SERA TR-056-11-02-02b

Chlorpyrifos:
WorksheetMaker Workbook Documentation
Final Report

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REVISION NOTE

This report is a modification to SERA TR-056-1-02-01a, Chlorpyrifos: WorksheetMaker Workbook Documentation: PARTIAL (pending Forest Service input) which was sent to the Forest Service with queries on November 26, 2014.

Changes to this report are based on the following comments from the Forest Service:

Notes from John Justin and Shawna Bautista in an EXCEL workbook (**Mancozeb SAMPLE Workbook-SB-JJ.xlsm**) via an email from Shawna Bautista dated 6/2/2015.

Comments from John Justin in a Microsoft Word file (**Query Template for WSM Input Effort.docx**) via an email from Shawna Bautista dated 12/30/2014.

The most recent set of comments (i.e., the EXCEL workbook from 6/2/2015) is given precedence when the feedback is inconsistent.

ACRONYMS, ABBREVIATIONS, AND SYMBOLS

ACGIH	American Conference of Governmental Industrial Hygienists
AChE	acetylcholine
AEL	adverse-effect level
a.i.	active ingredient
a.k.a.	also known as
a.s.	active substance
AOEL	acceptable occupational exposure limit
ATSDR	Agency for Toxic Substances and Disease Registry
BCF	bioconcentration factor
bw	body weight
calc	calculated value
CBI	confidential business information
ChE	cholinesterase
CI	confidence interval
cm	centimeter
CNS	central nervous system
COC	crop oil concentrates
DAA	days after application
DAT	days after treatment
DER	data evaluation record
d.f.	degrees of freedom
EC	emulsifiable concentrate
EC_x	concentration causing X% inhibition of a process
EC_{25}	concentration causing 25% inhibition of a process
EC_{50}	concentration causing 50% inhibition of a process
ECOTOX	ECOTOXicology (database used by U.S. EPA/OPP)
EFED	Environmental Fate and Effects Division (U.S. EPA/OPP)
ERA	ecological risk assessment
ExToxNet	Extension Toxicology Network
F	female
FH	Forest Health
FIFRA	Federal Insecticide, Fungicide and Rodenticide Act
FIRST	FQPA Index Reservoir Screening Tool
FQPA	Food Quality Protection Act
g	gram
GLP	Good Laboratory Practices
ha	hectare
HED	Health Effects Division (U.S. EPA/OPP)
HHRA	human health risk assessment
HIARC	Hazard Identification and Assessment Review Committee (part of U.S. EPA/OPP/HED)
HQ	hazard quotient
HRAC	Herbicide Resistance Action Committee
IARC	International Agency for Research on Cancer
IRED	Interim Reregistration Eligibility Decision
IRIS	Integrated Risk Information System

k_a	absorption coefficient
k_e	elimination coefficient
kg	kilogram
$K_{o/c}$	organic carbon partition coefficient
$K_{o/w}$	octanol-water partition coefficient
K_p	skin permeability coefficient
L	liter
lb	pound
LC_{50}	lethal concentration, 50% kill
LD_{50}	lethal dose, 50% kill
LOAEL	lowest-observed-adverse-effect level
LOC	level of concern
LR_{50}	50% lethal response [EFSA/European term]
m	meter
M	male
mg	milligram
mg/kg/day	milligrams of agent per kilogram of body weight per day
mL	milliliter
mM	millimole
mPa	millipascal, (0.001 Pa)
MITC	methyl isothiocyanate
MOS	margin of safety
MRID	Master Record Identification Number
MSDS	material safety data sheet
MSO	methylated seed oil
MW	molecular weight
NOAEL	no-observed-adverse-effect level
NOEC	no-observed-effect concentration
NOEL	no-observed-effect level
NOS	not otherwise specified
N.R.	not reported
OPP	Office of Pesticide Programs
ppm	parts per million
RBC	red blood cell
RED	re-registration eligibility decision
RfD	reference dose
SERA	Syracuse Environmental Research Associates
TCP	3,5,6-trichloro-2-pyridinol
T.G.I.A.	Technical grade active ingredient
UF	uncertainty factor
U.S.	United States
USDA	U.S. Department of Agriculture
U.S. EPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
WHO	World Health Organization

1. INTRODUCTION

1.1. General Information

This document supports the development of a WorksheetMaker EXCEL workbook for the subject pesticides. As detailed in SERA (2011a), WorksheetMaker is a utility that automates the generation of EXCEL workbooks that accompany Forest Service risk assessments, and these EXCEL workbooks are typically generated in the development of Forest Service risk assessments (SERA 2014a).

The development of full Forest Service risk assessments, however, is resource intensive. For some pesticides used in only relatively small amounts and/or only in few locations, the development of full Forest Service risk assessments is not feasible. Nonetheless, the Forest Service may be required to develop risk analyses supported by WorksheetMaker EXCEL workbooks. To meet this need, an MS Word utility was developed to facilitate the addition of pesticides and pesticide formulations into the Microsoft Access database used by WorksheetMaker (SERA 2011b). With this addition, WorksheetMaker can be used to generate EXCEL workbooks typical of those that accompany Forest Service risk assessments.

The current document is designed to serve as documentation for the application of this general method for the pesticide discussed in Section 1.2. The major difference between this approach to using WorksheetMaker and the typical use of WorksheetMaker in the development of Forest Service risk assessments involves the level of documentation and the sources used in developing the documentation. While standard Forest Service risk assessments involve a relatively detailed review and evaluation of the open literature and publically available documents from the U.S. EPA, as discussed further in Section 1.2, the current assessment relies primarily on secondary sources with minimal independent evaluation of the data.

1.2. Chemical Specific Information

1.2.1. Information Sources

The primary motivation for the development of this report involves the assessment of pesticide use at the J. Herbert Stone Nursery in Central Point, Oregon. While reference to this Forest Service facility is made in the current report as needed, the design of this report is intended to support other activities within the Forest Service with only minor modification—i.e., changes in input parameters related to pesticide use in WorksheetMaker.

The current document concerns chlorpyrifos. Most of the information on chlorpyrifos was identified at the U.S. EPA's Pesticide Chemical Search website (http://iaspub.epa.gov/apex/pesticides/f?p=CHEMICALSEARCH:1:5025550978400::NO:1::) using the search term "Chlorpyrifos". Chlorpyrifos is a well-studied insecticide. U.S. EPA's Pesticide Chemical Search website lists 22 regulatory action documents on chlorpyrifos, 453 cleared science reviews, and five E-Dockets for the period from 2007 to 2012. TOXLINE (http://toxnet.nlm.nih.gov) contains 8401 open literature citations for chlorpyrifos.

For the current documentation, information on human health effects is taken primarily from the preliminary human health risk assessment for the registration review of chlorpyrifos (U.S.

EPA/OPP/HED 2011a). The Interim Reregistration Eligibility Decision for Chlorpyrifos (U.S. EPA/OPP 2002), the EPA's human health risk assessment for the RED (U.S. EPA/OPP/HED 2000), and the EPA's assessment of human health effects related to volatilization (U.S. EPA/OPP/HED 2013) were also consulted. Information on ecological effects is taken from the EPA's assessment of the potential effects of chlorpyrifos on threatened and endangered species (U.S. EPA/OPP/EFED 2009). Information on chemical and physical properties and the environmental fate of chlorpyrifos is taken from the EPA documents, as discussed further in Section 2.

1.2.2. Forest Service Use at JH Stone Nursery

The JH Stone Nursery specified two formulations of chlorpyrifos—i.e., DuraGuard ME (20.0% chlorpyrifos) for greenhouse applications or Dursban 50W (50.0% chlorpyrifos) for field grown crops. The application rate for field crops is specified as 2 lbs./acre with an application volume of 30 gallons per acre. A total of 5 acres will be treated each year with single applications involving between 0.5 and 2.5 acres. The Forest Service also indicated that up to 5 applications may be made at an application interval as short as 14 days.

Dursban 50W may be applied by backpack (directed foliar) or tractor mounted spray boom. The application rate of 2 lbs/acre appears to pertain to the Dursban 50W formulation. Thus, the application rate in terms of a.i. is taken as 1 lb a.i./acre.

