitude. SEAWAVE-QEX fit a shallow, two-season wave to the data, likely due to sporadic use of chlorpyrifos at various times and locations within the watershed over the period examined. The 2SSD bounds are not large (i.e., less than an order of magnitude) with most data falling within the 2SSD bounds. The first season has a slightly sharper peak than the second, with seasons running mid-April through late June and the end of August through early December. There is a significant (α=0.05) positive correlation of adjusted concentration with MTFA and weakly positive correlation with STFA. There is an overall downward trend of concentrations from 1994 to 2000 and residuals are centered on zero. The empirical correlogram 95% confidence limits overlap with the fitted exponential correlation function at time intervals shorter than the average (to the left of the red line) with a CTS of 4.7 days.

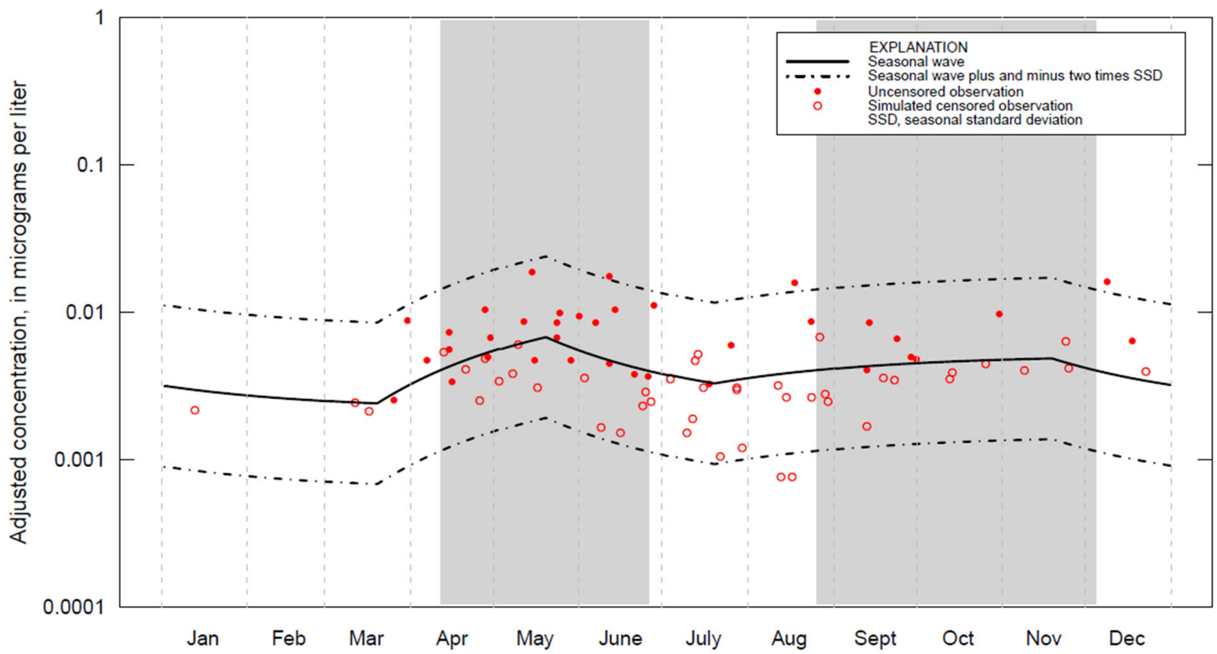

Figure 38. SEAWAVE-QEX Seasonal Wave Fit to Data for USGS-01654000

Based on the resulting estimated chemographs, concentrations of chlorpyrifos at this site are expected to be below well 1 µg/L. **Table 34** summarizes the 1- and 21-day estimated concentrations from SEAWAVE-QEX for each year based on the maximum of the 99th percentile concentrations. These do not range substantially higher than the highest measured concentration of 0.041 µg/L.

Table 34. Maximum of the 99th Percentile 1- and 21-day Concentrations of Chlorpyrifos at USGS-01654000

Year	1-day Conc. (µg/L)	21-day Conc. (µg/L)
1994	0.060	0.033
1995	0.045	0.036
1996	0.048	0.033

1997	0.033	0.016
1998	0.042	0.027
1999	0.026	0.011
2000	0.027	0.014

Sampling Bias Factor Development

SBFs developed for estimating the 1-day and 21-day average concentrations are shown in **Figure 39** and **Figure 40**, respectively. Again, these figures show median SBFs across SEAWAVE-QEX chemographs for each site year and sample number category.

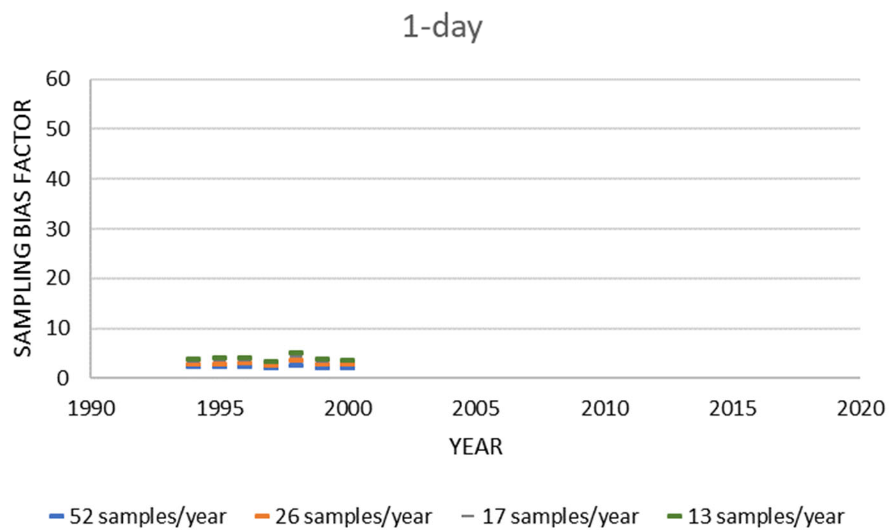

Figure 39. USGS Site 01654000: Sampling Bias Factors for Estimating the Upper Confidence Interval on the 1-day Average Concentration

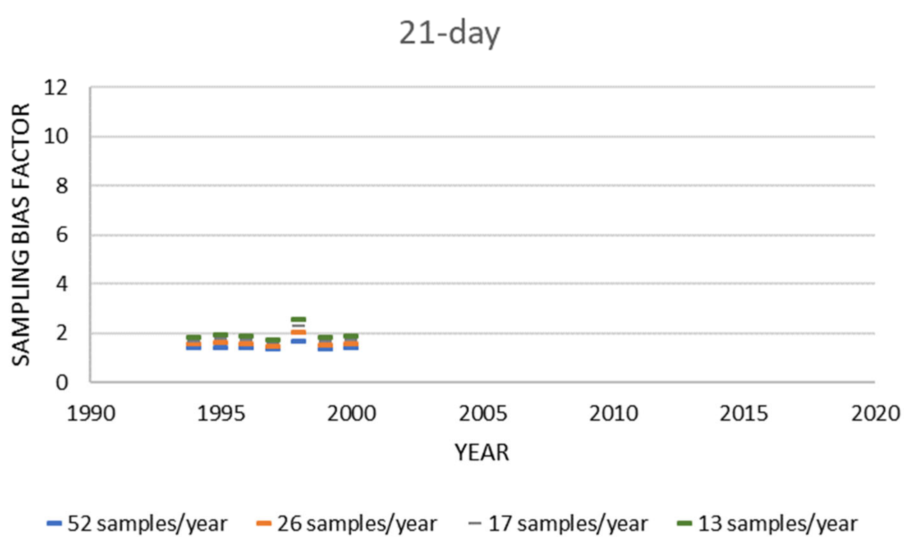

Figure 40. USGS Site 01654000: Sampling Bias Factors for Estimating the Upper Confidence Interval on the 21-day Average Concentration

Generally, the SBFs are consistent across all years for USGS-0165400 for estimating the upper confidence interval on the 1- and 21-day average concentration. One year, 1998, results in notably higher SBFs; however, all SBFs are roughly 5 or below for all sample number categories for calculating the 1-day average or below 3 for the 21-day average.

4. USGS-02174250

Site and Sampling Characterization

USGS site 02174250 (Cow Castle Creek near Bowman, SC) falls within a 24.9 mi^2 (64.4 km^2) watershed in HUC 03. The sampling location is in a watershed with 26% cropland and a high percentage of other natural areas (e.g., woody wetland, shrub, hay, evergreen forest) as described in **Figure 41.** Watershed Landcover Characteristics of Sampling Site USGS-02174250 . The sampling location is upstream of a drinking water intake with a 2-day time of travel between the sampling site and the intake. This indicates that the site is relevant for source drinking water.

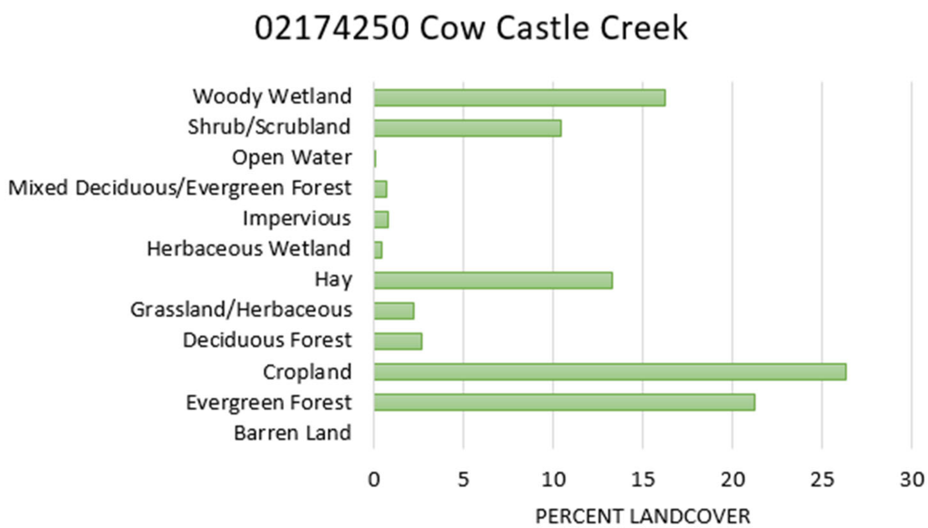

Figure 41. Watershed Landcover Characteristics of Sampling Site USGS-02174250

The site has a total of 83 chlorpyrifos detections out of 162 samples over 14 years of data between 1996 and 2012 (**Table 35**). Five of these years have 12 or more samples and a detection frequency greater than 25%. **Table 35** also includes information on the years simulated in SEAWAVE-QEX as well as the years SBFs were developed. SEAWAVE-QEX analysis and the developed SBFs are described in the subsections below.

Table 35. USGS-02174250 Data Summary

Year	Number of Samples Collected	Number of Detections	Detection Frequency	Years Simulated in SEAWAVE-QEX	Number of Samples Excluded by SEAWAVE-QEX[1]	Years Sampling Bias Factors Developed
1996	38	31	82%	✓	0	✓
1997	0	—	—	✓	0	✓
1998	1	1	100%	✓	0	✓
1999	15	10	67%	✓	0	✓
2000	17	10	59%	✓	0	✓
2001	10	6	60%	✓	0	✓
2002	9	2	22%	✓	0	✓
2003	7	2	29%	✓	0	✓
2004	8	2	25%	✓	0	✓
2005	8	5	63%	✓	0	✓
2006	14	5	36%	✓	0	✓
2007	3	1	33%	✓	0	✓
2008	14	8	57%	✓	0	✓
2009	0	—	—			
2010	0	—	—			
2011	4	0	0%			
2012	14	0	0%			

Gray shading highlights sites with at least 12 samples per year and a detection frequency of 25%
[1] Samples may be excluded by SEAWAVE-QEX when samples are spaced <3 days apart (see SEAWAVE-QEX SOP).

SEAWAVE-QEX Analysis

Several cuts of the data were attempted in SEAWAVE-QEX as well as adding a small constant (e.g., a fraction of the LOD of 0.004). This included the following splices of the data based on the diagnostic plots of the full run: 1996-2008 (with and without addition of 0.0012 or 0.0016), 1999-2006, 1996-2000, 2000-2008, 1996-2006. The best fit was determined to be for the period from 1996 to 2008 with the addition of a small constant, 0.0012, which improved the fit of the empirical correlogram.

The 80% confidence bounds on the estimated maximum for each year (blue boxes on first diagnostic plot) span less than an order of magnitude. The highest measured concentration occurs in 2005 (0.338 µg/L); the 80% confidence bounds on the estimated maximum for all other years falls below this value (**Figure 42**). The model shows a single, very shallow seasonal wave from early December to early March, with most data falling within the 2SSD bounds and several outliers of higher concentrations from July to September (i.e., outside of the 2SSD bounds). There is a significant (α=0.05) positive correlation of adjusted concentration with MTFA and STFA. There is an overall downward trend of concentrations from and residuals are centered on zero. The empirical correlogram 95% confidence limits overlap with the fitted exponential correlation function at time intervals shorter than the average (to the left of the red line) with a CTS of 20.5 days.

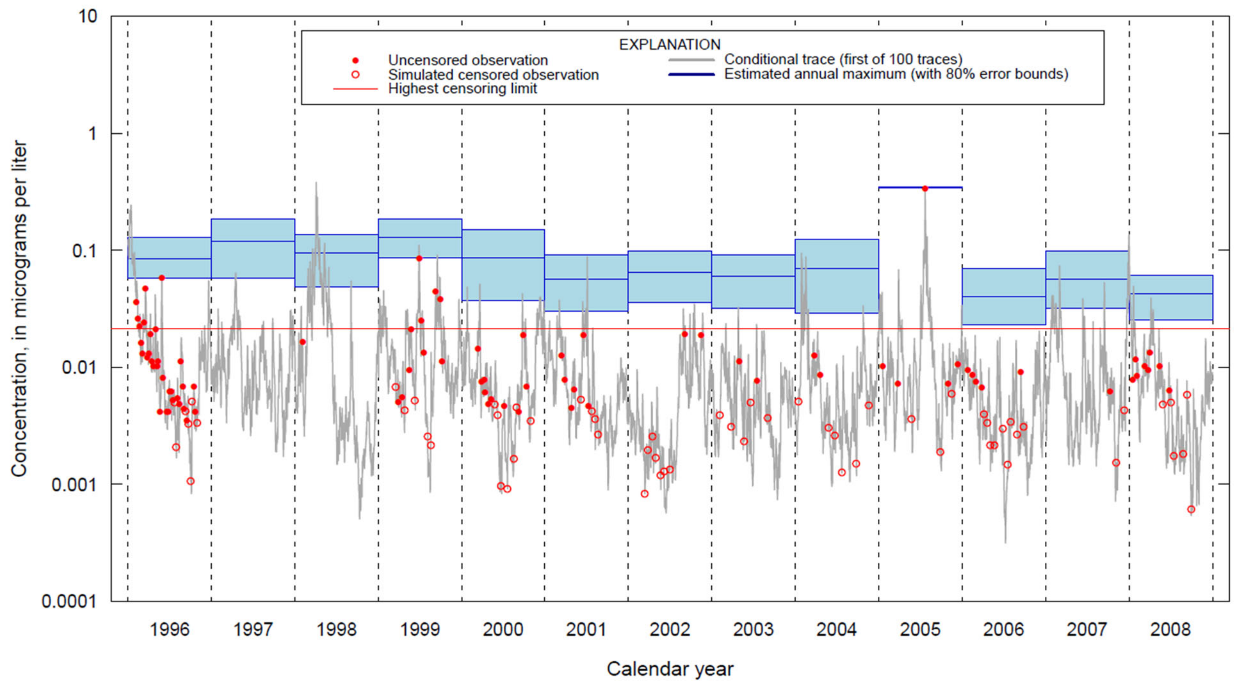

Figure 42. SEAWAVE-QEX Run Summary Diagnostic Plot for USGS-02174250

Table 36 summarizes the 1- and 21-day estimated concentrations from SEAWAVE-QEX for each year based on the maximum of the 99th percentile concentrations. From this table, choosing the maximum of the 99th percentile 1-day concentration ranges from 0.09-0.5 µg/L, encompassing the highest measured concentration from 2005 (0.338 µg/L) while accounting for uncertainty in infrequent sampling where the peak concentration might be higher than the highest measured.

Table 36. Maximum of the 99th Percentile 1- and 21-day Concentrations of Chlorpyrifos at USGS-02174250

Year	1-day Conc. (µg/L)	21-day Conc. (µg/L)
1996	0.22	0.14
1997	0.50	0.23
1998	0.33	0.15
1999	0.17	0.12
2000	0.18	0.12
2001	0.13	0.06
2002	0.09	0.06
2003	0.12	0.06
2004	0.19	0.15
2005	0.37	0.25
2006	0.09	0.07
2007	0.11	0.08
2008	0.10	0.06

Sampling Bias Factor Development

SBFs developed for estimating the 1-day and 21-day average concentrations are shown in **Figure 43** and **Figure 44**, respectively. These figures show the median SBFs across SEAWAVE-QEX chemographs for each site year and sample number category.

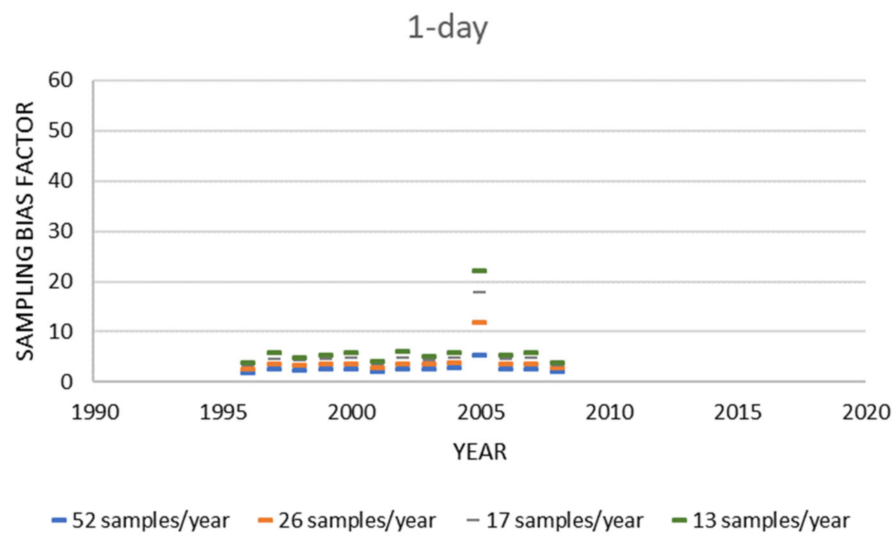

Figure 43. USGS Site 02174250: Sampling Bias Factors for Estimating the Upper Confidence Interval on the 1-day Average Concentration

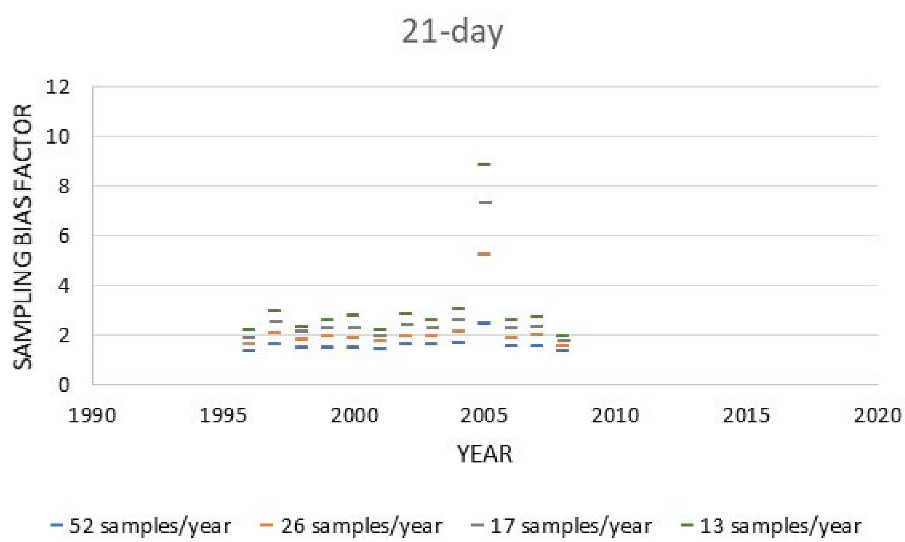

Figure 44. USGS Site 02174250: Sampling Bias Factors for Estimating the Upper Confidence Interval on the 21-day Average Concentration

Generally, the SBFs are consistent across all years for USGS-02174250 for estimating the upper confidence interval on the 1- and 21-day average concentration except for one year, 2005, which are much higher than for other years. Investigation of these higher SBFs reveal that the 2005 SBFs are driven by a measured concentration. This introduces uncertainty in the other years of data where peak occurrence concentrations may have gone without being measured. Furthermore, since the other years have SBFs in the range of other sampling sites derived for other sites, it is possible that peak occurrence concentration may have gone undetected for other sites that would have resulted in generation of higher SBFs.