The JH Stone Nursery specified that personal protective equipment will include coveralls over long sleeve shirt and pants, chemical resistant gloves, chemical resistant apron when mixing or loading, chemical resistant footwear plus socks, and a NIOSH approved respirator with any N,R,P, or HE filter. This array of personal protective equipment is required on the product labels for Dursban 50W and DuraGuard ME.

As noted in Section 3.2.1, a key input for worker exposure assessments is the amount of the pesticide that a worker would handle in 1 day. The Forest Service indicated (in the annotated workbook from 6/2/2015) that the maximum exposure would involve treating 2.5 acres per hour for 2 hours of application. Thus, the maximum amount handled by a worker would be 5 lbs a.i./day [1 lb a.i./acre x 2.5 acres/hour x 2 hours/day]. Applications could be made with either tractor mounted spray booms or directed foliar backpack spray. Modifications to the workbook necessary to assess backpack applications are given in Section 3.2.1.

The WorksheetMaker workbook that accompanies this risk assessment is based on an October 7, 2008 label for Dursban 50W obtained from Syngenta web site (http://www.syngentacropprotection.com/pdf/labels/daconilweastik0100.pdf). Based on information from the Forest Service (the illustration in **JH Stone Nursery Information-v3 Shawna Aug 21.docx**), the JH Stone nursery is about 220 acres in size. Using a 5-acre treated area, a proportion of about 0.023 [5 acres ÷ 220 acres ≈ 0.0227] of the nursery area would be treated. As discussed further in Section 3.2.2, this proportion is used to modify the water contamination rates.

2. CHEMICAL/PHYSICAL PROPERTIES

Chlorpyrifos has been in use in the United States since 1965 (U.S. EPA/OPP 2006). This insecticide was developed by Dow Chemical Company, and current formulations of Dursban and Lorsban are currently registered to Dow AgroSciences. Chlorpyrifos is off-patent, and formulations such as DuraGuard are supplied by other manufacturers. From 1987 to 1998, the annual use of chlorpyrifos in the United States ranged from 21 to 24 million pounds with about 11 million pounds used in non-agricultural sites (U.S. EPA/OPP 2006). Chlorpyrifos has been available in over 400 formulations (U.S. EPA/OPP 2006); however, only 137 formulations are currently active in the United States (Kegley et al. 2014). The U.S. EPA registration review program operates on a 15-year cycle. Chlorpyrifos has been under registration review since 2009 and is not scheduled for completion until 2015.

Table 1 summarizes the chemical and physical properties of chlorpyrifos. As discussed further in Section 3 (Human Health) and Section 4 (Ecological Effects), chlorpyrifos is an inhibitor of acetylcholinesterase (e.g., U.S. EPA/OPP 2009). As reviewed in U.S. EPA/OPP/EFED (2009), aerobic and anaerobic metabolism is the major route of degradation for chlorpyrifos in the environment. As summarized in Table 1, the aerobic soil half-lives for chlorpyrifos range from 11 to 180 days and the anaerobic soil half-lives range from 39 to 51 days. While the ranges of half-lives, particularly those for aerobic soil metabolism may be viewed as somewhat wide, high variability in rates of soil metabolism are common and often reflect differences in the nature and density of microbial populations in the soil. As also summarized in Table 1, the data on the binding of chlorpyrifos to soils also display substantial variability with K_{oc} values ranging from 360 to 31,000 mL/g. As discussed further in Section 3.2.2, the variability in soil binding and soil metabolism are the primary factors in the estimates of surface water concentrations of chlorpyrifos. No data are available on the aquatic metabolism of chlorpyrifos. Following the standard approach used by U.S. EPA/OPP, the rates of aerobic and anaerobic aquatic metabolism are estimated as twice the half-lives for the aerobic and anaerobic soil half-lives. Chlorpyrifos is relatively lipophilic with reported K_{ow} values of about 50,000 to 90,000. As with most lipophilic compounds, chlorpyrifos will bioconcentrate in fish and has a reported BCF of about 2700 in rainbow trout.

As also summarized in Table 1, the major environmental metabolite of chlorpyrifos is 3,5,6-trichloro-2-pyridinol (TCP). TCP is also a major environmental metabolite of triclopyr that is discussed extensively in the Forest Service risk assessment on triclopyr (SERA 2011). If chlorpyrifos and triclopyr are applied in the same location, the impact of both pesticides on the formation of TCP may require additional consideration. Unlike the case with triclopyr, chlorpyrifos is much more toxic than TCP and is not a metabolite of major concern in applications of chlorpyrifos in terms of either human health (U.S. EPA/OPP/HED 2000, p. 2) or ecological effects (U.S. EPA/OPP/EFED 2009, p. 10). Consequently, TCP is not addressed further in the current document.

3. HUMAN HEALTH

3.1. Hazard Identification

While full Forest Service risk assessments provide a detailed discussion of the available toxicity data on the pesticide under consideration, this approach is not taken in the current document, in the interest of economy.

Chlorpyrifos acts by reversibly inhibiting acetylcholinesterase (AChE). Malathion is another insecticide that inhibits AChE, and the Forest Service risk assessment on malathion (SERA 2008) provides a relatively detailed discussion of biological mechanisms and toxicity of AChE inhibition. In short, acetylcholine is a neurotransmitter, a compound that facilitates transmission of neural impulses between nerve cells as well as the activation of muscle and other effector cells by nerve cells. Normally, the acetylcholine is rapidly degraded to inactive agents (acetate ion and choline) by AChE. Inhibitors of AChE lead to the accumulation of acetylcholine in synapses (i.e., spaces between cells) which causes a continuous stimulation of the cholinergic system and may lead to paralysis because of nerve cell fatigue. Depending on the degree of AChE inhibition, a broad spectrum of clinical effects may be induced ranging from mild signs of toxicity (e.g., salivation or lacrimation) to convulsions and death (SERA 2008).

As discussed in U.S. EPA/OPP/HED (2000), the inhibition of acetylcholinesterase is a mechanism of action common to numerous insecticides (e.g., azinphos methyl, chlorpyrifos-methyl, diazinon, dichlorvos, dicrotophos, dimethoate, disulfoton, methamidophos, methidathion, monocrotophos, oxydemeton methyl, phorate, phosmet, and pirimiphos-methyl). As also detailed in U.S. EPA/OPP/HED (2000), the EPA assesses cumulative effects of inhibitors of AChE in situations where exposures to multiple AChE inhibitors may occur. Based on a list of pesticides used at the J. Herbert Stone Nursery (i.e., **JHSN_Pesticide_List_REVISED-08_07_14 (1).xlsx**), chlorpyrifos is the only AChE inhibitor used at this nursery. Consequently, there is no apparent need to assess cumulative effects involving the inhibition of AChE.

3.2. Exposure Assessment

3.2.1. Workers

As discussed in SERA (2014b), the Forest Service risk assessments use a standard set of worker exposure rates (Table 14 in SERA 2014b). As discussed in SERA (2014b), worker exposure rates for directed foliar applications are also used for greenhouse applications, and the rates are adjusted as necessary for dermal absorption.

U.S. EPA/OPP/HED (2000, p. 3) uses a dermal absorption rate of 3% for chlorpyrifos. This rate is intended to reflect the proportion of chlorpyrifos absorbed over an 8-hour work day and, therefore, corresponds to a first-order dermal absorption rate coefficient (k_a) of 0.00375 hour^{-1} [0.03 ÷ 8 hours]. As detailed in Worksheet B03b of the WorksheetMaker workbook that accompanies this report, the central estimate of the first-order dermal absorption rate based on algorithms commonly used in Forest Service risk assessments (SERA 2014a, Section 3.1.3.2.2) is about 0.0041 hour^{-1} with a 95% confidence interval of about 0.0015 to 0.012 hour^{-1}. Rounding to one significant digit, the rate of 0.00375 $hour^{-1}$ and 0.0041 $hour^{-1}$ are identical—i.e., 0.004 $hour^{-1}$. Consequently, the first-order dermal absorption rates from Worksheet B03b are used in the current analysis to reflect the underlying uncertainty in the estimates using the 95% confidence interval. These first-order dermal absorption rates of 0.0041 $hour^{-1}$ (0.0015 to 0.012 $hour^{-1}$) from Worksheet B03b are entered into Worksheet B01 and are used for all exposure assessments that require estimates of the first-order dermal absorption rates.