5. USGS-03353637

Site and Sampling Characterization

USGS site 03353637 (Little Buck Creek near Indianapolis, IN) falls within a 19.5 mi^2 (50.6 km^2) urban watershed in HUC 05, comprising of 6% cropland and 25% impervious surfaces (**Figure 45.** Watershed Landcover Characteristics of Sampling Site USGS-03353637). The sampling location is upstream of several community water systems with intakes on the Ohio River. The time of travel between the sampling site on Little Buck Creek and the intakes range from 12-14 days.

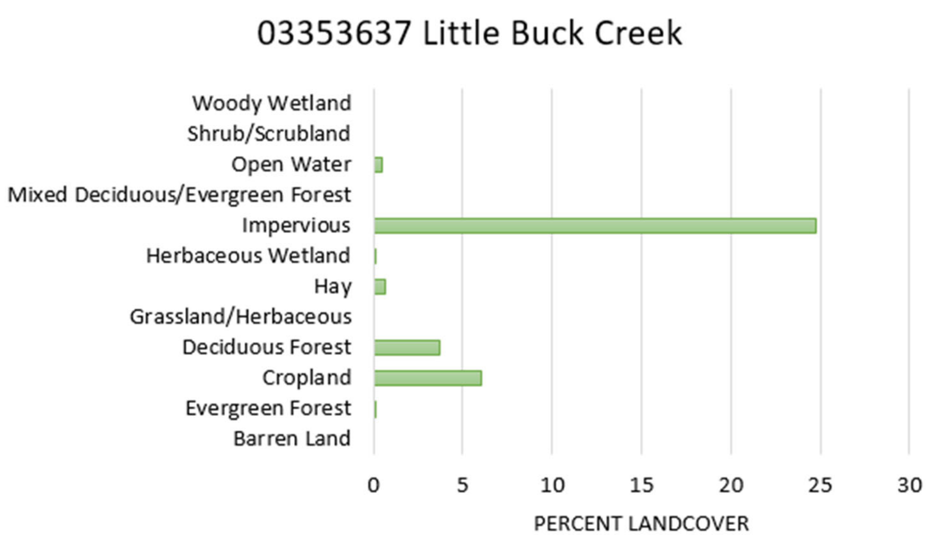

Figure 45. Watershed Landcover Characteristics of Sampling Site USGS-03353637

This site had a total of 96 detections out of 223 samples over 13 years between 1992 and 2004. Only 4 years of data have 12 or more samples and a detection frequency greater than 25% as shown in **Table 37**. **Table 37** also includes information on the years simulated in SEAWAVE-QEX as well as the years SBFs were developed. SEAWAVE-QEX analysis and the developed SBFs are described in the subsections below.

Table 37. USGS-03353637 Data Summary

Year	Number of Samples Collected	Number of Detections	Detection Frequency	Years Simulated in SEAWAVE-QEX	Number of Samples Excluded by SEAWAVE-QEX[1]	Years Sampling Bias Factors Developed
1992	49	42	86%	✓	19	✓
1993	32	24	75%	✓	3	✓
1994	14	5	36%	✓	0	✓
1995	11	6	55%	✓	0	✓
1996	13	6	46%	✓	0	✓
1997	9	5	56%			
1998	11	2	18%			
1999	8	0	0%			
2000	13	2	15%			
2001	20	3	15%			
2002	22	1	5%			
2003	14	0	0%			
2004	7	0	0%			

Gray shading highlights sites with at least 12 samples per year and a detection frequency of 25%
[1] Samples may be excluded by SEAWAVE-QEX when samples are spaced <3 days apart (see SEAWAVE-QEX SOP).

SEAWAVE-QEX Analysis

Data for 1992-1996 were input into SEAWAVE-QEX. Other subsets of years were explored (i.e., 1992-1994, 1993-1996) and data for 1992 to 1996 had the best model fit. As seen in **Table 37**, SEAWAVE-QEX excluded a number of samples in 1992 due to the temporal intensity of sampling (see **Figure 46**).

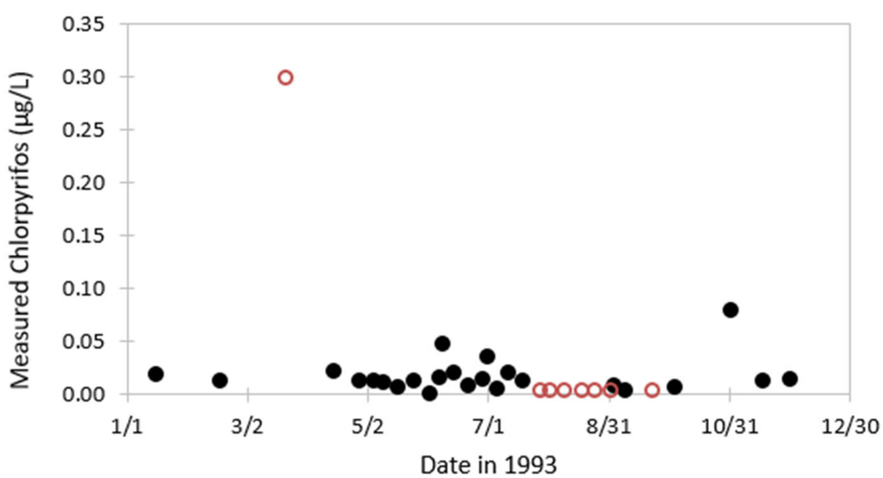

Figure 46. Sampling Intensity in 1993 of Measured Concentrations Above (black) and Below (red) the LOD

The final selected model had 80% confidence bounds on the estimated maximum for each year spanning less than an order of magnitude. The highest measured concentration occurs in 1996 (0.11 µg/L) which is encompassed by the 80% confidence bounds on the estimated maximum for several years, indicating that the model estimated concentrations at and above this concentration. There was a shallow "inverse" seasonal wave with 2SSDs of less than one order of magnitude. This means that SEAWAVE-QEX fit a very long, flat seasonal wave (from mid-October to early July), with a period of lower concentrations in other months (**Figure 47**). While most of the measured observations fall within the 2SSD bounds, it is unclear that concentrations are substantially lower outside of the season. The low seasonality of concentrations combined with the high amount of impervious land cover at this site suggest that the measured concentrations may have resulted from residential applications.

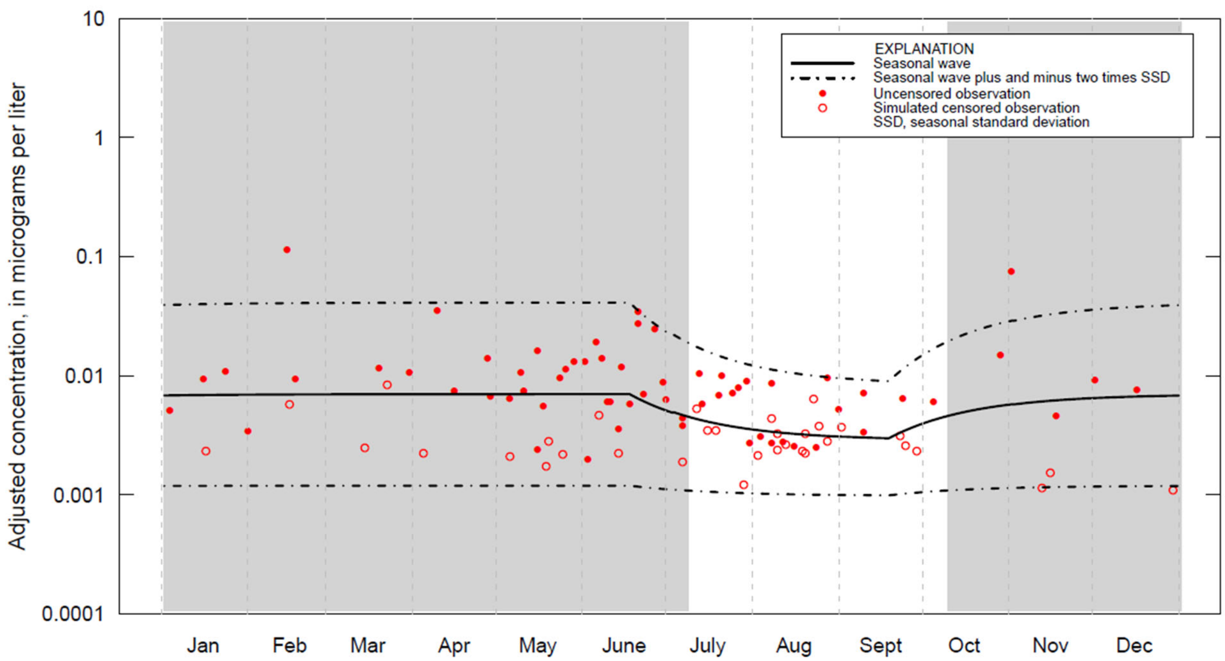

Figure 47. SEAWAVE-QEX Seasonal Wave for USGS-03353637

There is a significant (α=0.05) positive correlation of adjusted concentration with MTFA and STFA. There is an overall downward trend of concentrations from and residuals are mostly centered on zero with a slightly positive skew. The empirical correlogram 95% confidence limits overlap with the fitted exponential correlation function at time intervals shorter than the average (to the left of the red line) with a CTS of 3.6 days. **Table 38** summarizes the 1- and 21-day estimated concentrations from SEAWAVE-QEX for each year based on the maximum of the 99th percentile concentrations.

Table 38. Maximum of the 99th Percentile 1- and 21-day Concentrations of Chlorpyrifos at USGS-03353637

Year	1-day Conc. (µg/L)	21-day Conc. (µg/L)
1992	0.152	0.077
1993	0.244	0.107
1994	0.152	0.073
1995	0.134	0.046
1996	0.147	0.075

Sampling Bias Factor Development

SBFs developed for estimating the 1-day and 21-day average concentrations are shown **Figure 48** and **Figure 49**, respectively. These figures show the median SBFs across SEAWAVE-QEX chemographs for each site year and sample number category.

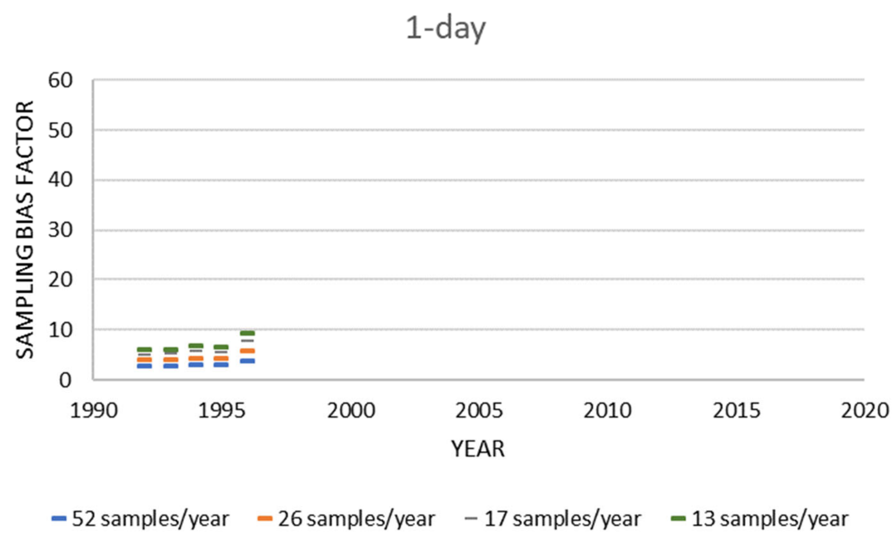

Figure 48. USGS Site 03353637: Sampling Bias Factors for Estimating the Upper Confidence Interval on the 1-day Average Concentration

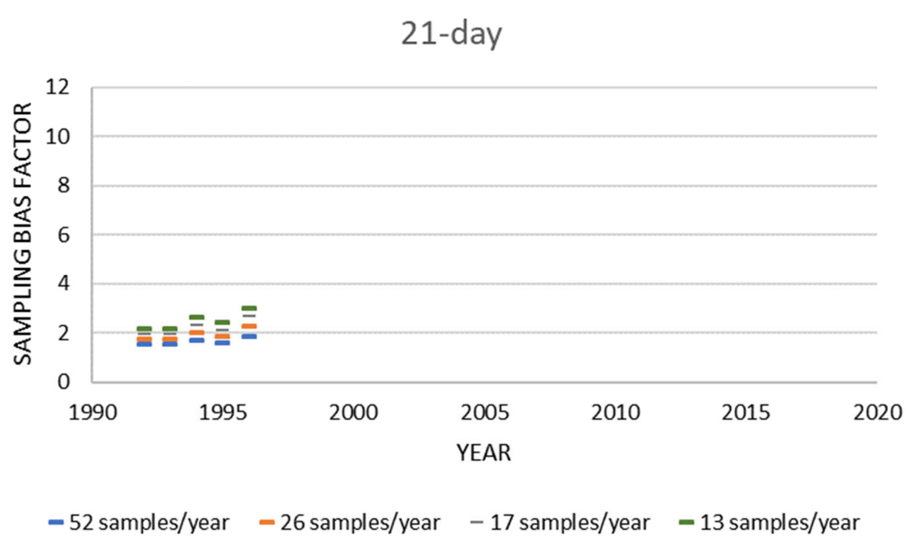

Figure 49. USGS Site 03353637: Sampling Bias Factors for Estimating the Upper Confidence Interval on the 21-day Average Concentration

The SBFs are consistent across 4 of the 5 years. The 1996 SBFs are higher than for other years. In general, SBFs for this site are consistently higher for 1-day SBFs when compared to other sites; however, 21-day SBFs calculated for this site are consistent with other sites. SBFs for all sample number categories are below 10 for estimating the upper confidence interval on the 1-day average concentration and below 4 for estimating the upper confidence interval on the 21-day average concentration.

6. USGS-14211720

Site and Sampling Characterization

USGS site 14211720 (Willamette River at Portland, OR) is in a 11,167 mi^2 (28,922 km^2) watershed in HUC 17. The watershed is 8% cropland with a high percentage of evergreen forest (49%). The sampling location is upstream of a drinking water intake. The time of travel between the sampling site and the intake is less than a day, making the site relevant for drinking water.

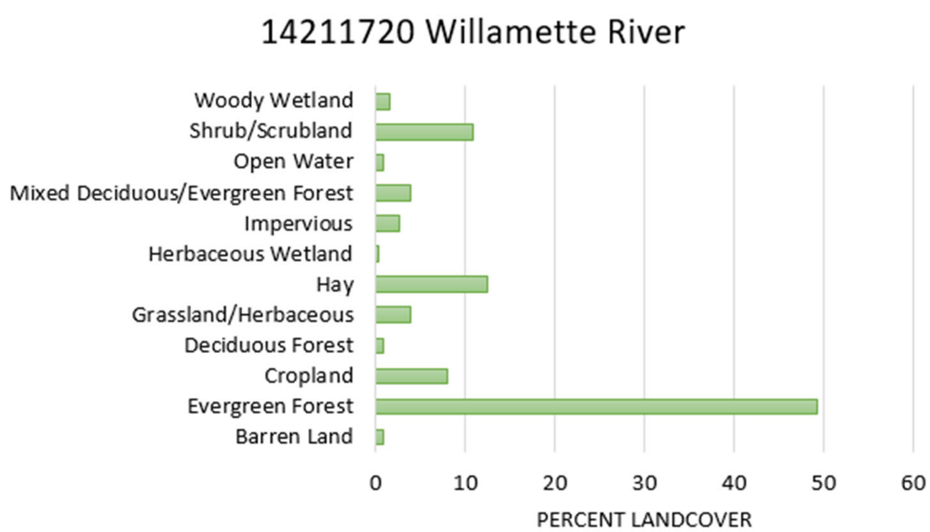

Figure 50. Watershed Landcover Characteristics of Sampling Site USGS-14211720

This site had a total of 69 detections out of 392 samples over 27 years between 1993 and 2019. Only 5 years of data have 12 or more samples and a detection frequency greater than 25% as shown in **Table 39**. **Table 39** also includes information on the years simulated in SEAWAVE-QEX as well as the years SBFs were developed. SEAWAVE-QEX analysis and the developed SBFs are described in the subsections below.

Table 39. USGS-14211720 Data Summary

Year	Number of Samples Collected	Number of Detections	Detection Frequency	Years Simulated in SEAWAVE-QEX	Number of Samples Excluded by SEAWAVE-QEX[1]	Years Sampling Bias Factors Developed
1993	3	0	0%			
1994	12	1	8%			
1995	8	1	13%			
1996	9	5	56%			
1997	17	12	71%	✓	1	✓
1998	13	7	54%	✓	0	✓
1999	15	4	27%	✓	0	✓
2000	13	6	46%	✓	0	✓
2001	14	0	0%	✓	0	✓
2002	16	1	6%	✓	0	✓
2003	13	1	8%	✓	0	✓
2004	15	0	0%	✓	0	✓
2005	9	2	22%	✓	0	✓
2006	9	2	22%	✓	0	✓
2007	19	6	32%	✓	0	✓
2008	18	3	17%			
2009	20	0	0%			
2010	19	4	21%			
2011	19	3	16%			
2012	19	4	21%			
2013	18	0	0%			
2014	18	0	0%			
2015	17	1	6%			
2016	18	4	22%			
2017	19	2	11%			
2018	18	0	0%			
2019	4	0	0%			

Gray shading highlights sites with at least 12 samples per year and a detection frequency of 25%
[1] Samples may be excluded by SEAWAVE-QEX when samples are spaced <3 days apart (see SEAWAVE-QEX SOP).

SEAWAVE-QEX Analysis

Data encompassing the 5 years of data meeting the SEAWAVE-QEX criteria were used in modeling (i.e., 1997-2007). Another subset of years was explored (i.e., 1997-2000) but did not have an acceptable model fit. The years 1997-2007 gave an acceptable model fit and included the most years of measured data possible.

The annual estimated maximum concentrations (with 80% confidence bounds) generated are well below 0.1 µg/L and are all less than 0.03 µg/L. The model produces a single flat wave with most data within 2SSD bounds, which suggests that there is similar use throughout the year with a period of no use (off-season) from late June to late September (**Figure 51**). Adjusted concentration has a weakly positive correlation with MTFA and significantly positive correlation with STFA, and concentrations increase slightly between 1997-2007. Normalized residuals are centered on zero both within years and across years. The 95% confidence limits on the empirical correlogram overlaps with the fitted exponential correlation function at time intervals less than the average with a CTS of 11.7 days.