For general exposures to workers, estimates of worker exposure rates are required for ground broadcast applications of Dursban 50W (Section 1.2.2). As discussed in Section 2, the WorksheetMaker workbook that accompanies this risk assessment is based on ground broadcast applications. As detailed in Table 14 of SERA (2014b), the reference chemical for this application method is 2,4-D with a first-order dermal absorption rate of 0.00066 $hour^{-1}$. As discussed above, central estimates of the dermal absorption rates used for chlorpyrifos in this analysis are 0.0015 $hour^{-1}$. The central estimate of the worker exposure rate for ground broadcast applications of 2,4-D is 0.0001 with a 95% prediction interval of 0.000002 to 0.005 mg/kg bw per lb a.i. handled. To account for differences in the estimated dermal absorption of chlorpyrifos and 2,4-D, the worker exposure rates for 2,4-D are multiplied by the ratio of the dermal absorption rate coefficient for chlorpyrifos to the corresponding value for 2,4-D—i.e., 0.0014 ÷ 0.00066 ≈ 2.1212…. These calculations are detailed in Table 2-1. Following the convention in SERA (2014b), the resulting worker exposure rates are rounded to one significant digit, and the occupational exposure rates for ground broadcast applications of chlorpyrifos are estimated as 0.0002 (0.000004 to 0.01) mg/kg bw per lb handled. These worker exposure rates are entered in Worksheet C01 of the EXCEL workbook that accompanies this risk assessment. Note that Table 2 is a compound table. Table 2-1 gives the worker exposure rates for ground broadcast applications. Table 2-2 gives the worker exposure rates for directed foliar backpack applications as discussed further below.

The Forest Service indicated that Dursban 50W may be applied by backpack applications and DuraGuard ME may be used in greenhouse applications. As discussed in SERA (2014b, Section 3.2.3.4.2), worker exposure rates for greenhouse applications may be based on the rates for backpack applications. As a convenience for the worker exposure assessment of backpack and greenhouse applications, Table 2-2 gives the derivation of worker exposure rates for backpack applications. As detailed in Table 14 of SERA (2014b), three reference chemicals with corresponding worker exposure rates are given for backpack and greenhouse applications—i.e., glyphosate (k_a = 0.00041 $hour^{-1}$), 2,4-D (k_a = 0.00066 $hour^{-1}$), and triclopyr BEE (k_a = 0.0031 $hour^{-1}$). To minimize extrapolation, triclopyr BEE is used as the reference chemical for chlorpyrifos. As noted above, the central estimate of the first-order dermal absorption rate coefficient for chlorpyrifos is taken as 0.0041$hour^{-1}$. The central estimate of the worker exposure rate for triclopyr BEE is 0.01 with a 95% prediction interval of 0.002 to 0.06 mg/kg bw per lb a.i. handled. To account for differences in the estimated dermal absorption of chlorpyrifos and triclopyr BEE, the worker exposure rates are multiplied by the ratio of the dermal absorption rate coefficient for chlorpyrifos to the corresponding value for triclopyr BEE [0.0014 ÷ 0.0031 ≈ 0.4516]. As detailed in Table 2-2, the resulting estimates of the worker exposure rates for chlorpyrifos are about 0.00451 (0.000903 to 0.027096) mg/kg bw per lb handled. Following the convention in SERA (2014b), the resulting worker exposure rates are rounded to one significant digit—i.e., 0.005 (0.0009 to 0.03) mg/kg bw per lb handled.

As discussed in Section 1.2.2, the Forest Service indicated that workers will handle up to 5 lbs a.i./day. This amount is used in Worksheets C01 to estimate doses for workers.

In addition to general exposures, four standard accidental exposure scenarios discussed in SERA (2014a, Section 3.2.2.2) are also considered, and they are detailed in Worksheets C02a,b and C03a,b.

3.2.2. General Public

As detailed in SERA (2014a, Section 3.2.3), Forest Service risk assessments provide a standard set of exposure scenarios for members of the general public. These exposure scenarios are applicable to standard forestry applications of pesticides and these scenarios are included in the WorksheetMaker workbook that accompanies this document. The applicability of these scenarios to nursery applications, particularly applications within greenhouses, is probably minimal.

While most of the exposure scenarios given in the WorksheetMaker workbook are standard for Forest Service risk assessments, one notable exception is the surface water modelling. Full Forest Service risk assessments typically estimate concentrations of a pesticide in surface water using GLEAMS-Driver (SERA 2014a, Section 3.2.3.4.3). In the interest of economy, the current analysis uses FIRST (FQPA Index Reservoir Screening Tool). FIRST is a Tier 1 model developed by the U.S. EPA to estimate concentrations of pesticide in surface water and details of the FIRST model are available at http://www.epa.gov/oppefed1/models/water/first_description.htm.

The input parameters and the estimated surface water concentrations of chlorpyrifos are summarized in Table 3. The output files from FIRST are given in Appendix 1. Most of the chemical specific inputs are taken from Table 1. As with standard GLEAMS-Driver modeling, a unit application rate of 1 lb a.i./acre is used. The results from the modeling are entered into Worksheet B04Rt as water contamination rates—i.e., mg/L per lb a.i./acre applied. These concentrations are adjusted for the functional application rate discussed in Section 2. Note that the number of applications and the application interval are sensitive input parameters for FIRST. Based on information from the JH Stone Nursery, a total of 5 applications with an application interval of 14 days are used. Decreasing the number of applications or increasing the application interval will lead to lower estimates of chlorpyrifos concentrations in water.

One very important input parameter for FIRST is the proportion of the watershed that is treated. As indicated in Table 2, the FIRST modeling was conducted using a proportion of 1.0—i.e., the entire watershed is treated. Based on inputs from the Forest Service (Section 2), the raw output values from FIRST in Table 2 are reduced using a proportion of 0.023 as derived in Section 1.2.2. These values are labeled as “Adjusted Output” in Table 3 and are entered into Worksheet B04Rt in units of mg a.i./L per lb a.i./acre and rounded to two significant places.

Forest Service risk assessments also include an accidental spill scenario. Typically, Forest Service risk assessments use a spill volume of 100 (20 to 200) gallons. As discussed in Section 1.2.2, chlorpyrifos will be applied to only 5 acres at an application volume of 30 gallons/acre. Thus, the maximum amount available for an accidental spill would be 150 gallons. Thus, the upper bound of the spill volume is Worksheet A01 is set to 150 gallons rather than the typical upper bound of 200 gallons.

Another major set of standard exposure scenarios for members of the general public involves the consumption of contaminated vegetation. These exposure scenarios are described fully in SERA (2014a, Section 3.2.3.7). These exposure scenarios were developed for forestry applications of pesticides to areas with edible vegetation that might be consumed by the general public. As discussed further in Section 3.4.2 (risk characterization for members of the general public), these exposure scenarios may be of limited relevance to a nursery environment.

3.3. Dose-Response Assessment

The dose-response assessment for chlorpyrifos is summarized in Table 4 from the most recent EPA human health risk assessment (U.S. EPA/OPP/HED 2011a). Three toxicity values are used in the WorksheetMaker workbook: an acute RfD of 0.0036 mg/kg bw/day, a chronic RfD of 0.0003 mg/kg bw/day, and an intermediate RfD of 0.0015 mg/kg bw/day. All of the toxicity values are based on cholinesterase (ChE) inhibition in red blood cells using an uncertainty factor of 100. For all three toxicity values, the uncertainty factor of 100 is based on a factor of 10 for interspecies extrapolation and a factor of 10 for intraspecies variation (i.e., differences in sensitivity among individuals). The intermediate RfD is based on a standard NOAEL. The acute and chronic RfDs, however, are based on benchmark doses, specifically doses associated with a 10% inhibition of ChE in red blood cells. As detailed in U.S. EPA (2012b), benchmark doses are treated in a manner similar to NOAELs and are particularly useful for responses such as ChE inhibition for which detailed dose/response data are available. Benchmark doses are beneficial in that they more fully account for the response data at several doses rather than relying on a single experimental dose (i.e., the NOAEL).

Additional details on the analyses of the neurotoxicity studies are presented in U.S. EPA/OPP/HED (2011b).

No chronic (i.e., lifetime) exposures are anticipated at the JH Stone Nursery. Consequently, the acute RfD of 0.0036 mg/kg bw is used for the risk characterization of acute/single exposure scenariosm and the intermediate RfD of 0.0015 is used for exposures that may occur over the course of several months (e.g., longer-term dietary exposures).

3.4. Risk Characterization

3.4.1. Workers

The risk characterization for workers is given in Worksheet E02 of the WorksheetMaker EXCEL workbook that accompanies this report.

All of the accidental exposure scenarios exceed the level of concern at the upper bounds. The exposure scenarios for wearing contaminated gloves lead to much higher HQs (up to 800) than the accidental exposure scenarios involving spills onto the hands (maximum HQ of 1.3) or lower legs (maximum HQ of 3). These exposure scenarios, particularly those for contaminated gloves, underscore the need for proper and careful handling of chlorpyrifos. In the event of an accidental exposure, aggressive measures to limit exposure are clearly warranted, and medical follow-up would be advisable in the event of any signs of neurological impairment.

For non-accidental exposure scenarios, HQs are given for both acute (1-day) exposures based on the acute RfD of 0.0036 mg/kg bw/day and for intermediate exposures (several months) based on the intermediate toxicity value of 0.0015 mg/kg bw/day. No chronic exposures are anticipated, given the limited use of chlorpyrifos at the JH Stone Nursery. The HQs for acute exposures are 0.3 (0.006 to 14) and the HQs for intermediate exposures are 0.7 (0.01 to 33). The most reasonable interpretation of these HQs is that chlorpyrifos may be applied with no substantial risks to workers at typical (i.e., central estimates) exposure levels. Poor handling practices or other factors that would increase exposure could lead to unacceptable exposure levels for workers.

The EPA uses a substantially different methodology in assessing worker exposure (SERA 2009, Section 4.1). A direct and detailed comparison of the most recent EPA risk characterization for workers to the risk characterization given in Worksheet E02 cannot be made. Nonetheless, the qualitative assessment from EPA is similar to that given in the current analysis:

> *Of the 305 exposure scenarios assessed 134 had risk estimates that did not exceed the level of concern at some level of personal protection (i.e. ARIs are > 1). Ninety-one (91) exposure scenarios had risk estimates not of concern when engineering controls were considered. The remaining 80 scenarios resulted in risk estimates of concern (i.e. ARIs are < 1) at all levels of personal protection and engineering controls considered.*
>
> U.S. EPA/OPP/HED (2011a, p. 83).

Note that an ARI (Aggregate Risk Index) of less than 1 is analogous to an HQ of greater than 1. In other words, the EPA notes that some applications of chlorpyrifos can result in risks to workers that are a concern. This conclusion is essentially identical to that given in the current analysis.

3.4.2. General Public

The HQs for members of the general public are summarized in Worksheet E04 for the WorksheetMaker EXCEL workbook that accompanies this report.

All accidental exposure scenarios (i.e., an accidental spray of a child or a woman or an accidental spill of chlorpyrifos into a small body of water) lead to HQs that exceed the level of concern (HQ=1). Even the lower bounds of the HQs (the least severe accidents considered) exceed the level of concern, except for the direct spray of a woman's legs (HQ=0.6), which approaches a level of concern. The highest HQs are associated with the upper bounds for the consumption of contaminated fish by members of the general public (upper bound HQ=1823) or subsistence populations (upper bound HQ=8882). The HQs require little interpretation. As with worker exposures, accidents involving members of the general public could lead to exposure levels that grossly exceed acceptable levels. Also as with workers, aggressive measures to limit exposure are clearly warranted, and medical follow-up could be advisable in the event of any signs of neurological impairment.

As also summarized in Worksheet E04, many non-accidental acute and longer-term exposure scenarios lead to HQs that exceed the level of concern. The higher HQs are associated with the consumption of contaminated vegetation—i.e., HQs of up to 375. The relevance of these HQs to a nursery application of any pesticide would depend on the public access to the vegetation and whether the treated vegetation treated is edible. These factors should be considered on a case-by-case basis.

The HQs associated with the consumption of contaminated fish are lower than those for contaminated vegetation (i.e., an upper bound HQ of 25 for the acute consumption of contaminated fish). These HQs, however, may be of greater practical concern. Given the nature of the FIRST modeling (Section 3.2.2), the estimated surface water concentrations would represent expected contamination of surface water. If individuals might take fish from contaminated water in the area of a nursery, more refined site-specific modeling may be justified.

4. ECOLOGICAL EFFECTS

4.1. Hazard Identification

As with the hazard identification for human health (Section 3.2), the hazard identification for ecological effects is highly abbreviated in the current document. The overall database for ecological effects is discussed in detail in U.S. EPA/OPP/EFED (2009), the most recent ecological risk assessment on chlorpyrifos. Specific toxicity values for different groups of receptors are discussed in Section 4.3.

Mechanistically, the inhibition of AChE is the endpoint of concern in most groups of ecological receptors. This endpoint, however, is not relevant to terrestrial plants; accordingly, standard toxicity studies on terrestrial plants were not conducted. Based on incident data, however, U.S. EPA/OPP/EFED (2009, p. 155) indicates a qualitative concern that chlorpyrifos may damage terrestrial plants, but not to a significant degree (p. 161).

4.2. Exposure Assessment

As detailed in SERA (2014a), most Forest Service risk assessments are based on a series of exposure assessments for mammals, birds, terrestrial invertebrates, plants, and aquatic organisms. These exposure assessments are detailed in the WorksheetMaker book that accompanies this document. Details of and the rational for these exposure assessments are given Section 4.2 of SERA (2014a) and are not discussed further in the current assessment. One exception, however, involves terrestrial plants. Because standard toxicity studies are not available on terrestrial plants, standard exposure assessments for terrestrial plants are not given in the WorksheetMaker workbook that accompanies this document.

4.3. Dose-Response Assessment

The dose response assessments for nontarget organisms are summarized in Table 5 and discussed in the following subsections on different groups of receptors.

4.3.1. Terrestrial Organisms

4.3.1.1. Mammals

As discussed in Section 3.3 and summarized in Table 4, the acute oral RfD is based on a 10% benchmark dose of 0.36 mg/kg bw in rats for ChE inhibition in red blood cells. Following standard practice in Forest Service risk assessments (SERA 2014a), the basis for the human health risk assessment is used as the basis for assessing effects in mammalian wildlife. Thus, the NOAEL of 0.36 mg/kg bw is used to characterize risks to mammals following short-term oral exposures to chlorpyrifos. Similarly, the NOAEL of 0.03 mg/kg bw/day from a study in pregnant rats (which is the basis for the chronic oral RfD) is used to assess the consequences of longer-term oral exposures of mammalian wildlife to chlorpyrifos.

4.3.1.2. Birds

In the most recent EPA ecological risk assessment, U.S. EPA/OPP/EFED (2009, Table 4.5, p. 106) cites three toxicity values for birds: an acute gavage LD_{50} of 5.62 mg/kg bw in the common grackle (MRID 40378401), an acute dietary LC_{50} of 136 ppm in mallard ducks (MRID 00095007), and a chronic dietary NOAEC of 25 ppm in mallard ducks with an LOAEC of 60 ppm based on a reduced number of eggs and reduced body weight in both sexes of the parental birds.

Forest Service risk assessments typically express toxicity values for birds in units of mg/kg bw rather than dietary concentrations. In converting dietary concentrations to mg/kg bw doses, approximate food consumption rates in acute dietary studies are about 0.4 kg food/kg bw for mallards and 0.3 kg food/kg bw for quail. These food consumption rates are from standard studies using very young birds. Approximate food consumption rates during reproduction studies are about 0.07 kg food/kg bw. Using these conversion factors, the acute dietary LC_{50} of 136 ppm in mallards corresponds to a dose of 54.4 mg/kg bw [136 mg/kg food x 0.4 kg food/kg bw ≈ 54.4 mg/kg bw] and the longer-term dietary concentration of 25 ppm corresponds to a dose of 1.75 mg/kg bw [25 mg/kg food x 0.07 kg food/kg bw/day ≈ 1.75 mg/kg bw/day].