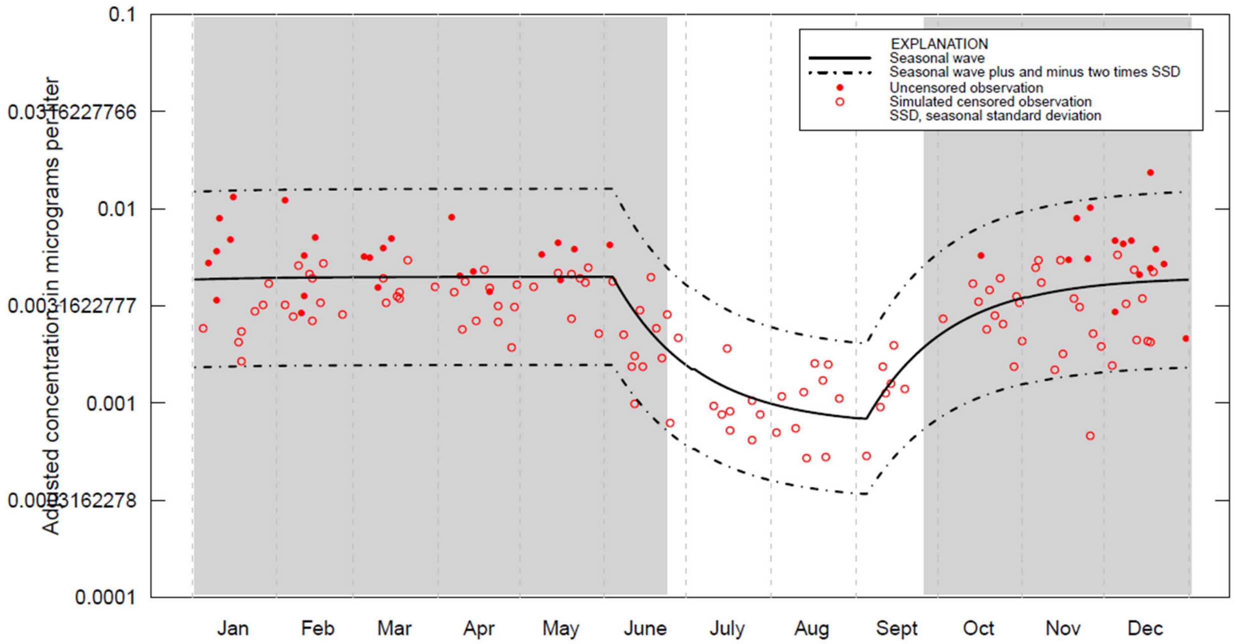

Figure 51. SEAWAVE-QEX Seasonal Wave for USGS-14211720

Table 40 summarizes the 1- and 21-day estimated concentrations from SEAWAVE-QEX for each year based on the maximum of the 99th percentile concentrations.

Table 40. Maximum of the 99th Percentile 1- and 21-day Concentrations of Chlorpyrifos at USGS-14211720

Year	1-day Conc. (µg/L)	21-day Conc. (µg/L)
1997	0.018	0.012
1998	0.015	0.011
1999	0.020	0.012
2000	0.020	0.015
2001	0.024	0.015
2002	0.019	0.012
2003	0.027	0.019
2004	0.021	0.011
2005	0.029	0.017
2006	0.027	0.019
2007	0.027	0.015

Sampling Bias Factor Development

SBFs developed for estimating the 1-day and 21-day average concentrations are shown **Figure 52** and **Figure 53**, respectively. These figures show the median SBFs across SEAWAVE-QEX chemographs for each site year and sample number category.

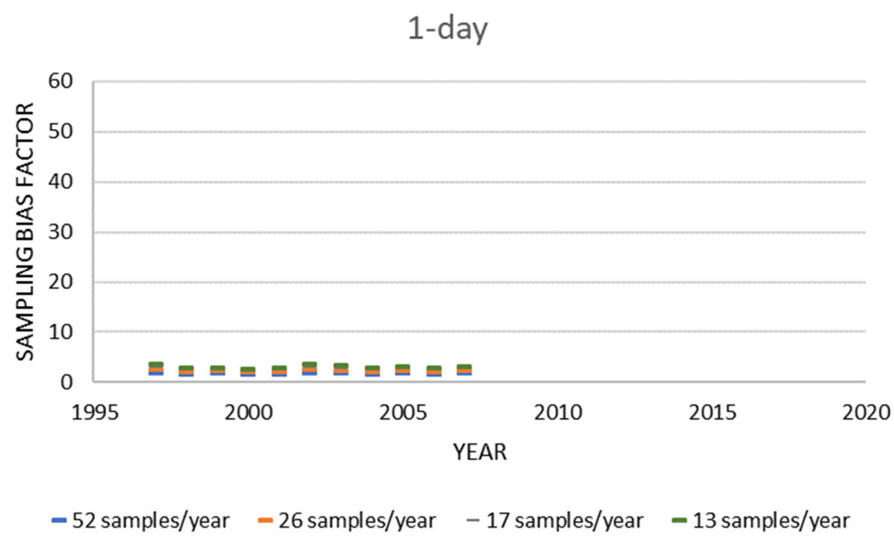

Figure 52. USGS Site 014211720: Sampling Bias Factors for Estimating the Upper Confidence Interval on the 1-day Average Concentration

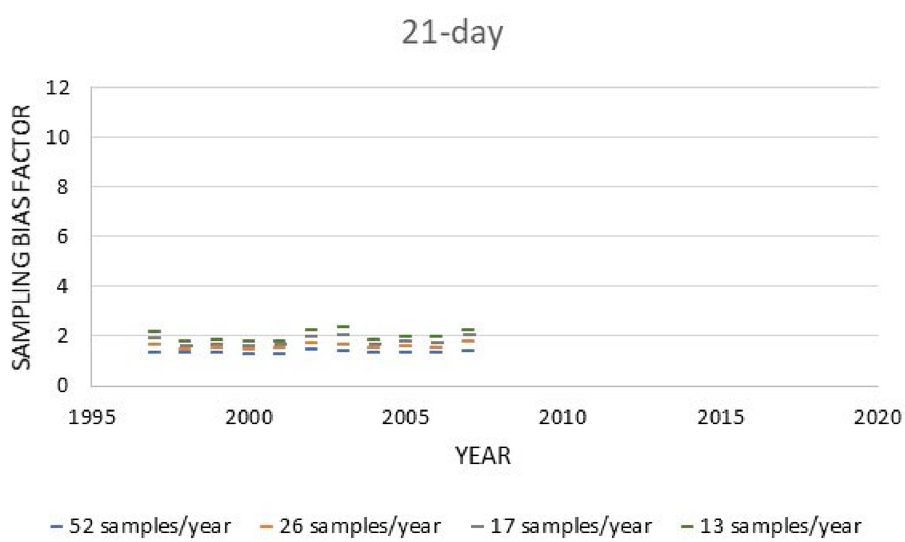

Figure 53. USGS Site 014211720: **Sampling Bias Factors for Estimating the Upper Confidence Interval on the 21-day Average Concentration**

The SBFs are consistent across all years. SBFs for all sample number categories are roughly equal to or below 3.5 for estimating the upper confidence interval on the 1-day average concentration and below 2.5 for estimating the upper confidence interval on the 21-day average concentration.

7. USGS-04208000

Site and Sampling Characterization

USGS site 04208000 (Cuyahoga River at Independence, OH) is a 706 mi^2 (1829 km^2) watershed in HUC 04. The watershed is 9% cropland, 11% impervious surfaces, with a high percentage of forestry. This watershed does not supply source drinking water, though it may be representative of other similar sites where chlorpyrifos is used.

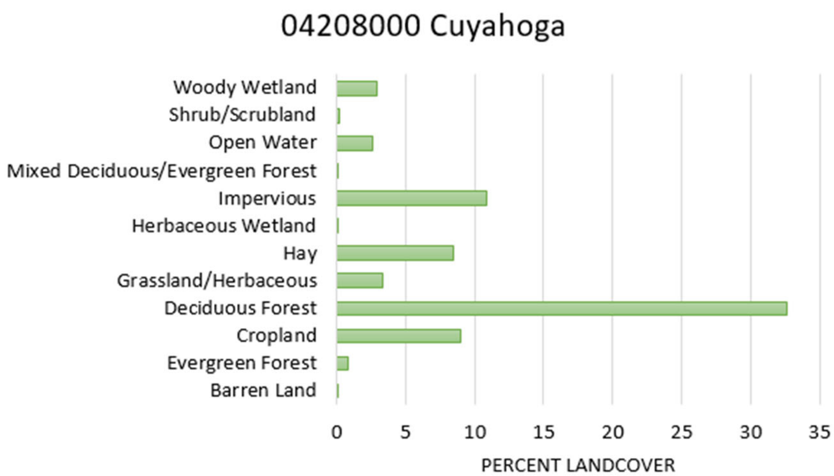

Figure 54. Watershed Landcover Characteristics of Sampling Site USGS-04208000

This site had a total of 40 detections out of 933 samples over 32 years between 1983 and 2015. Only 10 years have any detections, 3 years of which have 12 or more samples and a detection frequency greater than 25% (**Table 41**). **Table 41** also includes information on the years simulated in SEAWAVE-QEX as well as the years SBFs were developed. SEAWAVE-QEX analysis and the developed SBFs are described in the subsections below.

Table 41. USGS-04208000 Data Summary

Year	Number of Samples Collected	Number of Detections	Detection Frequency	Years Simulated in SEAWAVE-QEX	Number of Samples Excluded by SEAWAVE-QEX[1]	Years Sampling Bias Factors Developed
1983	23	0	0%			
1984	19	0	0%			
1985	28	0	0%			
1986	12	0	0%			
1987	12	6	50%	✓	1	✓
1988	20	6	30%	✓	1	✓
1989	25	4	16%	✓	2	✓
1990	17	7	41%	✓	0	✓
1991	11	10	90%	✓	0	✓
1992	12	1	8%			
1993	35	0	0%			
1994	34	1	3%			
1995	32	2	6%			
1996	32	2	6%			
1997	35	1	3%			
1998	41	0	0%			
1999	33	0	0%			
2000	41	0	0%			
2001	34	0	0%			
2002	38	0	0%			
2003	29	0	0%			
2004	31	0	0%			
2005	37	0	0%			
2006	30	0	0%			
2007	31	0	0%			
2008	33	0	0%			
2009	34	0	0%			
2010	32	0	0%			
2011	39	0	0%			
2012	38	0	0%			
2013	36	0	0%			
2014	29	0	0%			
2015	23	0	0%			

Gray shading highlights sites with at least 12 samples per year and a detection frequency of 25%

[1] Samples may be excluded by SEAWAVE-QEX when samples are spaced <3 days apart (see SEAWAVE-QEX SOP).

SEAWAVE-QEX Analysis

While only data from 1987 to 1990 met the SEAWAVE-QEX minimum criteria, the model fit was not acceptable using those years. Therefore, data for 1991 was included, which had a 90% detection frequency and 11 samples, and resulted in an acceptable fit.

The 80% confidence bounds on the estimated maximum concentrations for each year span roughly 1 to 10 µg/L for this site. The seasonal wave model selected has two shallow waves of similar amplitudes with most data within the 2SSD lines. The first season is from early March to early May and the second from early September to early January. There is not substantial correlation between adjusted concentrations and either MTFA or STFA and not much change in average concentration over time. Neither MTFA nor STFA are significantly correlated with the adjusted concentrations, and both correlations are generally flat (i.e., have little slope), suggesting that changes in streamflow do not have a strong impact on model outputs. The normalized residuals are centered around zero within years. The 95% confidence limits on the empirical correlogram overlaps with the fitted exponential correlation function with a CTS of 4.3 days.

Table 42 summarizes the 1- and 21-day estimated concentrations from SEAWAVE-QEX for each year based on the maximum of the 99th percentile concentrations. Concentrations were measured up to 0.5 µg/L, occurring in 1988.

Table 42. Maximum of the 99th Percentile 1- and 21-day Concentrations of Chlorpyrifos at USGS-04208000

Year	1-day Conc. (µg/L)	21-day Conc. (µg/L)
1987	4.9	1.9
1988	4.4	2.3
1989	4.6	2.9
1990	2.9	1.3
1991	12.7	4.7

SEAWAVE-QEX estimated concentrations are more than 10x larger than the measured concentrations. While the model assumptions are satisfied based on the diagnostic plots, there are two indicators to evaluate when considering the potential for overestimation. The first can be seen in the first diagnostic plot (**Figure 55**), in which the annual maximum concentration estimates (blue line) are somewhat higher than the midway point in the 80% confidence bounds (blue boxes), particularly for 1988, 1989, and 1991. This gives an indicator that the average concentration for that year is somewhat higher than the mean, suggesting a slightly skewed distribution of concentrations. Generally, unacceptable plots have mean concentrations that are highly skewed to the top of the plot. Additionally, while the 95% confidence limits on the empirical correlogram overlaps with the fitted exponential correlation, the overlap is toward the top of the confidence limits (gray boxes, **Figure 56**). When the empirical correlogram is entirely below the fitted exponential correlation, concentrations are estimated. In this case, it is not expected that the difference observed would cause substantial overestimation given that the confidence limits are overlapping. Variability in the degree of overlap is commonly observed in SEAWAVE-QEX diagnostic plots and not expected to indicate overestimation.

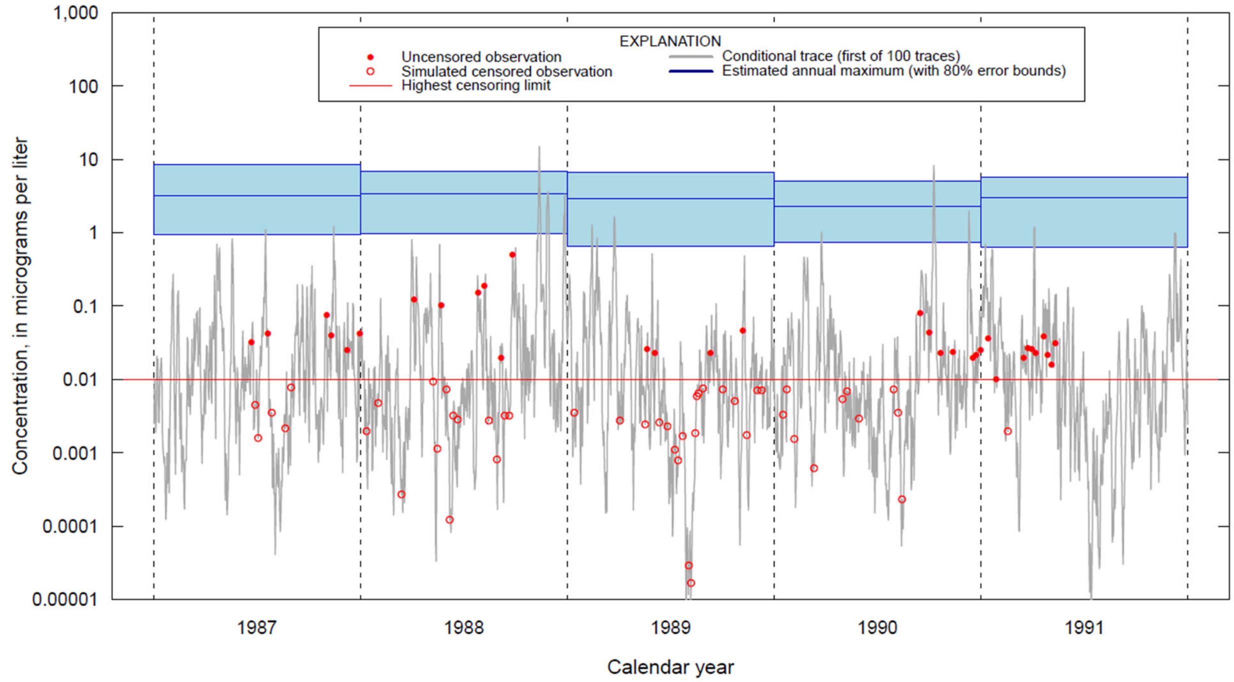

Figure 55. SEAWAVE-QEX Run Summary Diagnostic Plot for USGS-04208000

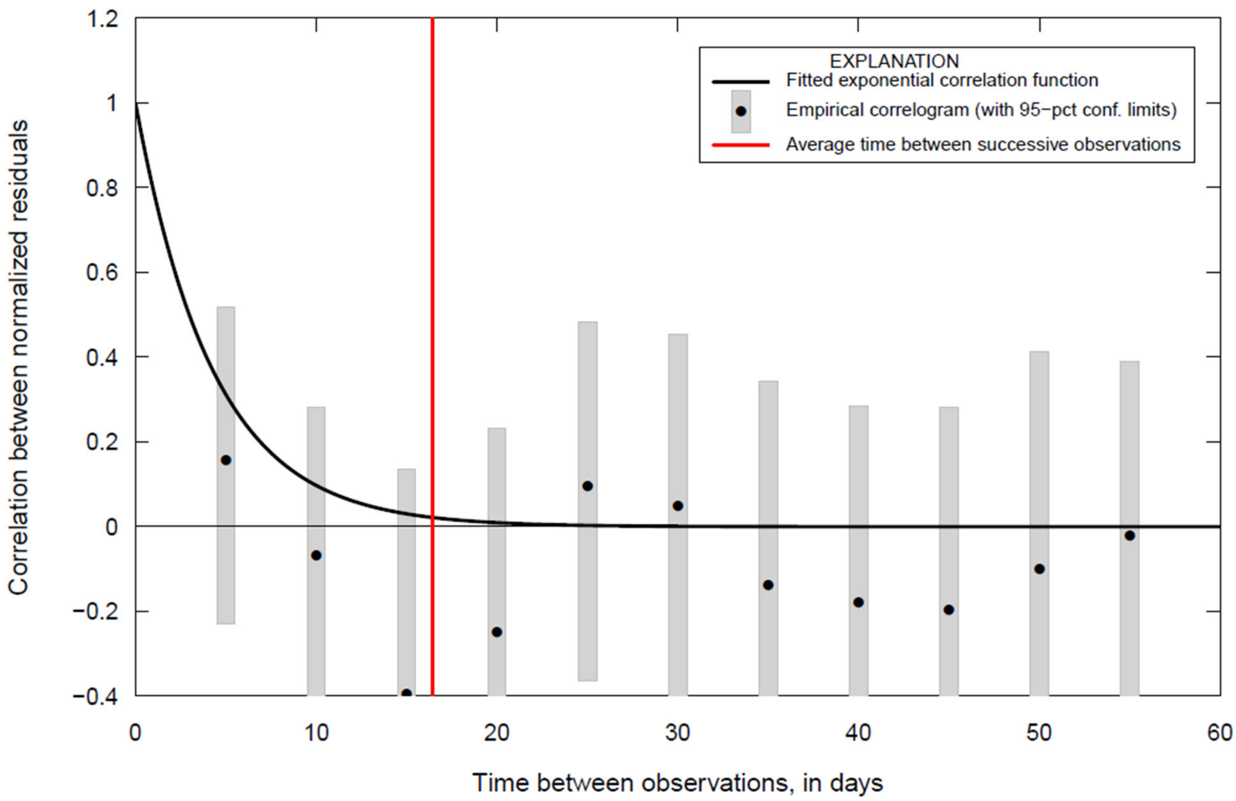

Figure 56. Plot of Correlation Between Normalized Residuals for USGS-04208000

Sampling Bias Factor Development

SBFs developed for estimating the 1-day and 21-day average concentrations are shown **Figure 57** and **Figure 58**, respectively. These figures show the median SBFs across SEAWAVE-QEX chemographs for each site year and sample number category.