The acute gavage LD_{50} of 5.62 mg/kg bw is substantially below the estimated acute dietary LD_{50} of 54.4 mg/kg bw. This pattern is not unusual and may reflect a higher bioavailability and/or higher peak body burdens in gavage studies, relative to dietary studies. As a conservative approach, the lower acute gavage LD_{50} of 5.62 mg/kg bw is used as the basis for the dose-response assessment in birds. Following the risk presumption approach used by U.S. EPA for terrestrial species (discussed in SERA 2014a, Section 4.3.2 and Table 19), the acute NOAEC for birds is estimated as 0.562 mg/kg bw—i.e., the LD_{50} is divided by a factor of 10 to approximate the NOAEC.

As discussed above, the longer-term dietary NOAEC is estimated as 1.75 mg/kg bw/day. This estimated longer-term NOAEC is higher than the estimated acute NOAEC by a factor of about 3 [1.75 mg/kg bw/day ÷ 0.562 mg/kg bw ≈ 3.114]. It is not sensible to use a chronic NOAEC that is higher than the acute NOAEC. As noted above, the acute toxicity value is based on a gavage study. Dietary studies are probably more relevant than gavage studies for the exposure scenarios considered in this document. Thus, the estimated longer-term dietary NOAEC is estimated as 1.75 mg/kg bw/day is applied to the risk characterization for acute and longer-term exposure of birds.

Note that the above approach is not the most conservative—i.e., using the lower estimated acute NOAECs for both acute and chronic exposures would result in lower toxicity values. Nonetheless, preference is given to experimental toxicity values (in this case the chronic toxicity values) rather than inherently conservative approximations.

4.3.1.3. Other Terrestrial Organisms

The only other toxicity value for terrestrial organisms discussed in U.S. EPA/OPP/EFED (2009) is an acute contact LD_{50} of 0.059 µg/bee (MRID 05001991), which is equivalent to 0.000059 mg/bee. Using a typical body weight of 116 mg (equivalent to 0.000116 kg) for a worker bee (SERA 2014a, Section 4.2.3.1), the dose of 0.000059 mg/bee is equivalent to about 0.51 mg/kg bw [0.000059 mg/bee ÷ 0.000116 kg bw ≈ 0.5086 mg/kg bw]. As with birds and for the same reason (i.e., the EPA risk presumption approach), the estimated LD_{50} of 0.51 mg/kg bw is divided by 10 to approximate an NOAEC of 0.051 mg/kg bw.

4.3.2. Aquatic Organisms

As discussed in the following sections, chlorpyrifos is classified as *very highly toxic* to aquatic animals, and U.S. EPA/OPP/EFED (2009) reports toxicity values in units of µg/L. In the WorksheetMaker workbook that accompanies this report, toxicity values are expressed in units of mg/L. In the following sections, toxicity values are generally discussed in units of µg/L to maintain consistency with the EPA source document. All toxicity values used in the WorksheetMaker workbook, however, are also expressed in units of mg/L (typically in parentheses) for clarity.

4.3.2.1. Fish

Following standard practice, U.S. EPA/OPP/EFED (2009, Table 4.1) summarizes toxicity data on freshwater and marine/estuarine fish. Unless there are obvious and substantial differences in the sensitivity of freshwater and saltwater fish, Forest Service risk assessments generally focus on identifying the most sensitive and most tolerant species of fish. Based on the data summarized in U.S. EPA/OPP/EFED (2009), no such substantial differences are apparent. The reported acute LC_{50} values are 1.8 µg/L for freshwater fish (bluegill sunfish) and 0.70 µg/L for saltwater fish (tidewater silverside). Following the risk presumption approach used by U.S. EPA for aquatic species (discussed in SERA 2014a, Section 4.3.2 and Table 19), acute LC_{50} values are divided by a factor of 20 to approximate the NOAEC. Thus, the estimated acute NOAECs would be 0.09 µg/L for bluegills and 0.035 µg/L for silversides.

U.S. EPA/OPP/EFED (2009) also reports chronic NOAEC values of 0.28 µg/L for Atlantic silversides and 0.57 µg/L for fathead minnows. As with birds (Section 4.3.1.2), the estimated acute NOAECs are below the experimental chronic NOAECs. Consequently, the chronic NOAECs are used to characterize risks from both acute and chronic exposures. While using the lower estimated acute NOAECs might be viewed as a more conservative approach, preference is given to the experimental NOAECs (i.e., the chronic values) rather than intentionally conservative approximations of the acute NOAECs.

There is not a substantial difference between the two chronic values—i.e., 0.57 µg/L ÷ 0.28 µg/L ≈ 2.03. In the absence of additional data on the chronic effects of chlorpyrifos in fish, however, the lower NOAEC of 0.28 µg/L (0.00028 mg/L) is used for potentially sensitive species of fish and the higher NOAEC of 0.57 (0.00057 mg/L) is used for potentially tolerant species of fish.

4.3.2.2. Amphibians

Two toxicity values are available on aquatic-phase amphibians in U.S. EPA/OPP/EFED (2009): an acute LC_{50} of 0.6 µg/L and a chronic LOAEC of 0.1 µg/L. Both of these toxicity values are for the African clawed frog tadpole (*Xenopus laevis*). Again using the risk presumption approach from U.S. EPA for aquatic species (discussed in SERA 2014a, Section 4.3.2 and Table 19), the acute LC_{50} value is divided by a factor of 20 to approximate an NOAEC of [0.6 µg/L ÷ 20 = 0.03 µg/ or 0.00003 mg/L].

LOAEL values are not used directly in Forest Service risk assessments. Following the general approach discussed in SERA (2014a, Section 3.3 and Table 15), the chronic LOAEC of 0.1 µg/L is divided by a factor of 10 to approximate an NOAEC of 0.01 µg/L or 0.00001 mg/L.

4.3.2.3. Aquatic Invertebrates

As summarized in U.S. EPA/OPP/EFED (2009, Table 4.1), for aquatic invertebrates, acute LC_{50} values are available in a freshwater species (i.e., 0.07 µg/L for *Daphnia magna*) and a saltwater species (0.035 µg/L in mysid shrimp, *Americamysis bahia*). Dividing these toxicity values by a factor of 20, the approximated acute NOAEC values are 0.0035 µg/L for *Daphnia magna* and 0.00175 µg/L for mysid shrimp.

For *Daphnia magna*, the reported chronic NOAEC is 0.025 µg/L (0.000025 mg/L). As with the toxicity values for fish, preference is given to the experimental chronic NOAEC, and this toxicity value is used to characterize risks associated with both acute and longer term exposures in presumably tolerant species of aquatic invertebrates.

For mysids, a chronic LOAEC of 0.0046 µg/L is available. Following the same approach used with amphibians (Section 4.3.2.2), the LOAEC of 0.0046 µg/L is divided by a factor of 10 to approximate a chronic NOAEC of 0.00046 µg/L (0.00000046 mg/L). This estimated chronic NOAEC is below the estimated acute NOAEC of 0.00175 µg/L for mysid shrimp. Consequently, the estimated acute NOAEC of 0.00175 µg/L (0.00000175 mg/L) is used to characterize risks of acute exposures, and the estimated chronic NOAEC 0f 0.00046 µg/L (0.00000046 mg/L) is used to characterize risks of longer-term exposures in presumably sensitive species of aquatic invertebrates.

4.3.2.4. Aquatic Plants

The only toxicity data on aquatic plants in U.S. EPA/OPP/EFED (2009, Table 4.1 and p. 161) is a reported 120-hour EC_{50} of 140 µg/L based on reduced cell density in a species of freshwater green alga (*Pseudokirchneriella subcapitata*). Dividing this EC_{50} by 20, the NOAEC is approximated as 7 µg/L (0.007 mg/L). As would be expected based on the known mechanism of action of chlorpyrifos, the EC_{50} in plants is substantially higher than EC_{50} values in aquatic animals—i.e., higher than the EC_{50} of 0.035 µg/L in sensitive aquatic invertebrates by a factor of 4000 [140 µg/L ÷ 0.035 µg/L].

No data on the toxicity of chlorpyrifos to aquatic macrophytes is presented in U.S. EPA/OPP/EFED (2009).