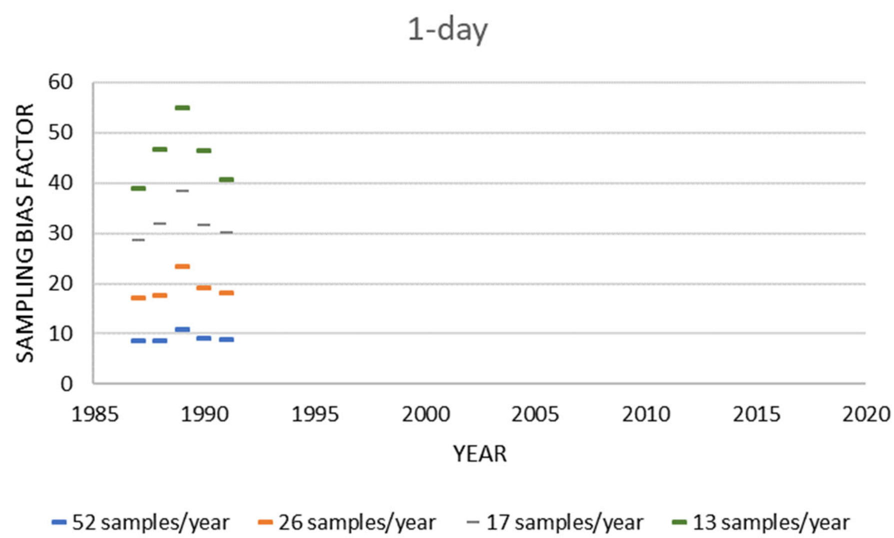

Figure 57. USGS Site 04208000: Sampling Bias Factors for Estimating the Upper Confidence Interval on the 1-day Average Concentration

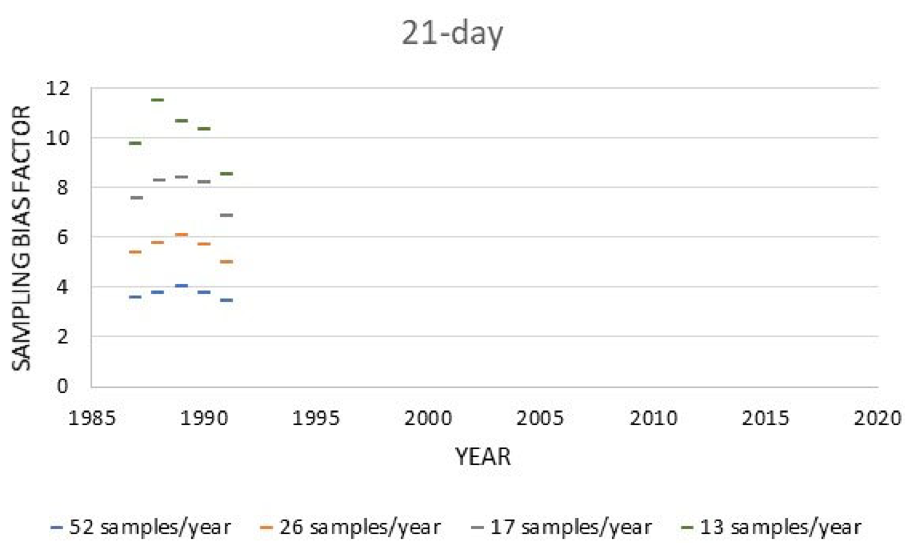

Figure 58. USGS Site 04208000: **Sampling Bias Factors for Estimating the Upper Confidence Interval on the 21-day Average Concentration**

The SBFs are consistently high across all years. SBFs for all sample number categories are much higher for all years than all the other sites. SBFs for estimating the upper confidence interval on the 1-day average concentration ranged from 9 to 11 for 52+ samples per year, 17 to 23 for 26-51 samples/year, 29 to 38 for 17-25 samples/year and 39 to 55 for 13-16 samples/year. SBFs for estimating the upper confidence interval on the 21-day average concentration ranged roughly 4 to almost 12 for 52+ samples per year and 13-16 samples/year, respectively.

8. USGS-02335870

Site and Sampling Characterization

USGS site 02335870 (Sope Creek near Marietta, GA) is in a 33.3 mi^2 (86.3 km^2) urban watershed in HUC 03. The watershed has no cropland but 20% impervious surfaces and 22% forested areas (**Figure 59**). The sampling location is upstream of seven drinking water intakes serving community water systems, with several pulling from the Chattahoochee River. Travel times of the water range from <1 day up to 3 days from the sampling site to each intake.

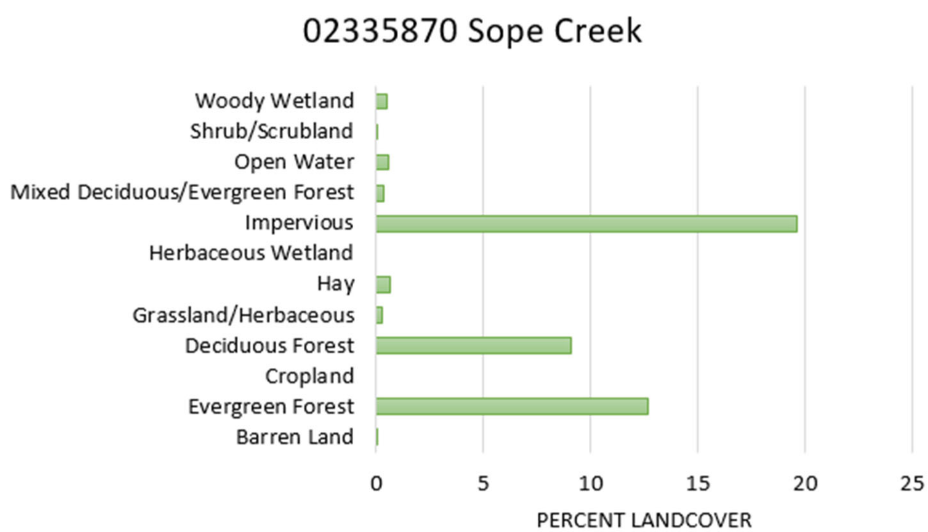

Figure 59. Watershed Landcover Characteristics of Sampling Site USGS-02335870 (2006 data)

This site had a total of 41 detections out of 401 samples over 26 years between 1993 and 2019. Only 3 years have 12 or more samples and a detection frequency greater than 25% (**Table 43**). **Table 43** also includes information on the years simulated in SEAWAVE-QEX as well as the years SBFs were developed. SEAWAVE-QEX analysis and the developed SBFs are described in the subsections below.

Table 43. USGS-02335870 Data Summary

Year	Number of Samples Collected	Number of Detections	Detection Frequency	Years Simulated in SEAWAVE-QEX	Number of Samples Excluded by SEAWAVE-QEX[1]	Years Sampling Bias Factors Developed
1993	32	17	53%	✓	0	✓
1994	12	7	58%	✓	0	✓
1995	3	1	33%	✓	0	✓
1996	0	—	—	✓	0	✓
1997	9	5	56%	✓	0	✓
1998	6	2	33%	✓	0	✓
1999	10	1	10%	✓	0	✓
2000	12	4	33%	✓	0	✓
2001	12	1	8%			
2002	23	0	0%			
2003	18	0	0%			
2004	7	0	0%			
2005	6	2	33%			
2006	6	0	0%			
2007	18	0	0%			
2008	22	0	0%			
2009	8	0	0%			
2010	18	0	0%			
2011	6	0	0%			
2012	24	0	0%			
2013	24	0	0%			
2014	27	0	0%			
2015	24	0	0%			
2016	23	0	0%			
2017	24	1	4%			
2018	22	0	0%			
2019	5	0	0%			

Gray shading highlights sites with at least 12 samples per year and a detection frequency of 25%
[1] Samples may be excluded by SEAWAVE-QEX when samples are spaced <3 days apart (see SEAWAVE-QEX SOP).

SEAWAVE-QEX Analysis

SEAWAVE-QEX was run only with the years encompassing the 3 years meeting the minimum requirements. The model did not produce an acceptable fit using SEAWAVE-QEX default parameters and the fitting was attempted by adding a small constant (0.0006 or 0.0009). Fitting with the addition of 0.0006 resulted in acceptable results with low confidence.

The 80% confidence bounds on the estimated maximum for each year are below 0.1 µg/L and the confidence bounds span much less than an order of magnitude. There are two shallow seasonal waves of similar amplitude; one season spanning early April to early August and the second from mid-December to early February. Most data are within the 2SSD bounds. There is a significant (α=0.05) positive correlation of adjusted concentration with MTFA and STFA. The adjusted concentrations trend slightly downward over time. The normalized residuals are centered on zero although have more spread (positive and negative) in 1993 compared to other years (**Figure 60**). The empirical correlogram 95% confidence limits overlap with the fitted exponential correlation function at time intervals shorter than the average (to the left of the red line) with a CTS of 3.5 days.

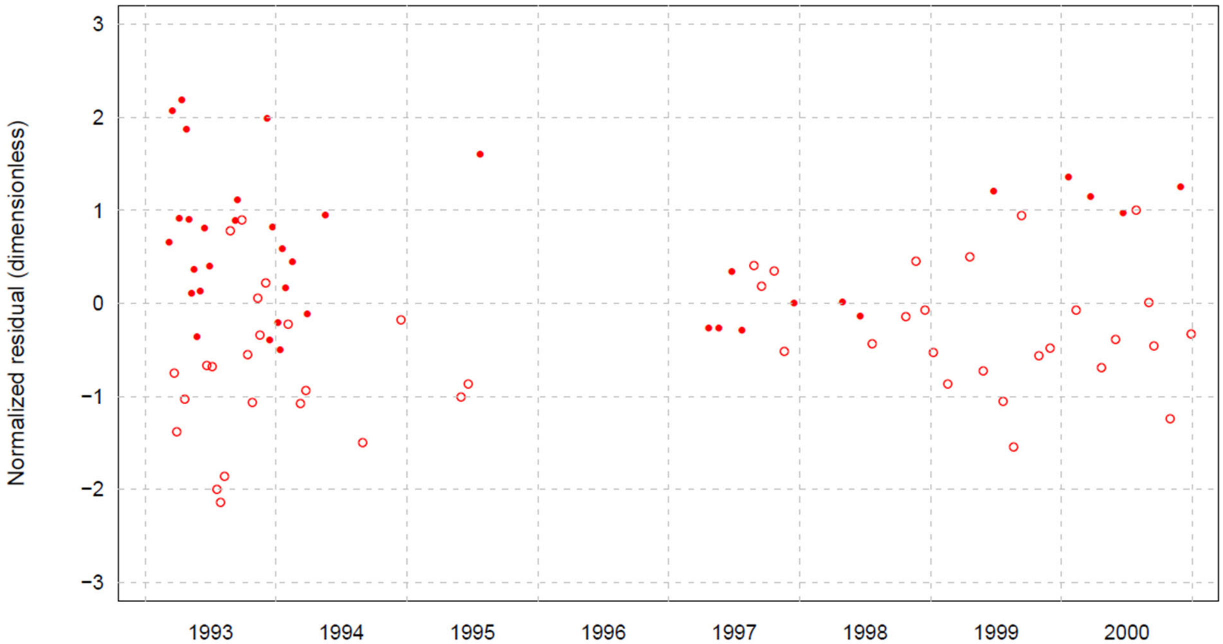

Figure 60. Normalized Residuals Across Years for USGS-02335870

Table 44 summarizes the 1- and 21-day estimated concentrations from SEAWAVE-QEX for each year based on the maximum of the 99th percentile concentrations.

Table 44. Maximum of the 99th Percentile 1- and 21-day Concentrations of Chlorpyrifos at USGS-02335870

Year	1-day Conc. (µg/L)	21-day Conc. (µg/L)
1993	0.085	0.041
1994	0.065	0.032
1995	0.040	0.020
1996	0.051	0.027
1997	0.052	0.021
1998	0.061	0.031
1999	0.056	0.022
2000	0.022	0.013

Sampling Bias Factor Development

SBFs developed for estimating the 1-day and 21-day average concentrations are shown **Figure 61** and **Figure 62** respectively. These figures show the median SBFs across SEAWAVE-QEX chemographs for each site year and sample number category.

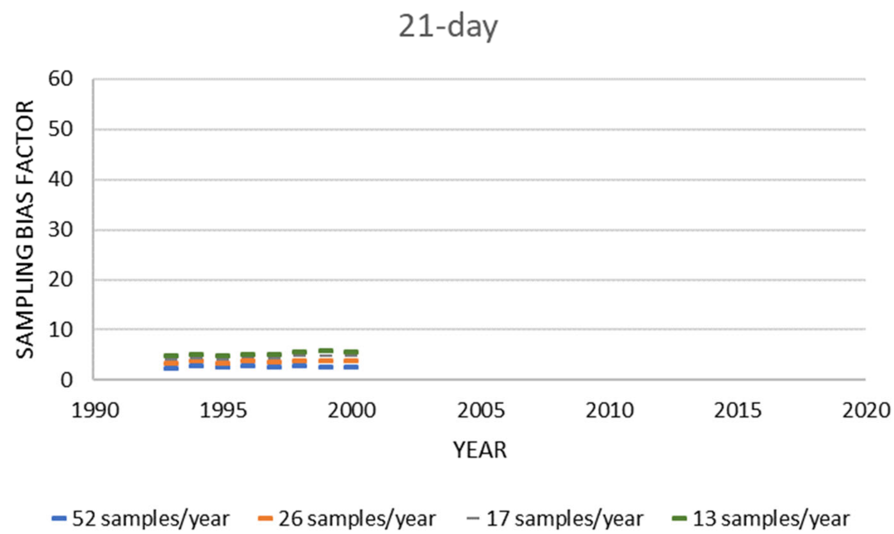

Figure 61. USGS Site 02335870: Sampling Bias Factors for Estimating the Upper Confidence Interval on the 1-day Average Concentration

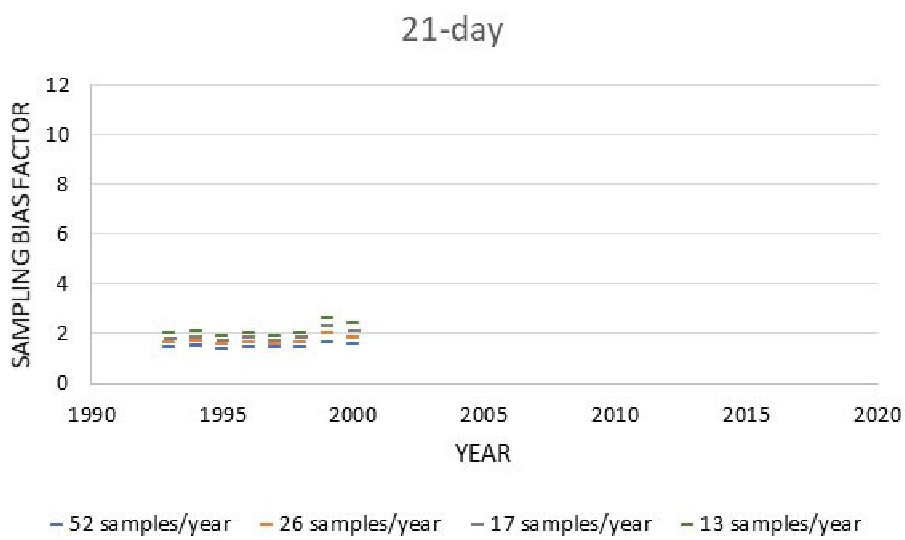

Figure 62. USGS Site 02335870: **Sampling Bias Factors for Estimating the Upper Confidence Interval on the 21-day Average Concentration**

SBFs for estimating the upper confidence interval on the 1-day and 21-day average concentration for all sampling intervals were below 6 and 3, respectively. The values were generally consistent across the years with the last two years (1999 and 2000) having the highest SBFs.

9. USGS-04193500

Site and Sampling Characterization

USGS site 04193500 (Maumee River at Waterville, OH) is in a 6,283 mi^2 (16,274 km^2) agricultural watershed in HUC 04 dominated by cropland (73% of landcover) (**Figure 63.** Watershed Landcover

Characteristics of Sampling Site USGS-04193500). This watershed does not supply source drinking water, though it may be representative of other similar sites where chlorpyrifos is used, particularly given the high percentage of cropland landcover. Additionally, the site is downstream of numerous intakes, several with travel times less than a day and it is unclear whether measured concentrations result from chlorpyrifos use within this watershed or upstream.

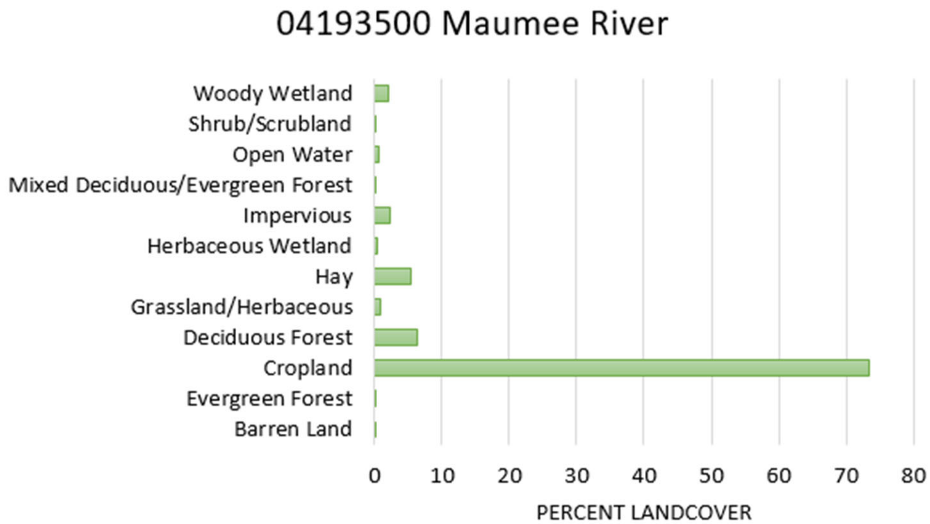

Figure 63. Watershed Landcover Characteristics of Sampling Site USGS-04193500

This site had a total of 29 detections out of 268 samples between 1996 and 2018 (**Table 45**)**. Table 45** also includes information on the years simulated in SEAWAVE-QEX as well as the years SBFs were developed. SEAWAVE-QEX analysis and the developed SBFs are described in the subsections below. Data from NCWQR was not included with the USGS data download as the sampling frequency was much higher (near-daily) and detection frequency was much lower.

Table 45. USGS-04193500 Data Summary

Year	Number of Samples Collected	Number of Detections	Detection Frequency	Years Simulated in SEAWAVE-QEX	Number of Samples Excluded by SEAWAVE-QEX[1]	Years Sampling Bias Factors Developed
1996	13	9	69%	✓	0	✓
1997	17	5	29%	✓	0	✓
1998	14	0	0%	✓	0	✓
1999	13	0	0%	✓	0	✓
2000	14	2	14%	✓	0	✓
2001	11	2	18%	✓	0	✓
2002	8	0	0%	✓	0	✓
2003	8	1	13%	✓	0	✓
2004	8	1	13%	✓	0	✓
2005	7	2	29%	✓	0	✓
2006	16	3	19%	✓	0	✓
2007	16	4	25%	✓	0	✓
2008	0	—	—			
2009	0	—	—			
2010	1	0	0%			
2011	16	0	0%			
2012	3	0	0%			
2013	18	0	0%			
2014	18	0	0%			
2015	19	0	0%			
2016	18	0	0%			
2017	18	0	0%			
2018	12	0	0%			

[redacted]

SEAWAVE-QEX Analysis

While only 3 years of the USGS data have 12 or more samples and a detection frequency greater than 25% (Table 45), these were able to be modeled. Data from the NCWQR was not included as no years of data met the minimum SEAWAVE-QEX criteria. The data for 1996-2007 were input into SEAWAVE-QEX as they encompassed the 3 years meeting the minimum requirements. Since the empirical correlogram did not overlap with the fitted exponential correlation function using SEAWAVE-QEX default parameters, several small constants were added to improve fit (i.e., 0.0004, 0.0008, 0.0012). Fitting with the addition of 0.0012 resulted in the best model fit with low confidence.

For many years in the simulation, the 80% confidence bounds on the estimated maximum for each year span roughly an order of magnitude. There is a broad, shallow wave with a season from early May to early January and all measured concentrations fitting within the 2SSD bounds. Adjusted concentration is significantly (α=0.05) positively correlated with both MTFA and STFA. There is not much trend in the concentration data over the years. The normalized residuals are somewhat negatively skewed by season; viewing normalized residuals by year shows that residuals in 1996 are skewed positive while 1998-2001 are skewed negative. However, these negatively skewed residuals include many censored values, meaning that the exact location of the residuals will change in each conditional simulation. The empirical correlogram 95% confidence limits overlaps well with the estimated correlation function at short sampling intervals (i.e., to the left of the red line) with a CTS of 19.9 days.

Table 46 summarizes the 1- and 21-day estimated concentrations from SEAWAVE-QEX for each year based on the maximum of the 99th percentile concentrations. In the year 2007, the mean estimated annual maximum (blue line) is high in the error bounds (blue box), indicating that the mean for that year is much higher than the median and the concentration data for 2007 may be skewed (**Figure 64**) and therefore may be overestimates.

Table 46. Maximum of the 99th Percentile 1- and 21-day Concentrations of Chlorpyrifos at USGS-04193500

Year	1-day Conc. (µg/L)	21-day Conc. (µg/L)
1996	0.36	0.17
1997	0.31	0.14
1998	0.18	0.08
1999	0.11	0.05
2000	0.08	0.05
2001	0.18	0.12
2002	0.13	0.07
2003	0.70	0.27
2004	0.20	0.12
2005	0.47	0.19
2006	0.20	0.13
2007	2.08	1.44

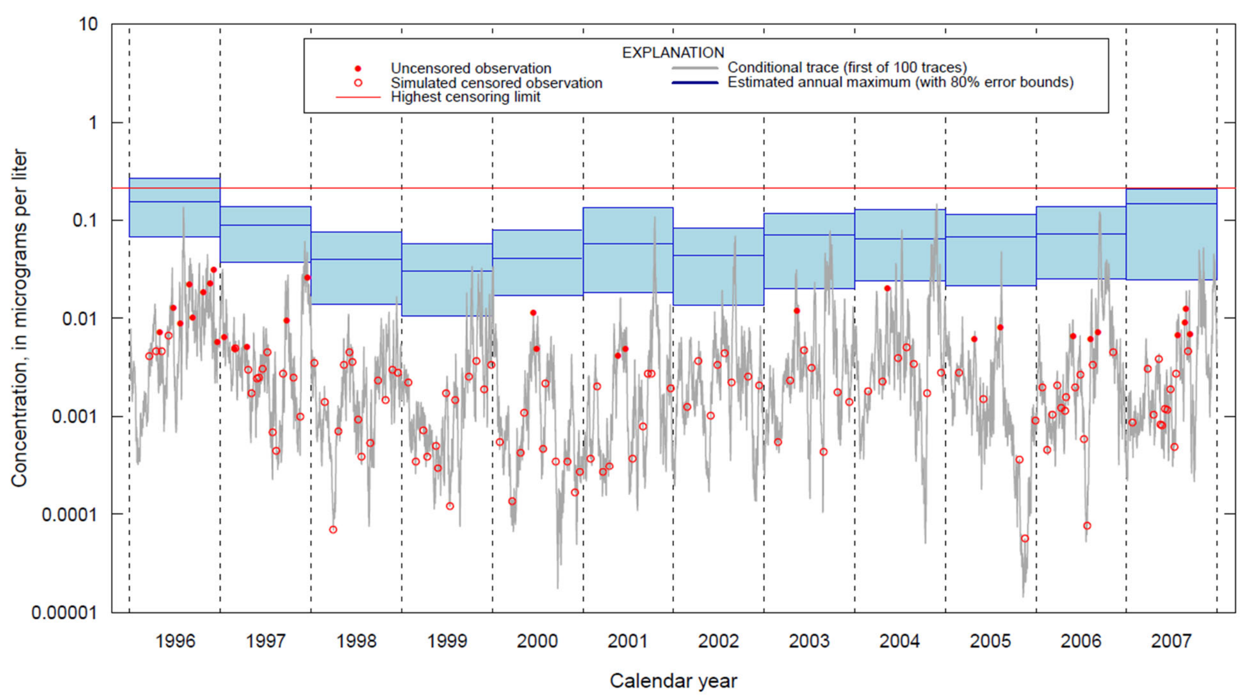

Figure 64. SEAWAVE-QEX Run Summary Diagnostic Plot for USGS-04193500 with High Mean in 2007

Sampling Bias Factor Development

SBFs developed for estimating the 1-day and 21-day average concentrations are shown **Figure 61** and **Figure 62** respectively. These figures show the median SBFs across SEAWAVE-QEX chemographs for each site year and sample number category.

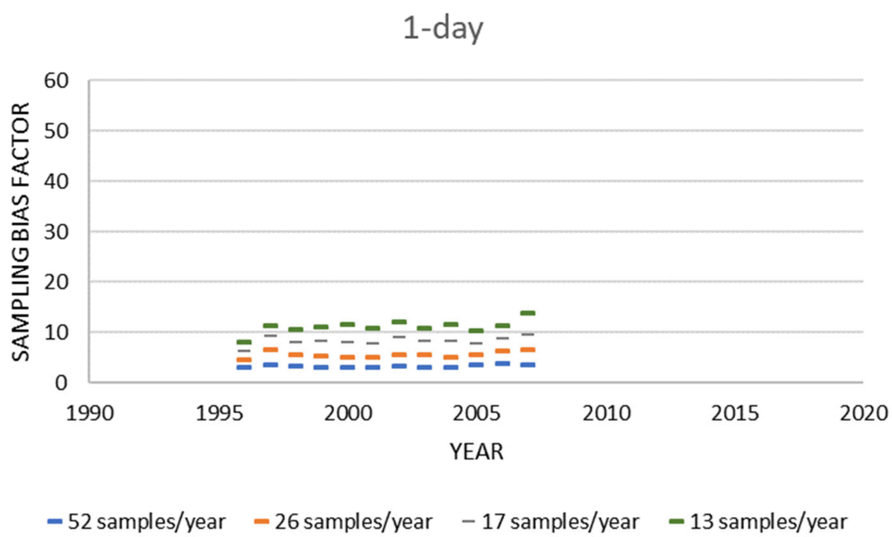

Figure 65. USGS Site 04193500: Sampling Bias Factors for Estimating the Upper Confidence Interval on the 1-day Average Concentration

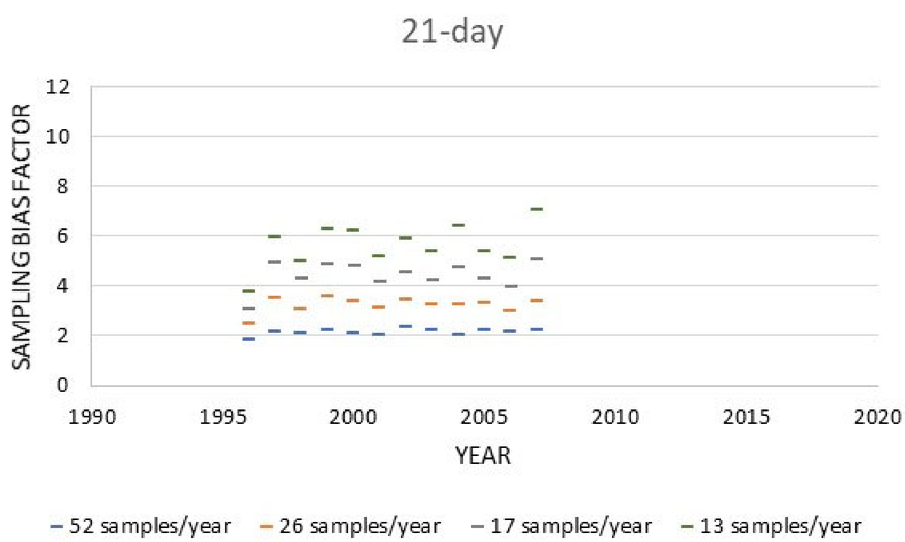

Figure 66. USGS Site 04193500: Sampling Bias Factors for Estimating the Upper Confidence Interval on the 21-day Average Concentration

SBFs for estimating the upper confidence interval on the 1-day and 21-day average concentration for all sampling intervals were below 11.5 and 8, respectively. The values were generally consistent across the years with the last year (2007) having the highest SBFs.

10. USGS-11274538

Site and Sampling Characterization

USGS site 11274538 (Orestimba Creek near Crows Landing, California) falls within a 180 mi^2 (465.2 km^2) watershed. The percent agriculture in 2006 in the sample site watershed was only 5% cropland and included a combined 74% of grassland and shrubs (**Figure 67.** Watershed Landcover Characteristics of Sampling Site USGS-11274538). This site is upstream of three community water system intakes, with two either on or receiving water through diversion of the San Joaquin River. These are the same three CWSs that the USGS site 11303500 is also upstream meaning water flow or pesticide loading from these sites would both likely occur at the downstream intake. The time of travel between the sample site on Orestimba Creek and each community water system intake is 1 day.

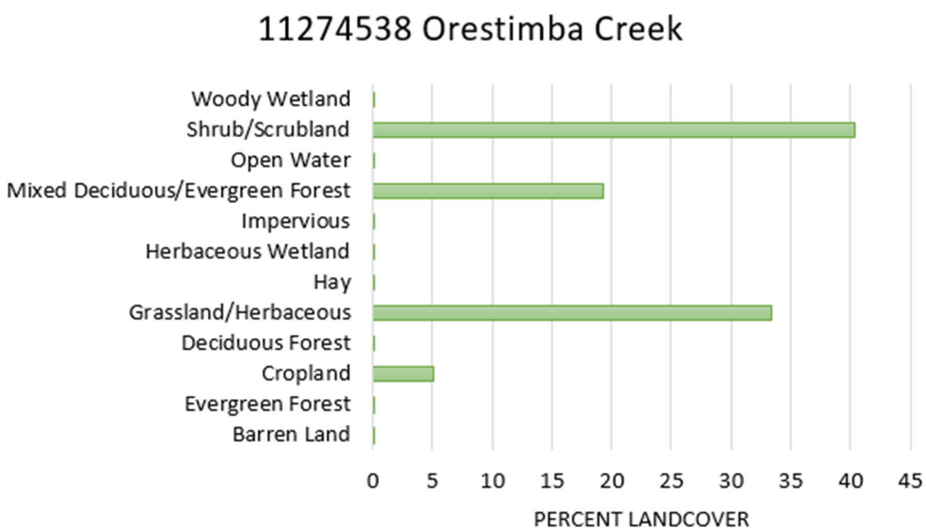

Figure 67. Watershed Landcover Characteristics of Sampling Site USGS-11274538

Based on available USGS data this site had a total of 163 detections out of 284 samples over 22 years between 1992 and 2017 (**Table 47**). Dow Agrosciences, currently known as Corteva Agriscience, also conducted a surface monitoring program in California on Orestimba Creek with daily and weekly sample collection (MRID 44711601). This program is described in more detail in the 2016 DWA (USEPA, 2016). USGS site 11274538 is “immediately above sampling location L1” where weekly samples were collected in 1996 and 1997 by Dow (Corteva Agriscience) for analysis of chlorpyrifos. **Table 47** also includes information on the years simulated in SEAWAVE-QEX as well as the years SBFs were developed. SEAWAVE-QEX analysis and the developed SBFs are described in the subsections below.

Table 47. USGS-11274538 Data Summary

Year	Number of Samples Collected	Number of Detections	Detection Frequency	Years Simulated in SEAWAVE-QEX	Number of Samples Excluded by SEAWAVE-QEX[1]	Years Sampling Bias Factors Developed
1992	44	40	91%	✓	21	✓
1993	40	22	55%	✓	4	✓
1994	1	1	100%	✓	0	✓
1995	1	1	100%	✓	0	✓
1996[2]	35	7	20%	✓	0	✓
1997[2]	26	15	58%	✓	0-3	✓
1998	14	9	64%	✓	0	✓
1999	16	5	31%	✓	0	✓
2000	20	15	75%	✓	2	✓
2001	43	24	56%	✓	8	✓
2002	18	8	44%	✓	0	✓
2003	16	8	50%	✓	0	✓
2004	8	5	63%	✓	0	✓
2005	6	4	67%	✓	0	✓
2006	4	3	75%	✓	0	✓
2007	0	—	—	✓	0	✓
2008	0	—	—	✓	0	✓
2009	1	1	100%	✓	0	✓
2010	15	5	33%	✓	0	✓
2011	0	—	—			
2012	2	0	0%			
2013	12	1	8%			
2014	3	0	0%			
2015	1	0	0%			
2016	4	2	50%			
2017	5	0	0%			

Gray shading highlights sites with at least 12 samples per year and a detection frequency of 25%

[1] Samples may be excluded by SEAWAVE-QEX when samples are spaced <3 days apart (see SEAWAVE-QEX SOP).

[2] 1996-1997 include additional data. Without additional data, 1996 has no samples and 1997 has 10 with 90% detection rate. No samples excluded without addition of data in 1997 and 3 samples excluded with extra data.

SEAWAVE-QEX Analysis

Initial SEAWAVE-QEX trials used chlorpyrifos concentration data from USGS. Nine years of data have 12 or more samples and a detection frequency greater than 25%, as shown in **Table 47**. The maximum measured concentration at this site is 0.3 μg/L (April 24, 1992). Several iterations of inputs to SEAWAVE-QEX were attempted to find the best fit to the data, such as including only the years 1998-2003 or 1998-2010. Ultimately, using data from the years 1998-2010 had the best model fit for USGS data although 1992-2010 also had an acceptable, low confidence fit and encompassed more years of data.

Given that additional data, from Dow Agrosciences (referred to Dow in this section, and is now Corteva Agriscience), was available with high frequency sampling directly downstream of the site, SEAWAVE-QEX output from the USGS data model run was compared to unadjusted measured chlorpyrifos data for

1996 and 1997 from Dow at site L1. These data added 51 samples with 13 detections (**Table 47**). The maximum measured concentration at L1 in 1996 and 1997 was 1.126 µg/L and 1.066 µg/L, respectively. Since the model fit by SEAWAVE-QEX is dependent on the input data, and the USGS data from 1992-2010 produced a poorer model fit than the data from 1998-2010, the latter was used for comparison to the more robust data set of USGS and supplemental Dow data from 1992-2010. Both the USGS (1998-2010) and USGS with Dow (1992-2010) data produced SEAWAVE-QEX results with medium confidence based on the diagnostic plots.

The data from USGS alone encompassed the highest measured concentration in the Dow data from the site (1.126 µg/L), however, the summary statistics used as point estimates of concentration (i.e., the maximum of the 99th 1- and 21-day average concentrations) did not reflect the maximum measured in the other data set. This can be seen in **Figure 68**, which shows the upper centiles (> 95 percentile) of all conditional simulations overlaid in blue, the maximum measured concentration as a red line, and each of the annual point estimates encircled along the top. Conversely, the USGS with Dow data in green has enough estimates beyond the measured maximum that the concentration is captured by the point estimates and better reflect the expected concentrations at that site. The full distributions of estimated concentrations from both runs, shown in **Figure 69**, shows that the addition of the Dow data increased the percentage of concentrations at the lower tail of the distribution. Overall, this comparison suggests that SEAWAVE-QEX may underestimate chlorpyrifos concentrations at the upper tail if run for datasets with high censorship and infrequent sampling (≥7-day sampling). Therefore, the USGS data along with the more frequent (i.e., weekly) sampling collected by Dow were combined and analyzed using SEAWAVE-QEX for the years 1992-2010 and used in the development of SBFs.

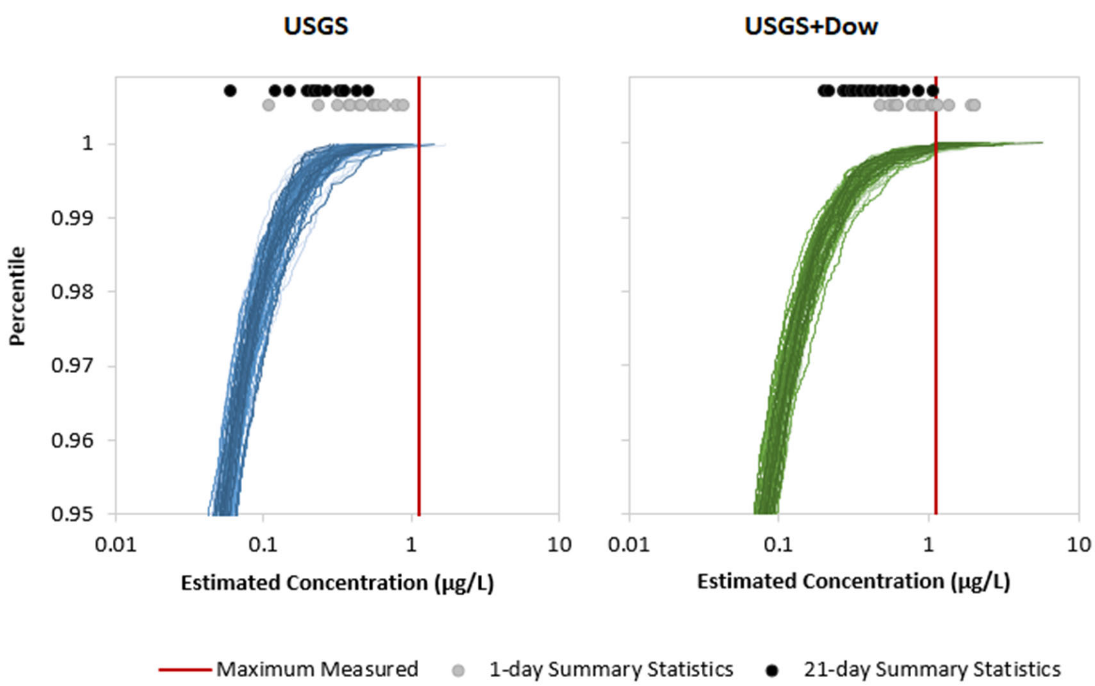

Figure 68. Upper Tail of Distribution of Estimated Concentrations from SEAWAVE-QEX and Associated Summary Statistics for USGS-11274538 With and Without Dow Monitoring Data

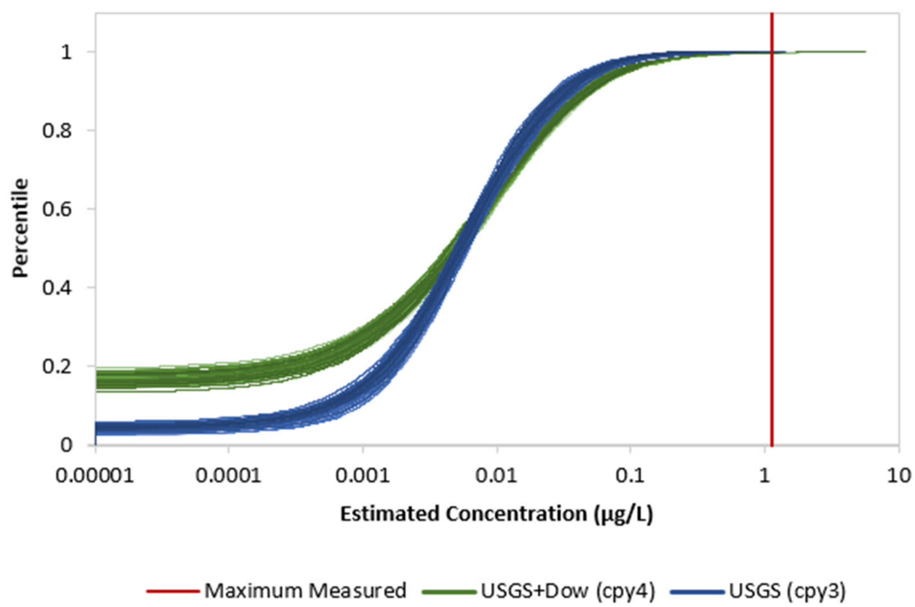

Figure 69. Distribution of Estimated Concentrations from SEAWAVE-QEX for USGS-11274538 With and Without Dow Monitoring Data Compared to Maximum Measured Concentration in 1996

SEAWAVE-QEX fit a shallow, long seasonal wave to the data and the 2xSSD on the model are approximately one order of magnitude. The season extends first of February to mid-October. The shape and season of the wave are very similar to that produced for the USGS data alone. The measured data are mostly within the 2xSSD lines and other model assumptions are satisfied (all diagnostic plots are provided in **ATTACHMENT 4**).

For just the USGS data from 1998-2010 (file name cpy3), the 80% confidence bounds on the estimated maximum for each year span up to an order of magnitude and all are below 1 µg/L. SEAWAVE-QEX fit a broad, shallow wave with a season from early April to early October and most measured concentrations fitting within the 2SSD bounds. Adjusted concentration is generally not correlated with MTFA but has a slight negative weak correlation with STFA. Concentration data trends somewhat upward over the years. The normalized residuals are somewhat positively skewed viewed across season and seem to be particularly skewed positive in 2000, 2006, and 2010. The empirical correlogram 95% confidence limits overlaps well with the estimated correlation function at short sampling intervals (i.e., to the left of the red line) with a CTS of 9.3 days.

When including the daily sampling data taken from another sample location on Orestimba Creek from 1996-1997 (file name cpy4), the 80% confidence bounds on the estimated maximum for each year similarly span up to an order of magnitude but include concentrations above 1 µg/L. The 80% error bounds for the two years with weekly samples added (i.e., 1996-1997) are much tighter (i.e., low uncertainty) than for the years of USGS data only, though the upper bound (i.e., top of the blue box) is not substantially higher than those of other years. SEAWAVE-QEX fits a single broad wave for these data as well, with an extended season from late January to mid-October and several measured data points falling outside the 2SSD bounds. Adjusted concentration is weakly negatively correlated with both MTFA and STFA; the negative correlation with STFA is present in both SEAWAVE-QEX runs but does not significantly impact the model. Measured concentrations trend somewhat downward from 1992-2010 and normalized residuals are still positively skewed in this run. There are several data points in season that have the maximum residual value (+3); these are all from the extra measured data in 1996-1997 that are at higher concentrations. Additionally, 2006 and 2010 remain skewed positive relative to other years. The empirical correlogram 95% confidence limits overlaps well with the estimated correlation function at short sampling intervals (i.e., to the left of the red line) with a CTS of 7.7 days.