4.4. Risk Characterization

4.4.1. Terrestrial Organisms

4.4.1.1. Mammals and Birds

The HQs for mammals and birds are summarized in Worksheet G02a (mammals) and Worksheet GO2b (birds) of the WorksheetMaker workbook that accompanies this risk assessment. As summarized in Table 5, the NOAECs for mammals are much less than those for birds. While this leads to much lower HQs for mammals, relative to birds, the qualitative risk characterization is similar for both groups of organisms.

The exposure scenarios for the consumption of contaminated water do not lead to HQs that exceed the level of concern, even in the event of an accidental spill (HQ=1). Some of the upper bound estimates of exposures associated with the consumption of contaminated fish exceed the level of concern for mammals (maximum HQ of 39) and birds (maximum HQ of 3).

Most of the upper bound HQs for the consumption of contaminated vegetation, grass, and fruit exceed the level of concern for both mammals (maximum HQ of 1382) and birds (maximum HQ of 976). Even at the lower bounds of the HQs, exceedances occur for mammals (maximum HQ of 30) and birds (maximum HQ of 22).

While the EPA uses a somewhat different approach to estimating exposures in mammals and birds from that used in Forest Service risk assessments (SERA 2009, Section 4.3, Table 5), the risk characterization for mammals and birds given in the current report is qualitatively similar to that in the EPA's most recent ecological risk assessment on chlorpyrifos:

> *…the acute and chronic avian and mammalian dose and dietary-based RQs estimated with T-REX exceed the LOCs listed species for all uses of chlorpyrifos, including granular and seed treatment uses.*
>
> U.S. EPA/OPP/EFED (2009, Section 5.5.1.2, p. 150).

Note that T-REX is a spreadsheet tool used by EPA which, similar to WorksheetMaker, is used to conduct exposure assessments and RQs (Risk Quotients). RQs are analogous to HQs used in Forest Service risk assessments.

The severe risk characterization for birds is supported by field incidents in which birds were killed following applications of chlorpyrifos with an association of "probably" or "highly probably" (U.S. EPA/OPP/EDED 2009, p. 154).

As discussed in Section 3.4.2, the high HQs for humans associated with the consumption of contaminated vegetation may have limited practical relevance, because the general public may have limited access to the JH Stone Nursery, and it does not seem likely that the Forest Service would be cultivating edible/agricultural crops. The extent to which these reservations would apply to mammalian wildlife and birds is not clear.

4.4.1.2. Invertebrates

The HQs for the direct spray or drift exposures of the honeybee (with or without foliar interception) are given in Worksheet G09. As would be expected with an effective insecticide, the direct spray of honeybees with chlorpyrifos leads to a very high HQ (1345). Depending on the extent of foliar interception, HQs can exceed the level of concern (HQ=1) at distances of up to 500 feet downwind. As detailed in SERA (2011a, Section 3.3.2), drift modeling should be site specific, and more elaborate estimates of drift could be made on a case-by-case basis.

As with the risk characterization for birds, the severe risk characterization for bees is supported by field incidents in which bees were killed following applications of chlorpyrifos with an association of "probably" or "highly probably" (U.S. EPA/OPP/EDED 2009, p. 154).

4.4.2. Aquatic Organisms

The HQs for aquatic organisms are summarized in Worksheet G03 for accidental, acute non-accidental, and longer-term exposure scenarios. The lower bounds of HQs following an accidental spill exceed the level of concern (HQ=1) for all groups of organisms for which HQs can be derived (i.e., fish, aquatic invertebrates, amphibians, and algae) with lower bound HQs ranging from 43 (algae) to 173,029 (sensitive species of aquatic invertebrates). The upper bound HQs for an accidental spill range from 324 (algae) to over 1-million (sensitive species of aquatic invertebrates). These HQs require little elaboration. In the event of even a mild spill of chlorpyrifos into surface water, adverse effects on all groups of aquatic invertebrates are to be expected.

Based on anticipated (non-accidental) concentrations of chlorpyrifos in surface water, the HQs for algae approach, but do not exceed, the level of concern—i.e., HQs = 0.3 (0.09-0.9). For sensitive species of fish, amphibians, and aquatic invertebrates the HQs exceed the level of concern even at the lower bounds. The exceedances for aquatic invertebrates are the greatest – HQs = 1086 (337-3714)—followed by amphibians—HQs = 63 (22-217) and then fish—HQs = 7 (2-23). For tolerant species of fish and aquatic invertebrates, the HQs are lower but also exceed the level of concern even at the lower bounds.

The above risk characterization is qualitatively similar to the risk characterization in the most recent ecological risk assessment from EPA:

> *Effects to aquatic-phase amphibians, as well as both freshwater and saltwater fish are significant and not discountable. Runoff may cause effects wherever chlorpyrifos is used...*
>
> U.S. EPA/OPP/EFED (2009, Section 5.5.1.1, p. 144).

> *In general, all aquatic invertebrate data reviewed (Section 5.2.1.2) had similar effect levels. … A strong potential exists for significant effects to the California freshwater shrimp* [applicable to other aquatic invertebrates] *and these are not discountable. Runoff may cause effects wherever chlorpyrifos is used…*
>
> U.S. EPA/OPP/EFED (2009, Section 5.5.1.1, p. 147-148).

In discussing numerous incident reports involving chlorpyrifos applications …*from the legal, registered uses of chlorpyrifos as well as misuses*…, the EPA concludes that:

> *Overall, the incident data that are available indicate that exposure pathways for chlorpyrifos are complete and that exposure levels are sufficient to result in field-observable effects.*
>
> U.S. EPA/OPP/EFED (2009, Section 5.5.1.1, p. 148).

As discussed in Section 3.2.2, the estimates of chlorpyrifos in surface water are based on relatively crude approximations from a simple Tier 1 model (FIRST). Nonetheless, the magnitude of HQs for aquatic organisms derived in the current analysis and the risk characterization presented above by EPA using a Tier 2 model (PRZM/EXAMS) leave little doubt that the use of chlorpyrifos near surface water would likely lead to adverse effects on aquatic organisms, unless effective methods are used to essentially eliminate the potential for the runoff of chlorpyrifos from the treated field to surface water. Considerations of lower but still effective application rates, the number of applications per season, and the application interval would not be likely to markedly impact this conclusion.

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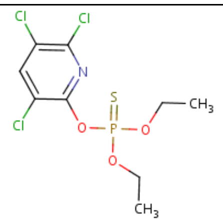
Table 1: Chemical and Physical Properties

Item	Value	Reference[1]
	Identifiers	
Common name:	Chlorpyrifos (a.k.a. chlorpyriphos)	Tomlin 2004
CAS Name	O,O-diethyl O-(3,5,6-trichloro-2-pyridinyl) phosphorothioate	
IUPAC Name	O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate	Tomlin 2004
CAS No.	2921-88-2	Tomlin 2004; U.S. EPA/OPP /HED 2013
Chemical Group	Organophosphate	Tomlin 2004
Development Codes	Dowco 179	Tomlin 2004
Molecular formula	$C_9H_{11}Cl_3NO_3PS$	Tomlin 2004
Mechanistic group	Acetylcholinesterase inhibitor	U.S. EPA/OPP 2009
EPA PC Code	059101	U.S. EPA/OPP/HED 2013
Smiles Code	`CCOP(=S)(OCC)Oc1nc(Cl)c(Cl)cc1Cl`	Tomlin 2004
	`S=P(OC1=NC(=C(C=C1Cl)Cl)Cl)(OCC)OCC`	U.S. EPA/OPP/HED 2013
Structure		ChemIDplus 2014
	Chemical Properties(1)	
Aqueous photolysis	29.6 days at pH 7	U.S. EPA/OPP/EFED 2009, Tables 2.2 and 3.2
Boiling point		
Density	1.44 (20 °C)	Tomlin 2004
Form	Colorless crystals, with a mild mercaptan odour	Tomlin 2004
	White granular crystals	U.S. EPA/OPP/EFED 2009, Table 2.2
Henry's Law Constant	2.93×10^{-6} atm-m^3/mole (20°C)	ChemIDplus 2014
	6.2×10^{-6} atm - m^3/mole	U.S. EPA/OPP/HED 2013
Hydrolysis	**DT_{50} (days)** / **pH at 25°C** 72 / 5 72 / 7 16 / 9	U.S. EPA/OPP/EFED 2009, Table 2.2
K_{ow}	≈50,100 [log K_{ow} = 4.7] (experimental?)	Tomlin 2004; U.S. EPA/OPP /HED 2013
	≈91,200 [log K_{ow} = 4.96] (experimental)	ChemIDplus 2014; EPI Suite 2011
Molecular weight (g/mole)	350.6	Tomlin 2004
	350.59	EPI Suite 2011
Melting point	42-43.5 °C	Tomlin 2004
Photolysis	29.6 days	U.S. EPA/OPP/EFED 2009, Table 2.2
Vapor concentration, saturated	489 µg/m^3 (experimental) 353 µg/m^3 (calculated)	U.S. EPA/OPP/HED 2013
Vapor pressure	2.7 mPa (25 °C)	Tomlin 2004

Item	Value	Reference[1]
	2.03x10^{-5} mm Hg	ChemIDplus 2014
	1.87x10^{-5} torr	U.S. EPA/OPP/HED 2013
Water solubility	1.4 mg/L (25 °C)	Tomlin 2004; U.S. EPA/OPP /HED 2013
	1.12 mg/L (24 °C)	ChemIDplus 2014; EPI Suite 2011
	0.4 mg/L	Knisel and Davis 2000
	Environmental Properties	
Aerobic aquatic metabolism	153.8 days [2x aerobic soil metabolism]	U.S. EPA/OPP/EFED 2009, Table 3.2
Anaerobic aquatic metabolism	81.5 days [2x anaerobic soil metabolism]	U.S. EPA/OPP/EFED 2009, Table 3.2
Bioconcentration in fish (BCF)	870.2 (wet-wt) [log BCF = 2.940]	EPI Suite 2011
	2727 (rainbow trout, whole body)	U.S. EPA/OPP/EFED 2009, Table 2.2
Field dissipation	33 to 56 days	U.S. EPA/OPP/EFED 2009, Table 2.3
Foliar washoff fraction	0.65	Knisel and Davis 2000
Foliar half-life	3.3 days	Knisel and Davis 2000
K_{oc} (ads/des in mL/g)	360 to 31000	U.S. EPA/OPP/EFED 2009, Table 2.3
	6070 [Used by U.S. EPA/OPP/EFED 2009 in water modeling]	Knisel and Davis 2000
Soil half-life (NOS)	30 days	Knisel and Davis 2000
Soil half-life, aerobic	11 to 180 days	U.S. EPA/OPP/EFED 2009, Table 2.3
	73.9 days	U.S. EPA/OPP/EFED 2009, Table 3.2
Soil half-life, anaerobic	39 to 51 days (2 soils); TCP metabolite	Soil half-life, aerobic
Soil photolysis	Stable	U.S. EPA/OPP/EFED 2009, Table 2.3

See Section 2 for discussion.

Table 2: Derivation of Worker Exposure Rates

Table 2-1 Ground Broadcast Applications

Item	Value	Reference/Note	Row
Reference Chemical	2,4-D	Section 3.2.1	2
First-order dermal absorption rate coefficient for reference chemical (hour^{-1}) [ka_{Ref}]	0.00066	SERA 2014b	3
Occupational Exposure Rates for Reference Chemical			4
Central Estimate	0.0001	SERA 2014b, Table 14	5
Lower 95% Prediction Bound	0.000002	SERA 2014b, Table 14	6
Upper 95% Prediction Bound	0.005	SERA 2014b, Table 14	7
Subject Chemical	Chlorpyrifos		8
First-order dermal absorption rate coefficient for subject chemical (hour^{-1}) [ka_P]	0.0014	Section 3.2.1.	9
$ka_P \div ka_{Ref}$	2.121212121		10
Occupational Exposure Rates for Reference Chemical			11
Central Estimate	0.000212121	SERA 2014b, Eq. 22	12
Lower 95% Prediction Bound	0.000004242	SERA 2014b, Eq. 22	13
Upper 95% Prediction Bound	0.010606061	SERA 2014b, Eq. 22	14

See Section 3.2.1. for discussion.

See Backpack Applications and documentation for table structure on next page.

Table 2-2 Backpack/Greenhouse Applications

Item	Value	Reference/Note	Row
Reference Chemical	Triclopyr BEE	Section 3.2.1	2
First-order dermal absorption rate coefficient for reference chemical (hour^{-1}) [ka_{Ref}]	0.0031	SERA 2014b	3
Occupational Exposure Rates for Reference Chemical			4
Central Estimate	0.01	SERA 2014b, Table 14	5
Lower 95% Prediction Bound	0.002	SERA 2014b, Table 14	6
Upper 95% Prediction Bound	0.06	SERA 2014b, Table 14	7
Subject Chemical	Chlorpyrifos		8
First-order dermal absorption rate coefficient for subject chemical (hour^{-1}) [ka_P]	0.0014	Section 3.2.1.	9
$ka_P \div ka_{Ref}$	0.4516129		10
Occupational Exposure Rates for Reference Chemical			11
Central Estimate	0.0045161	SERA 2014b, Eq. 22	12
Lower 95% Prediction Bound	0.00090323	SERA 2014b, Eq. 22	13
Upper 95% Prediction Bound	0.02709677	SERA 2014b, Eq. 22	14

Documentation for Table: The above table implements the adjustment of worker exposure rates based dermal absorption rates. The table uses MS Word "fields" rather than macros.

- Determine the first-order dermal absorption rate coefficient for the chemical under review. See SERA 2014a, Section 3.1.3.2.2.
- Select the reference chemical. See SERA 2014b, Section 4.1.6.1.
- Fill in the information on the reference chemical in the upper section of the above table.
- Fill in the first-order dermal absorption rate coefficient for the chemical under review in the Value column of Row 9 in the above table.
- Update the estimated values for ration of the k_a values and the occupational exposure rates for the chemical under review – i.e., the green shaded cells in the above table. The simplest way to update these fields is to select each of the 4 green shaded cells (one at a time and in order), press the right mouse button, and select 'Update field'.

Assuming that you will construct an EXCEL workbook, it is a good idea to check the above calculations in EXCEL. Also note that you should round the values in the green shaded cells to one significant figure in the EXCEL workbook if you want to maintain compatibility with SERA (2014b).

Table 3: Inputs and Outputs for FIRST Simulations

Parameter	Central Estimate of Concentration in Water	Lower Bound of Concentration in Water	Upper Bound of Concentration in Water
Input Values			
Aerobic soil metabolism half-life (days) [1]	73.9	11	180
Aerobic aquatic metabolism (days) [2]	153.8	22	360
K_{oc} (mL/g) [3]	6070	31,000	360
Aqueous Photolysis half-life (days) [4]	29.6	29.6	29.6
Water solubility (mg/L) [4]	1.4	1.4	1.4
Raw Output			
Gross Peak Concentration (µg/L per lb/acre)	83.328	28.574	283.413
Gross Longer-term Concentration (µg/L per lb/acre)	11.407	0.837	78.369
Proportion of Treated Watershed	0.023		
Adjusted Output			
Peak Concentration Used in Analysis (µg/L per lb/acre)	1.917	0.657	6.518
Longer-term Concentration Used in Analysis (µg/L per lb/acre)	0.262	0.0193	1.802

Other General Inputs Used for FIRST runs: Application rate: 1 lb/acre, 5 applications with an application interval of 14 days; Proportion of watershed treated used for run: 1.0; Wetted in: No; Drift: None (analogous to GLEAMS-Driver runs); Incorporation Depth: 0 cm.

[1] Central estimate from U.S. EPA/OPP/EFED (2009, Table 3.2) with range from U.S. EPA/OPP/EFED (2009, Table 2.3).

[2] Approximated as 2x soil aerobic metabolism per U.S. EPA/OPP/EFED (2009, Table 3.2).

[3] Central estimate from Knisel and Davis (2000) as used by U.S. EPA/OPP/EFED 2009 with range from U.S. EPA/ OPP/EFED (2009).

[4] From U.S. EPA/OPP/EFED (2009, Tables 2.2 and 3.2).

Note: The adjusted water contamination rates are entered into Worksheet B04Rt of the EXCEL workbook that accompanies this document in units of mg a.i./L per lb a.i./acre applied and rounded to 2 significant places.