Table 48 summarizes the 1- and 21-day estimated concentrations from SEAWAVE-QEX for each year based on the maximum of the 99th percentile concentrations.

Table 48. Maximum of the 99th Percentile 1- and 21-day Concentrations of Chlorpyrifos at USGS-11274538

Year	USGS		USGS+Dow	
	1-day Conc. (µg/L)	21-day Conc. (µg/L)	1-day Conc. (µg/L)	21-day Conc. (µg/L)
1992	—	—	1.11	0.54
1993	—	—	0.48	0.20
1994	—	—	1.95	1.09
1995	—	—	1.04	0.56
1996	—	—	1.39	0.59
1997	—	—	2.05	0.69
1998	0.38	0.20	0.63	0.27
1999	0.32	0.15	0.88	0.43
2000	0.47	0.22	0.61	0.31
2001	0.11	0.06	0.61	0.22
2002	0.24	0.12	0.59	0.31
2003	0.45	0.27	0.94	0.40
2004	0.39	0.22	0.79	0.36
2005	0.60	0.24	1.07	0.39
2006	0.57	0.33	1.17	0.49
2007	0.80	0.51	2.06	0.87
2008	0.66	0.35	0.61	0.32
2009	0.55	0.35	0.55	0.36
2010	0.90	0.43	0.81	0.28

Sampling Bias Factor Development

SBFs developed for estimating the 1-day and 21-day average concentrations are shown in **Figure 70** and **Figure 71**, respectively. These figures show the median SBFs across SEAWAVE-QEX chemographs for each site year and sample number category.

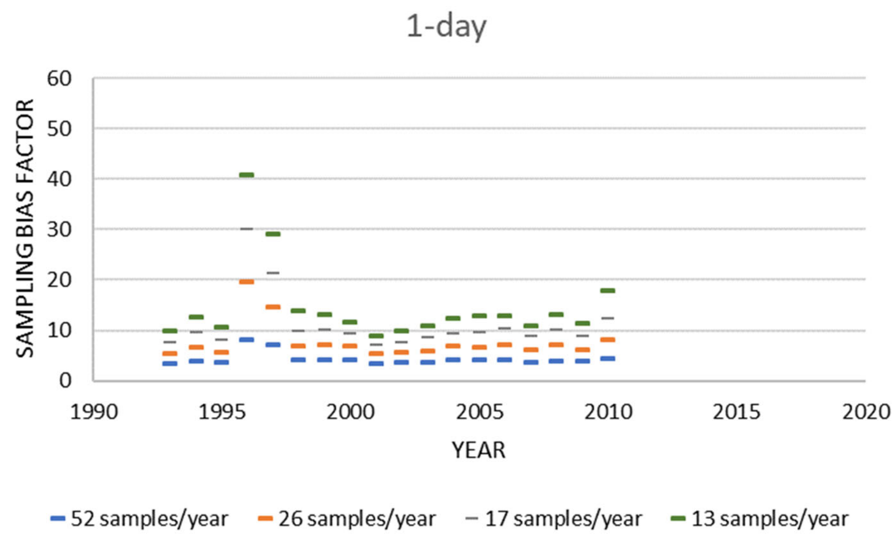

Figure 70. USGS Site 11274538: Sampling Bias Factors for Estimating the Upper Confidence Interval on the 1-day Average Concentration

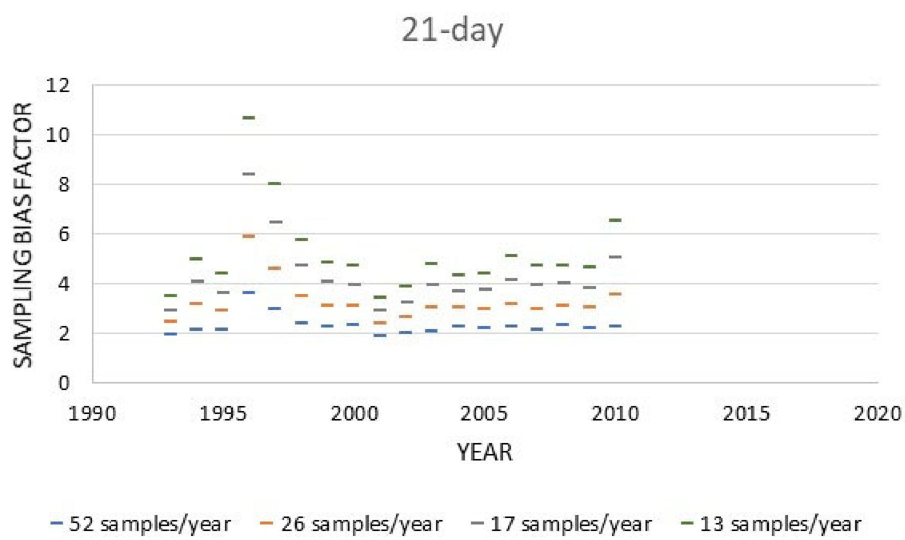

Figure 71. USGS Site 04193500: **Sampling Bias Factors for Estimating the Upper Confidence Interval on the 21-day Average Concentration**

SBFs varied across years. The highest SBFs were estimated for the years (1996 and 1997) with the most monitoring data (i.e., daily). Like USGS-02174250, the highest SBFs are driven by measured concentrations. Again, this calls into question the ability to estimate accurate SBFs when infrequent sampling (i.e., non-daily) is conducted or misses peak occurrence concentrations.

11. USGS-03612500

Site and Sampling Characterization

USGS site 03612500 (Ohio River at Dam 53 near Grand Chain, IL) is in HUC-06 in a 203,100 mi^2 (526,000 km^2) drainage area. The watershed has roughly 20% cropland, 15% hay, and 46% deciduous forests (**Fig**).

The sampling location is upstream of several drinking water intakes serving community water systems, pulling from the Ohio River. Travel times from the sampling site to each intake is less than a day, making the site very relevant for source drinking water.

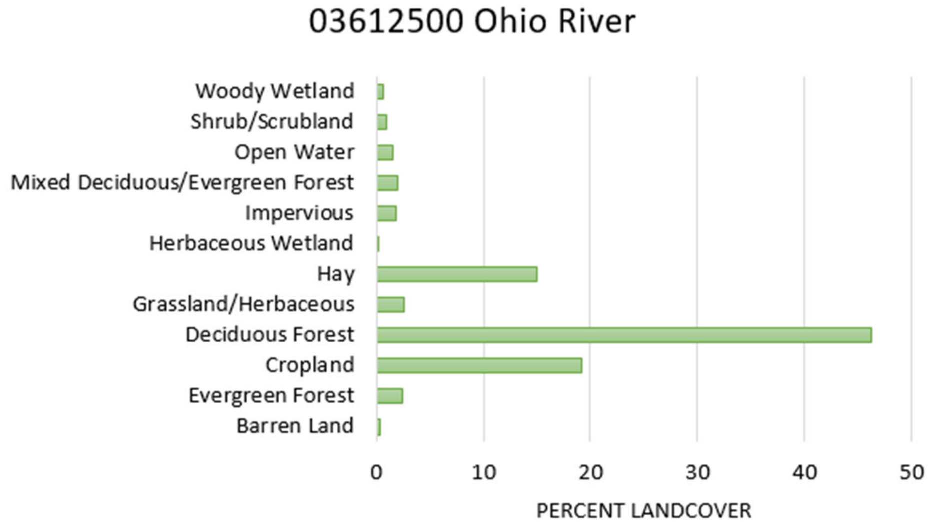

Figure 72. Watershed Landcover Characteristics of Sampling Site USGS-11274538

The site has 42 chlorpyrifos detections out of 262 samples from 1992-2014 (**Table 49**). **Table 49** also includes information on the years simulated in SEAWAVE-QEX as well as the years SBFs were developed. SEAWAVE-QEX analysis and the developed SBFs are described in the subsections below.

Table 49. USGS-03612500 Data Summary

Year	Number of Samples Collected	Number of Detections	Detection Frequency	Years Simulated in SEAWAVE-QEX	Number of Samples Excluded by SEAWAVE-QEX[1]	Years Sampling Bias Factors Developed
1992	10	10	100%	✓	0	✓
1993	1	1	100%	✓	0	✓
1994	0	—	—	✓		✓
1995	0	—	—	✓		✓
1996	12	10	83%	✓	0	✓
1997	15	6	40%	✓	0	✓
1998	13	3	23%	✓	0	✓
1999	11	3	27%	✓	0	✓
2000	13	7	54%	✓	0	✓
2001	15	1	7%			
2002	15	0	0%			
2003	13	0	0%			
2004	15	0	0%			
2005	14	0	0%			
2006	12	0	0%			
2007	13	0	0%			
2008	12	0	0%			
2009	12	0	0%			
2010	12	0	0%			
2011	15	1	7%			
2012	12	0	0%			
2013	14	0	0%			
2014	13	0	0%			

Gray shading highlights sites with at least 12 samples per year and a detection frequency of 25%
[1] Samples may be excluded by SEAWAVE-QEX when samples are spaced <3 days apart (see SEAWAVE-QEX SOP).

SEAWAVE-QEX Analysis

The site has 42 chlorpyrifos detections out of 262 samples from 1992-2014, with only 3 years meeting the minimum criteria for SEAWAVE-QEX as outlined earlier (**Table 49**). The site does not have daily streamflow measurements to use as a covariate in SEAWAVE-QEX. However, in a USGS study (Aulenbach et al., 2007), streamflow from a nearby site is used in conjunction with water quality data from this site. Therefore, streamflow from USGS-03611500 (Ohio River at Metropolis, IL) is also used in this analysis as a surrogate for USGS-03612500. The site was run in SEAWAVE-QEX unsuccessfully using years 1996-2000 with and without adding a constant (0.004 and 0.012). The analysis was repeated with a start date of 1992, since 1992 has 10 samples with 100% detection frequency. Including 1992 improved the fit and was considered acceptable after subtracting a constant of 0.012 within the model.

The 80% confidence bounds on the estimated maximum for each year span less than an order of magnitude. The estimated concentrations have a clear downward trend from 1992 to 2000 of nearly an order of magnitude. Similarly, the adjusted concentrations trend significantly downward over the timeframe analyzed. However, it is notable that several measured concentrations from 1996-1998 are in the mid-range of the measured concentrations from 1992, implying that the estimated concentrations for 1992 continue to be relevant for peak values throughout the time period. There are two shallow seasonal waves of similar amplitude; one season spanning early February to late June and the second from late October to late December. All but one measured concentration is within the 2SSD bounds. There is a significant (α=0.05) negative correlation of adjusted concentration with MTFA and weakly negative correlation with STFA. The normalized residuals are mostly centered on zero with slightly positive skew seeming to result from data in 2000. The empirical correlogram 95% confidence limits overlap with the fitted exponential correlation function at time intervals shorter than the average (to the left of the red line) with a CTS of 20.5 days.

Table 50 summarizes the 1- and 21-day estimated concentrations from SEAWAVE-QEX for each year based on the maximum of the 99th percentile concentrations.

Table 50. Maximum of the 99th Percentile 1- and 21-day Concentrations of Chlorpyrifos at USGS-03612500

Year	1-day Conc. (µg/L)	21-day Conc. (µg/L)
1992	0.35	0.23
1993	0.20	0.14
1994	0.32	0.21
1995	0.10	0.068
1996	0.059	0.042
1997	0.036	0.023
1998	0.046	0.033
1999	0.031	0.023
2000	0.040	0.021

Sampling Bias Factor Development

SBFs developed for estimating the 1-day and 21-day average concentrations are shown in **Figure 73** and **Figure 74**, respectively. These figures show the median SBFs across SEAWAVE-QEX chemographs for each site year and sample number category.

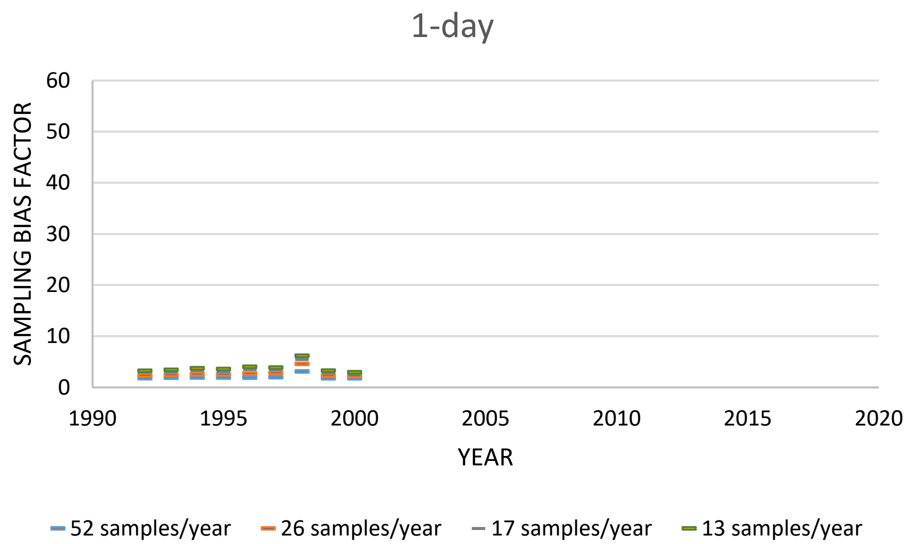

Figure 73. USGS Site 03612500: Sampling Bias Factors for Estimating the Upper Confidence Interval on the 1-day Average Concentration

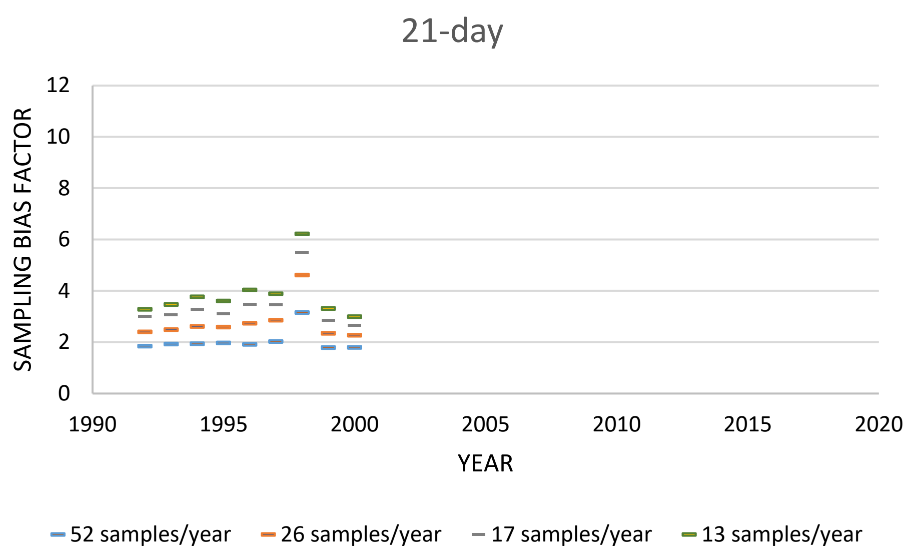

Figure 74. USGS Site 03612500: **Sampling Bias Factors for Estimating the Upper Confidence Interval on the 21-day Average Concentration**

SBFs are consistent across years except 1998. There is nothing notable about the diagnostic plots that would suggest that the estimated concentrations from SEAWAVE-QEX would be out of line for 1998. Like USGS site 03612500, the highest bias factors are driven by measured concentrations. The confidence bounds on the 1998 simulation are tight around the measured concentration. Giving confidence in the estimated SBFs. Again, this calls into question the ability to estimate accurate SBFs using SEAWAVE-QEX when infrequent (i.e., non-daily) sampling is conducted or misses peak occurrence concentrations.

12. USGS-11447360

Site and Sampling Characterization

USGS site 11447360 (Arcade Creek near Del Paso Heights, CA) falls has a 38 mi^2 (98.5 km^2) urban watershed in HUC 18, with 42% impervious surfaces and no cropland (**Figure 75.** Watershed Landcover Characteristics of Sampling Site USGS-11447360). The water travel time is noted to be less than a day to a community water system intake.

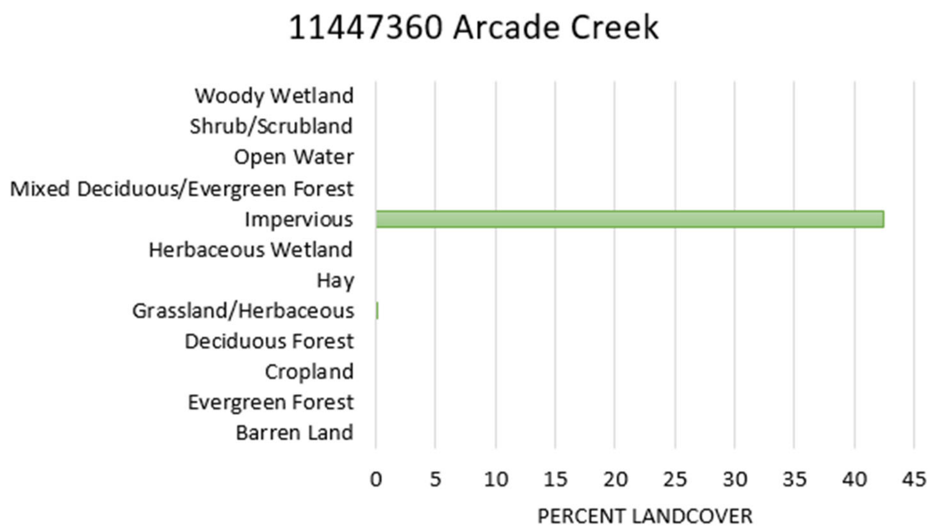

Figure 75. Watershed Landcover Characteristics of Sampling Site USGS-11447360

This site had a total of 57 detections out of 128 samples between 1996 and 2012. Four years of data have 12 or more samples and a detection frequency greater than 25% as shown in **Table 51**. SEAWAVE-QEX analysis is described in the subsection below.

Table 51. USGS-11447360 Data Summary

Year	Number of Samples Collected	Number of Detections	Detection Frequency	Years Simulated in SEAWAVE-QEX	Number of Samples Excluded by SEAWAVE-QEX[1]	Years Sampling Bias Factors Developed
1996	2	2	100%			
1997	24	18	75%	✓	0	✓
1998	4	2	50%	✓	0	✓
1999	0	—	—	✓	0	✓
2000	0	—	—	✓	0	✓
2001	10	6	60%	✓	0	✓
2002	9	2	22%	✓	0	✓
2003	9	4	44%	✓	0	✓
2004	13	6	46%	✓	0	✓
2005	20	8	40%	✓	0	✓
2006	4	3	75%	✓	0	✓
2007	4	0	0%	✓	0	✓
2008	13	6	46%	✓	0	✓
2011	5	0	0%			
2012	11	0	0%			

Gray shading highlights sites with at least 12 samples per year and a detection frequency of 25%
[1] Samples may be excluded by SEAWAVE-QEX when samples are spaced <3 days apart (see SEAWAVE-QEX SOP).

SEAWAVE-QEX Analysis

Data for 1997-2008 were input into SEAWAVE-QEX. Other subsets of years were explored; however, the best fit was determined to be for the period from 1997 to 2008 with the addition of a small constant (0.0012), which resulted in an acceptable model fit of low confidence. The maximum measured concentration at this site is 0.04 μg/L (January 13, 1997).

The 80% error bounds on the estimated maximum are <1 μg/L for each year and span much less than 1 order of magnitude. The seasonal wave is very shallow in an extended season from September to early May, which is the wetter time of year in California, with few measured concentrations outside of the 2SSD bounds. Adjusted concentration has a significant positive correlation with MTFA and weakly positive correlation with STFA. The adjusted concentrations decrease over time (1997 to 2008) and the residuals are centered on zero. The 95% confidence limits on the empirical correlogram overlaps with the fitted exponential correlation function at time intervals less than the average. However, there is more uncertainty at the shortest time intervals (large 95% confidence limits without much overlap). The CTS is 22.6 days and all other model assumptions are satisfied (diagnostic plots are provided in **ATTACHMENT 4**).

Further analysis of the streamflow data indicates that results from SEAWAVE-QEX for this site may not be appropriate to use quantitatively, based on feedback from the SAP. This is because 6.5% of the streamflow values are zero for this site (see **Figure 76**). Therefore, SEAWAVE-QEX chemographs from this site were not used for the development of SBFs.

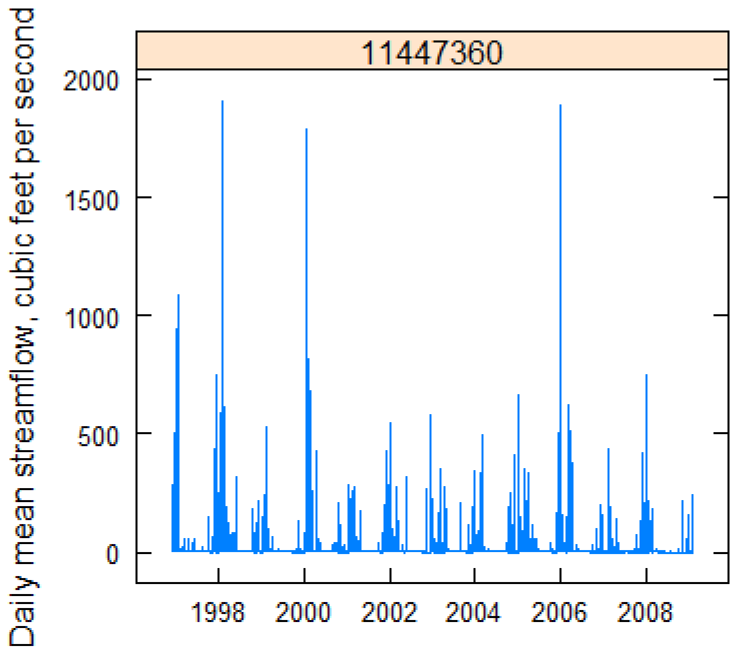

Figure 76. USGS-04193500 Streamflow Data

13. USGS-14201300

Site and Sampling Characterization

USGS site 14201300 (Zollner Creek near Mount Angel, OR) is in a 15.7 mi^2 (40.6 km^2) watershed in HUC 17 with 53% cropland and 35% hay landcover (**Figure 77.** Watershed Landcover Characteristics of Sampling Site USGS-14201300). The time of travel of water from the sampling site to a community water system intake is one day.

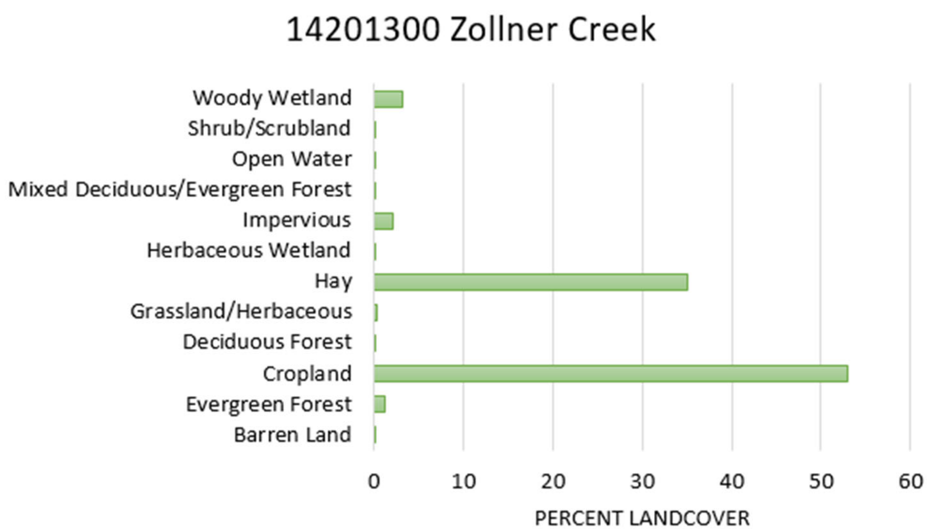

Figure 77. Watershed Landcover Characteristics of Sampling Site USGS-14201300

This site had a total of 205 detections out of 354 samples over 25 years between 1993 and 2019. Twelve years of data have 12 or more samples and a detection frequency greater than 25% (**Table 52**) spanning from 1993-2018.

Table 52. USGS-14201300 Data Summary

Year	Number of Samples Collected	Number of Detections	Detection Frequency	Years Simulated in SEAWAVE-QEX	Number of Samples Excluded by SEAWAVE-QEX[1]	Years Sampling Bias Factors Developed
1993	14	9	64%	✓	8	
1994	11	8	73%	✓	0	
1995	5	3	60%	✓	0	
1996	3	2	67%	✓	0	
1997	9	7	78%	✓	0	
1998	11	5	45%	✓	0	
1999	12	5	42%	✓	0	
2000	11	9	82%	✓	0	
2001	19	14	74%	✓	0	
2002	24	20	83%	✓	0	
2003	13	4	31%	✓	0	
2004	9	8	89%	✓	0	
2005	6	6	100%	✓	0	
2006	4	4	100%	✓	0	
2007	5	5	100%	✓	0	
2008	17	14	82%	✓	0	
2009	0	—	—	✓	n/a	
2010	0	—	—	✓	n/a	
2011	5	5	100%	✓	0	
2012	23	19	83%	✓	0	
2013	24	6	25%	✓	0	
2014	24	9	38%	✓	0	
2015	31	7	23%	✓	0	
2016	24	11	46%	✓	0	
2017	24	13	54%	✓	0	
2018	23	11	48%	✓	0	
2019	3	1	33%		n/a	

Gray shading highlights sites with at least 12 samples per year and a detection frequency of 25%
[1] Samples may be excluded by SEAWAVE-QEX when samples are spaced <3 days apart (see SEAWAVE-QEX SOP).

SEAWAVE-QEX Analysis

The years 1993-2018 were included in the SEAWAVE-QEX modeling with default parameters, resulting in a low confidence fit. Due to the limitations of site relevance due to intermittent flow, additional fits were not pursued further.

The 80% error bounds on the estimated maximum vary in size by year, but all are <1 µg/L and appear to span less than 1 order of magnitude. The seasonal wave is very shallow in an extended season from late September to late June, with few measured concentrations outside of the 2SSD bounds. Adjusted concentration has a weakly positive correlation with MTFA and significantly positive correlation with STFA; however, both diagnostic plots indicate that there are a number of flow days where the flow anomaly does not correlate with concentration at all, typically observed for sites with zeros in the flow data (see **Figure 78**).

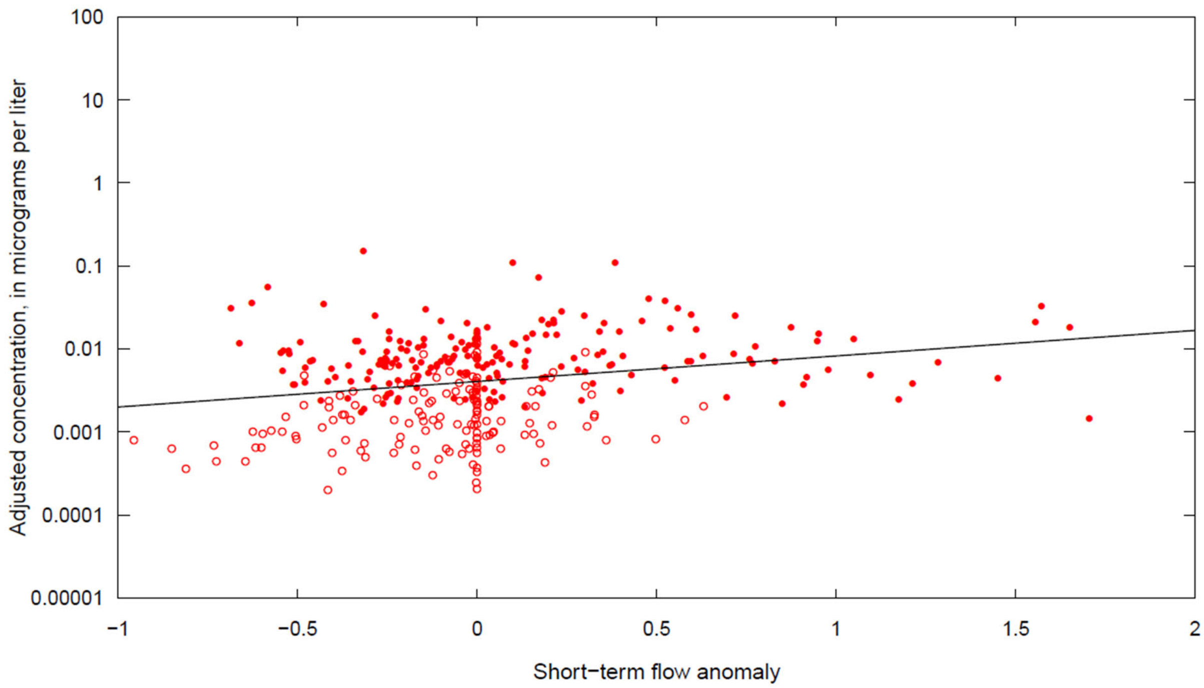

Figure 78. Correlation Between Adjusted Concentration and Short-term Flow Anomaly for USGS-14201300

The adjusted concentrations decrease over time (1993 to 2018) and the residuals are centered on zero with a few individual residuals skewing positive. By year, the residuals skew positive from roughly 2001 to 2008, suggesting that further subsets of the data (e.g., 2012 to 2018) may produce improved results. The 95% confidence limits on the empirical correlogram does not always overlap with the fitted exponential correlation function at time intervals less than the average; when there is not overlap, the empirical correlogram is lower, indicating the potential to overestimate concentrations. The CTS is 43.9 days.

While the flow data for the site does not have measurements of zero, the seasonality of flow (**Figure 79**) and unusual diagnostic plots have decreased confidence in quantitative use of the SEAWAVE-QEX output to an unacceptable level. Therefore, SEAWAVE-QEX chemographs from this site were not used for the development of SBFs.

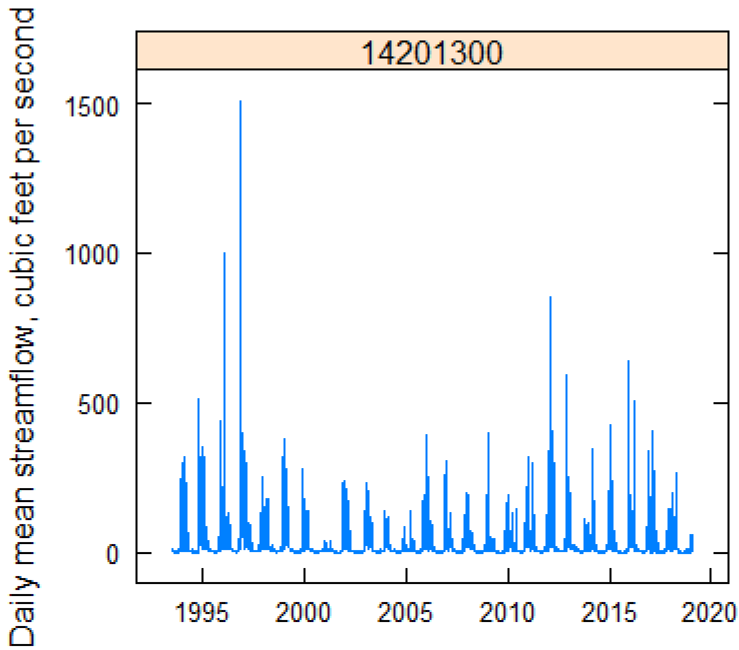

Figure 79. USGS-14201300 Streamflow Data

14. OREGONDEQ-32010-ORDEQ

Site and Sampling Characterization

OREGONDEQ-32010-ORDEQ sampling site (West Prong Little Walla Walla River south of Stateline Road, OR) is in a 24.1 mi^2 (62.3 km^2) watershed in HUC 17 with 55% evergreen forest, 14.5% grassland, 12% cropland and <1% hay landcover (**Figure 80.** Watershed Landcover Characteristics of Sampling Site OREGONDEQ-32010-ORDEQ). This sample site is located upstream of two community water system intakes. Based on flow data, this site is within a 2-day travel time of one community water system intake and within in a 3-day travel time of a second community water system intake.

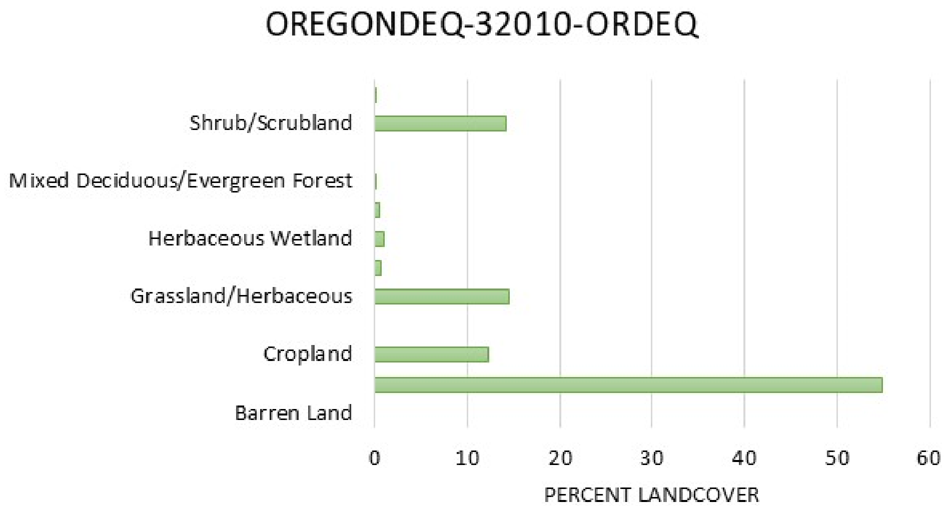

Figure 80. Watershed Landcover Characteristics of Sampling Site OREGONDEQ-32010-ORDEQ

A summary of the data collected for OREGONDEQ-32010-ORDEQ is provided in **Table 53**. Sample collection began in 2005 and continues today. Between 9 and 15 samples have been collected each year. Detection frequencies at this site are high in most years. All quantifiable detections at this site occurred in the months of March or April (**Figure 81**).

Table 53. OREGONDEQ-32010-ORDEQ Data Summary

Year	Number of Samples Collected	Number of Detections	Detection Frequency
2005	15	6	40%
2006	14	5	36%
2007	10	3	30%
2008	12	6	50%
2009	14	3	21%
2010	10	2	20%
2011	10	1	10%
2012	10	3	30%
2013	11	1	9%
2014	11	2	18%
2015	13	1	8%
2016	12	2	17%
2017	12	2	17%
2018	10	4	40%
2019	9	0	0%

Gray shading highlights sites with at least 12 samples per year and a detection frequency of 25%

[1] Flow data or alternatively suitable covariate data are not available for SEAWAVE-QEX analysis.

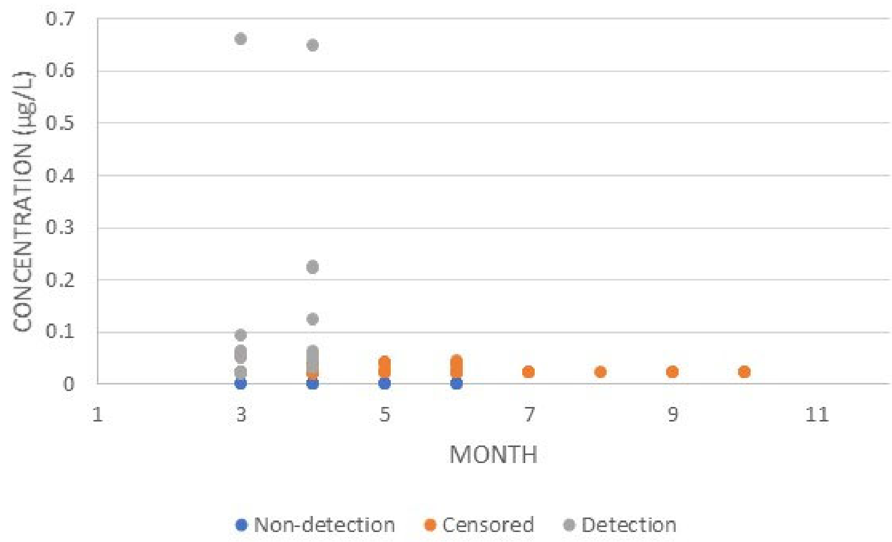

Figure 81. OREGONDEQ-32069-ORDEQ Monthly Summary

Sampling Bias Factor Application

The maximum 1- or 21-day sampling bias factor SBFs for the respective time periods (i.e., 1987-2012 or 2005-2012) were multiplied by the by the maximum measured concentration (1-day) or the maximum estimated (log-linear interpolated) 21-day average concentration. The results are shown in **Table 57**.

Table 54. Sampling Bias Factor Analysis Summary for OREGONDEQ-32010-ORDEQ

Year	Number of samples	Maximum Measured Concentration µg/L	Maximum Imputed 21-day Average Concentration	Maximum Sampling Bias Factor		Sampling Bias Factor Adjusted Upper Bound Concentration µg/L	
				1-day	21-day	1-day	21-day
2009	14	0.65	0.14	54.8 (22.2)	11.5 (8.9)	35.6 (14.41)	1.6 (1.2)
Bracketed values are for sub-set of SBFs for years 2005-2015							

15. OREGONDEQ-32068-ORDEQ

Site and Sampling Characterization

OREGONDEQ-32068-ORDEQ sampling site (Noyer Creek at Hwy 212, St. Paul Lutheran Church (North Fork, Deep Creek, Clackamas, OR) is in a 33.3 mi^2 (86.3 km^2) watershed in HUC 17 with 7.1% evergreen forest, 8.4% cropland, 39.3% hay landcover and 9.7% impervious (**Figure 82.** Watershed Landcover Characteristics of Sampling Site OREGONDEQ-32068-ORDEQ). This sample site is located upstream of 5 community water system intakes. Based on flow data, all 5 of these community water system intakes are located within a day's travel time from the monitoring site.

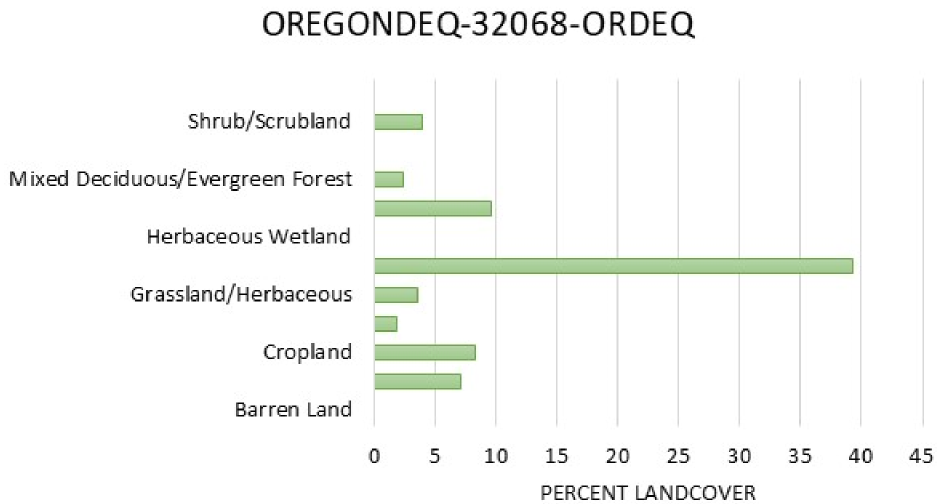

Figure 82. Watershed Landcover Characteristics of Sampling Site OREGONDEQ-32068-ORDEQ

A summary of the data collected for OREGONDEQ-32068-ORDEQ is provided in **Table 55**. Sample collection at this site began in 2005 and is ongoing. Detection frequencies are high with between 6 and 16 samples collected per year. With the highest detection frequency occurring in 2016. Quantifiable detections at this site occur throughout the year, mainly March through December with peak measured concentrations occurring in May and October.

Table 55. OREGONDEQ-32068-ORDEQ Data Summary

Year	Number of Samples Collected	Number of Detections	Detection Frequency
2005	12	5	42%
2006	16	6	38%
2007	14	5	36%
2008	10	1	10%
2009	9	4	44%
2010	6	2	33%
2011	8	2	25%
2012	11	2	18%
2013	15	4	27%
2014	13	0	0%
2015	15	2	13%
2016	13	9	69%
2017	14	4	26%
2018	13	4	31%
2019	8	1	13%
Gray shading highlights sites with at least 12 samples per year and a detection frequency of 25% [1] Flow data or alternatively suitable covariate data are not available for SEAWAVE-QEX analysis.			