See Section 3.2 for discussion.

Table 4: Summary of toxicity values used in human health risk assessment

Acute – single exposure

Element	Derivation of RfD
EPA Document	U.S. EPA/OPP/HED 2011, p. 43
Study	MRID 48139301 and Moser et al. (2006) as summarized in EPA document.
NOAEL Dose	0.36 mg/kg bw/day (10% benchmark dose)
LOAEL Dose	N/A
LOAEL Endpoint(s)	ChE inhibition in red blood cells
Species, sex	Rats, pups, males and females
Uncertainty Factor	100 (10X to account for interspecies extrapolation and 10X for intraspecies variation)
Acute RfD	0.0036 mg/kg bw/day

Chronic – lifetime exposure

Element	Derivation of RfD
EPA Document	U.S. EPA/OPP/HED 2011, p. 44
Study	MRID 44556901, developmental neurotoxicity
NOAEL Dose	0.03 mg/kg bw/day (10% benchmark dose)
LOAEL Dose	N/A
LOAEL Endpoint(s)	ChE inhibition in red blood cells
Species, sex	Rats, pregnant, females
Uncertainty Factor	100 (10X to account for interspecies extrapolation and 10X for intraspecies variation)
Chronic RfD	0.0003 mg/kg bw/day

Occupational – 1 to 6 month exposure periods

Element	Derivation of RfD
EPA Document	U.S. EPA/OPP/HED 2011, p. 44 and Table 8
Study	MRID 40972801
NOAEL Dose	0.15 mg/kg bw/day [estimated absorbed dermal dose]
LOAEL Dose	0.3 mg/kg bw/day [estimated absorbed dermal dose]
LOAEL Endpoint(s)	ChE inhibition in red blood cells
Species, sex	Rats
Uncertainty Factor/MOE	100 (10X to account for interspecies extrapolation and 10X for intraspecies variation)
Equivalent RfD	0.0015 mg/kg bw/day

Table 5: Summary of toxicity values used in ERA

Group/Duration	Organism	Endpoint	Toxicity Value (a.i.)	Reference
Terrestrial Animals				
Acute				
	Mammals (including canids)	10% benchmark dose for AChE	0.36 mg/kg bw	Section 4.3.1.1.
	Birds	Use chronic value	1.75 mg/kg bw/day	Section 4.3.1.2
	Honey Bee (contact)	Estimated NOAEL	0.051 mg/kg bw	Section 4.3.1.3
Longer-term				
	Mammals	NOAEL	0.03 mg/kg bw/day	Section 4.3.2.1
	Bird	Chronic NOAEL	1.75 mg/kg bw/day	Section 4.3.1.2.
Aquatic Animals				
Acute				
Amphibians	Sensitive	LC_{50} in frog ÷ 20	0.00003 mg/L	Section 4.3.3.2
	Tolerant	N/A		
Fish	Sensitive	Use chronic NOAEC	0.00028 mg/L	Section 4.3.3.1
	Tolerant	Use chronic NOAEC	0.00057 mg/L	
Invertebrates	Sensitive	EC_{50} in mysid ÷ 20	0.00000175 mg/L	Section 4.3.3.3
	Tolerant	Use chronic NOAEC	0.000025 mg/L	
Longer-term				
Amphibians	Sensitive	Chronic NOAEC in frog species	0.00001 mg/L	Section 4.3.3.2
	Tolerant	N/A		
Fish	Sensitive	NOAEC in silverside	0.00028 mg/L	Section 4.3.3.1
	Tolerant	NOAEC in minnows	0.00057 mg/L	
Invertebrates	Sensitive	Chronic NOAEC in mysid	0.00000046 mg/L	Section 4.3.3.3
	Tolerant	Chronic NOAEC in daphnid	0.000025 mg/L	
Aquatic Plants				
Algae	Sensitive	EC_{50} in green alga ÷ 20	0.007 mg/L	Section 4.3.3.4
	Tolerant	N/A		Section 4.3.3.4
Macrophytes	Sensitive	N/A		Section 4.3.3.4
	Tolerant	N/A		Section 4.3.3.4

Appendix 1: FIRST Runs

Central Estimate

```
RUN No.   1 FOR Chlorpyrifos     ON   None          * INPUT VALUES *
   --------------------------------------------------------------------
    RATE (#/AC)   No.APPS &   SOIL  SOLUBIL  APPL TYPE  %CROPPED INCORP
     ONE(MULT)    INTERVAL    Koc   (PPM )   (%DRIFT)     AREA    (IN)
   --------------------------------------------------------------------
  1.000(  3.912)   5  14    6070.0    1.4   GRANUL( 0.0) 100.0   0.0


   FIELD AND RESERVOIR HALFLIFE VALUES (DAYS)
   --------------------------------------------------------------------
   METABOLIC  DAYS UNTIL  HYDROLYSIS   PHOTOLYSIS   METABOLIC  COMBINED
    (FIELD)  RAIN/RUNOFF  (RESERVOIR)  (RES.-EFF)   (RESER.)   (RESER.)
   --------------------------------------------------------------------
     73.90        2           0.00   29.60- 3670.40  153.80     147.61


   UNTREATED WATER CONC (MICROGRAMS/LITER (PPB)) Ver 1.1.1  MAR 26, 2008
   --------------------------------------------------------------------
        PEAK DAY  (ACUTE)      ANNUAL AVERAGE (CHRONIC)
          CONCENTRATION             CONCENTRATION
   --------------------------------------------------------------------
             83.328                     11.407
```

Lower Bound

```
   RUN No.   2 FOR Chlorpyrifos     ON   None          * INPUT VALUES *
   --------------------------------------------------------------------
    RATE (#/AC)   No.APPS &   SOIL  SOLUBIL  APPL TYPE  %CROPPED INCORP
     ONE(MULT)    INTERVAL    Koc   (PPM )   (%DRIFT)     AREA    (IN)
   --------------------------------------------------------------------
  1.000(  1.685)   5  14   31000.0    1.4   GRANUL( 0.0) 100.0   0.0


   FIELD AND RESERVOIR HALFLIFE VALUES (DAYS)
   --------------------------------------------------------------------
   METABOLIC  DAYS UNTIL  HYDROLYSIS   PHOTOLYSIS   METABOLIC  COMBINED
    (FIELD)  RAIN/RUNOFF  (RESERVOIR)  (RES.-EFF)   (RESER.)   (RESER.)
   --------------------------------------------------------------------
     11.00        2           0.00   29.60- 3670.40   22.00      21.87


   UNTREATED WATER CONC (MICROGRAMS/LITER (PPB)) Ver 1.1.1  MAR 26, 2008
   --------------------------------------------------------------------
        PEAK DAY  (ACUTE)      ANNUAL AVERAGE (CHRONIC)
          CONCENTRATION             CONCENTRATION
   --------------------------------------------------------------------
             28.574                      0.837
```

Upper Bound

```
RUN No.   3 FOR Chlorpyrifos     ON   None          * INPUT VALUES *
 --------------------------------------------------------------------
  RATE (#/AC)   No.APPS &   SOIL  SOLUBIL  APPL TYPE  %CROPPED INCORP
   ONE(MULT)    INTERVAL    Koc   (PPM )   (%DRIFT)     AREA    (IN)
 --------------------------------------------------------------------
1.000(  4.502)   5  14     360.0    1.4   GRANUL( 0.0) 100.0   0.0

 FIELD AND RESERVOIR HALFLIFE VALUES (DAYS)
 --------------------------------------------------------------------
 METABOLIC  DAYS UNTIL  HYDROLYSIS   PHOTOLYSIS   METABOLIC  COMBINED
  (FIELD)  RAIN/RUNOFF  (RESERVOIR)  (RES.-EFF)   (RESER.)   (RESER.)
 --------------------------------------------------------------------
  180.00        2           0.00   29.60- 3670.40  360.00     327.84

 UNTREATED WATER CONC (MICROGRAMS/LITER (PPB)) Ver 1.1.1  MAR 26, 2008
 --------------------------------------------------------------------
      PEAK DAY  (ACUTE)      ANNUAL AVERAGE (CHRONIC)
        CONCENTRATION             CONCENTRATION
 --------------------------------------------------------------------
         283.413                     78.369
```