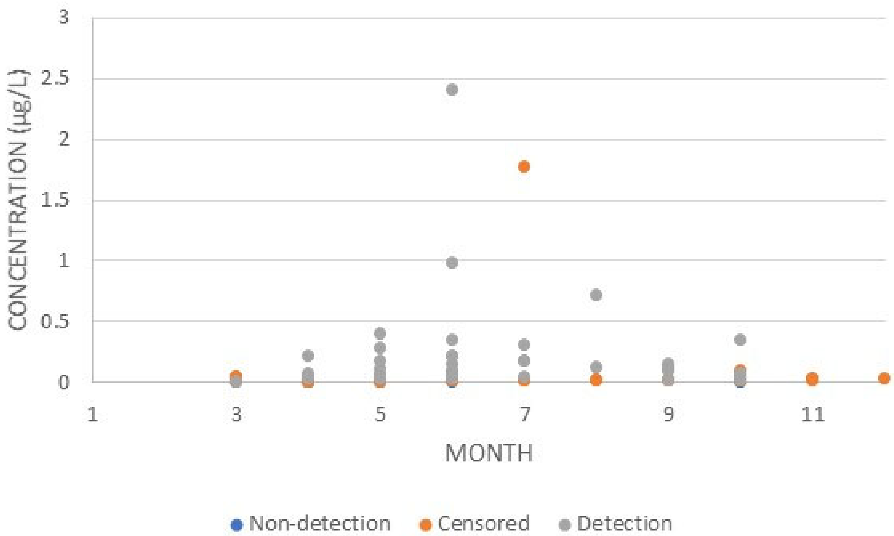

Figure 83. OREGONDEQ-32068-ORDEQ Monthly Summary

Sampling Bias Factor Application

The maximum 1- or 21-day sampling bias factor SBFs for the respective time periods (i.e., 1987-2012 or 2005-2012) were multiplied by the by the maximum measured concentration (1-day) or the maximum estimated (log-linear interpolated) 21-day average concentration. The results are shown in **Table 56**.

Table 56. Sampling Bias Factor Analysis Summary for OREGONDEQ-32068-ORDEQ

Year	Number of samples	Maximum Measured Concentration µg/L	Maximum Imputed 21-day Average Concentration	Maximum Sampling Bias Factor		Sampling Bias Factor Adjusted Upper Bound Concentration µg/L	
				1-day	21-day	1-day	21-day
2007	14	2.4	1.7	54.8 (22.2)	11.5 (8.9)	131.5 (53.3)	19.3 (14.9)
2015	15	1.8	0.7	54.8 (22.2)	11.5 (8.9)	97.0 (39.3)	7.6 (5.6)
2016	13	0.7	0.6	54.8 (22.2)	11.5 (8.9)	39.6 (16.0)	6.5 (5.0)
Bracketed values are for sub-set of SBFs for years 2005-2015							

16. OREGONDEQ-32069-ORDEQ

Site and Sampling Characterization

OREGONDEQ-32069-ORDEQ sampling site (NF Deep Creek at Springwater trail, Boring, between 2nd and 3rd towers from trailhead (Clackamas, OR)) is in a 19.5 mi^2 (50.6 km^2) watershed in HUC 17 with 7.1% evergreen forest, 27.3% cropland and 30.3% hay landcover (**Figure 84.** Watershed Landcover Characteristics of Sampling Site OREGONDEQ-32069-ORDEQ). This sample site is located upstream of 5 community water system intakes. All community water system intakes are located within a day's travel time of the monitoring site. These are the same community water system intakes downstream of OREGONDEQ-32068-ORDEQ.

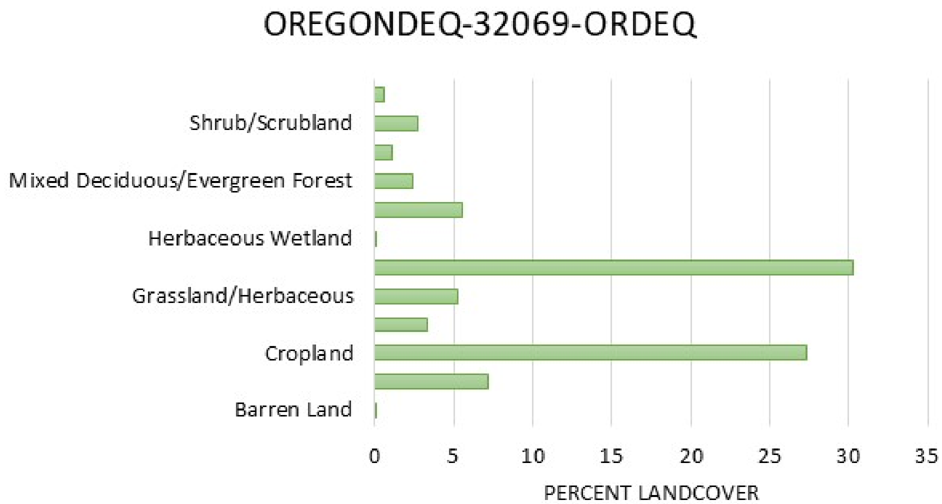

Figure 84. Watershed Landcover Characteristics of Sampling Site OREGONDEQ-32069-ORDEQ

A summary of the data collected for OREGONDEQ-32069-ORDEQ is provided in **Table 57**. Sample collection began in 2005; however, the last year of sampling collection at this site ended in 2011. Sample frequency ranged from 5 to 16 per year. Detection frequency was high in those years with the most samples collected. Quantifiable detections at this site occur throughout the year except for January and February. The maximum measured concentrations occurred in May and October (**Figure 85**).

Table 57. OREGONDEQ-32069-ORDEQ Data Summary

Year	Number of Samples Collected	Number of Detections	Detection Frequency
2005	12	8	67%
2006	16	1	6%
2007	13	7	54%
2008	9	1	11%
2009	9	0	0%
2010	5	1	20%
2011	8	0	0%

Gray shading highlights sites with at least 12 samples per year and a detection frequency of 25%

[1] Flow data or alternatively suitable covariate data are not available for SEAWAVE-QEX analysis.

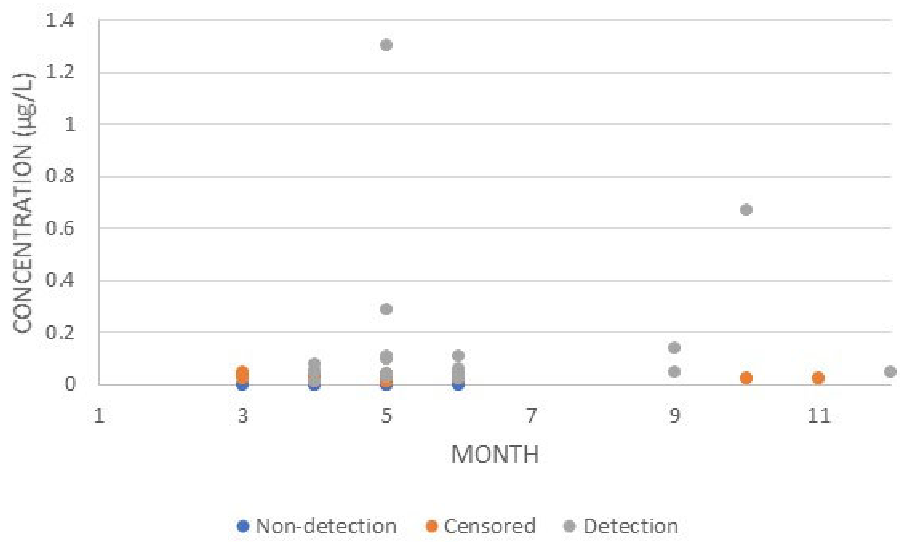

Figure 85. OREGONDEQ-32069-ORDEQ Monthly Summary

Sampling Bias Factor Application

The maximum 1- or 21-day sampling bias factor SBFs for the respective time periods (i.e., 1987-2012 or 2005-2012) were multiplied by the by the maximum measured concentration (1-day) or the maximum estimated (log-linearly interpolated) 21-day average concentration. The results are shown in **Table 58**.

Table 58. Sampling Bias Factor Analysis Summary for OREGONDEQ-32069-ORDEQ

Year	Number of samples	Maximum Measured Concentration µg/L	Maximum Imputed 21-day Average Concentration	Maximum Sampling Bias Factor		Sampling Bias Factor Adjusted Upper Bound Concentration µg/L	
				1-day	21-day	1-day	21-day
2007	13	1.3	0.4	54.8 (22.2)	11.5 (8.9)	71.2 (28.9)	4.8 (3.7)
Bracketed values are for sub-set of SBFs for years 2005-2015							

17. OREGONDEQ-34235-ORDEQ

Site and Sampling Characterization

OREGONDEQ-34235-ORDEQ sampling site (Middle Cozine at Old Sheridan Road (McMinnville, OR)) is in a 73.5 mi^2 (190.3 km^2) watershed in HUC 17 with 2.8% evergreen forest, 35.7% cropland, 9.4% hay landcover and 11.1% impervious (**Figure 86.** Watershed Landcover Characteristics of Sampling Site OREGONDEQ-34235-ORDEQ). This sample site is located upstream of 2 community water system intakes. Both community water system intakes have a 1-day travel time between the sampling site and the intake.

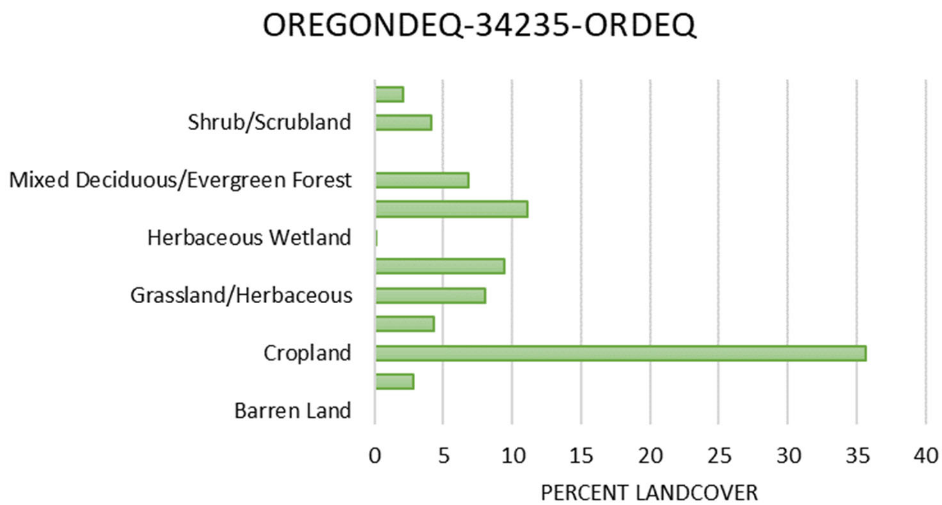

Figure 86. Watershed Landcover Characteristics of Sampling Site OREGONDEQ-34235-ORDEQ

A summary of the data collected for OREGONDEQ-34235-ORDEQ is provided in **Table 59**. Sample collection at this site began in 2007 and is ongoing. Detection frequencies are much lower at this site compared to other Oregon sites. Sample collection ranged between 7 and 15 samples per year. With the highest detection frequency occurring in 2017. Quantifiable detections at this site occur throughout the growing season (**Figure 87)**. The highest sample value for this site is for a censored sample collected on August 10, 2018. Additional information on these reported values was solicited but not additional information became available as of the writing of this assessment.

Table 59. OREGONDEQ-34235-ORDEQ Data Summary

Year	Number of Samples Collected	Number of Detections	Detection Frequency
2007	14	0	0%
2008	10	0	0%
2009	7	0	0%
2010	6	0	0%
2011	8	0	0%
2012	12	2	17%
2013	15	0	0%
2014	14	0	0%
2015	15	0	0%
2016	14	0	0%
2017	13	3	23%
2018	13	1	8%
2019	8	0	0%

Gray shading highlights sites with at least 12 samples per year and a detection frequency of 25%
[1] Flow data or alternatively suitable covariate data are not available for SEAWAVE-QEX analysis.

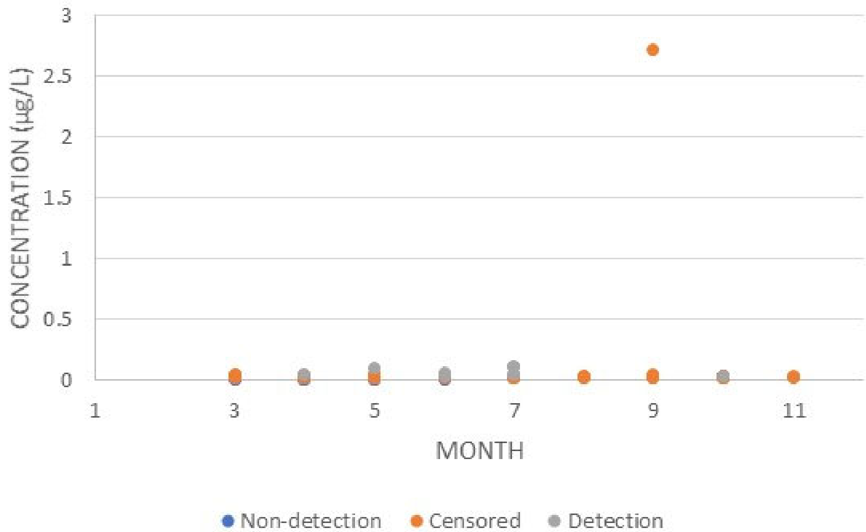

Figure 87. OREGONDEQ-34235-ORDEQ Monthly Summary

Sampling Bias Factor Application

The maximum 1- or 21-day sampling bias factor SBFS for the respective time periods (i.e., 1987-2012 or 2005-2012) were multiplied by the by the maximum measured concentration (1-day) or the maximum estimated (log-linearly interpolated) 21-day average concentration. The results are shown in **Table 60**.

Table 60. Sampling Bias Factor Analysis Summary for OREGONDEQ-34235-ORDEQ

Year	Number of samples	Maximum Measured Concentration µg/L	Maximum Imputed 21-day Average Concentration	Maximum Sampling Bias Factor		Sampling Bias Factor Adjusted Upper Bound Concentration µg/L	
				1-day	21-day	1-day	21-day
2018	13	2.72[1]	1.4	54.8 (22.2)	11.5 (8.9)	74.5 (30.2)	16.4 (12.7)
Bracketed values are for sub-set of SBFs for years 2005-2015 [1] value is a censored concentration.							

18. OREGONDEQ-37639-ORDEQ

Site and Sampling Characterization

OREGONDEQ-37639-ORDEQ sampling site (West Fork Palmer Creek at SE Palmer Creek Road) is in a 73.5 mi^2 (465.2 km^2) watershed in HUC 17 with 56.8% cropland, and 26.3% hay landcover (**Figure 88.** Watershed Landcover Characteristics of Sampling Site OREGONDEQ-37639-ORDEQ). This sample site is located upstream of 2 community water system intakes. Based on flow data, both community water system intakes are within a 1-day travel time from the monitoring site. These community water systems are the same systems in line with OREGONDEQ-34235-ORDEQ.

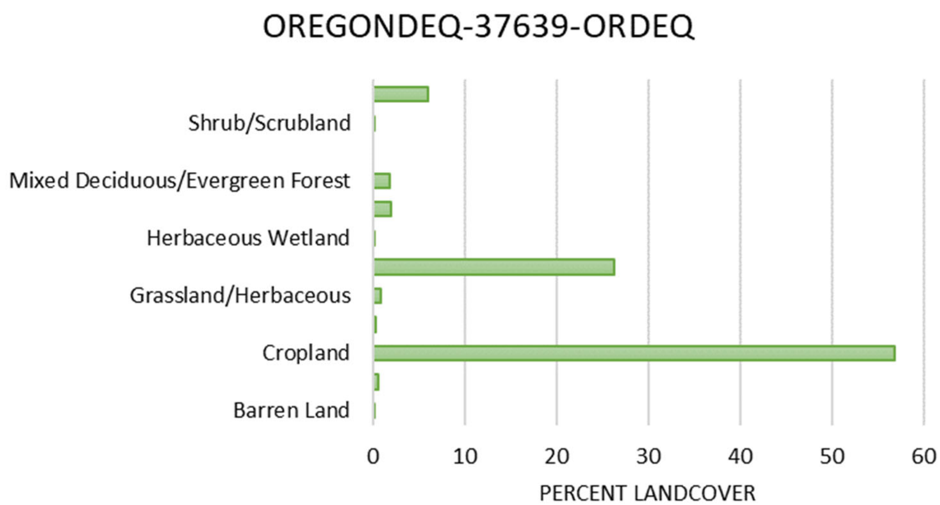

Figure 88. Watershed Landcover Characteristics of Sampling Site OREGONDEQ-37639-ORDEQ

A summary of the data collected for OREGONDEQ-34235-ORDEQ is provided in **Table 61**. Sample collection occurred between 2014 and 2018. Samples number ranged between 13 and 15 while detection frequencies ranged between 7 and 46 percent. With the highest detection frequency occurring in 2017.The highest quantifiable detections at this site occur in April (**Figure 89**).

Table 61. OREGONDEQ-37639-ORDEQ Data Summary

Year	Number of Samples Collected	Number of Detections	Detection Frequency
2014	14	4	29%
2015	15	1	7%
2016	14	2	14%
2017	13	6	46%
2018	13	1	8%
Gray shading highlights sites with at least 12 samples per year and a detection frequency of 25% [1] Flow data or alternatively suitable covariate data are not available for SEAWAVE-QEX analysis.			

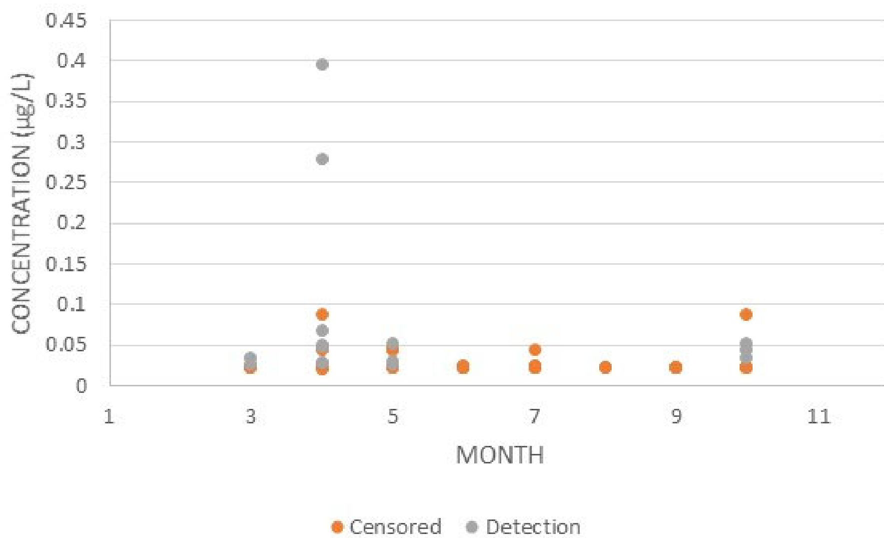

Figure 89. OREGONDEQ-37639-ORDEQ Monthly Summary

Sampling Bias Factor Application

The maximum 1- or 21-day sampling bias factor SBFs for the respective time periods (i.e., 1987-2012 or 2005-2012) were multiplied by the by the maximum measured concentration (1-day) or the maximum estimated (log-linearly interpolated) 21-day average concentration. This site was identified for additional analysis using the 1-day maximum measured concentration when estimating upper confidence bound for the 21-day average. Estimation on the 21-day average concentration for estimation of the upper bound are shown in **Table 62**.

Table 62. Sampling Bias Factor Analysis Summary for OREGONDEQ-34235-ORDEQ

Year	Number of samples	Maximum Measured Concentration µg/L	Maximum Imputed 21-day Average Concentration	Maximum Sampling Bias Factor		Sampling Bias Factor Adjusted Upper Bound Concentration µg/L	
				1-day	21-day	1-day	21-day
2014	14	0.09	0.22 (0.20)	-	2.5 (2.3)	-	23. (1.8)
Bracketed values are for sub-set of SBFs for years 2005-2015							