Properties and Uses of Chlorpyrifos in the United States

Keith R. Solomon, W. Martin Williams, Donald Mackay, John Purdy, Jeffrey M. Giddings, and John P. Giesy

1 Introduction

The physical and chemical properties of chlorpyrifos (O, O-diethyl O-3,5,6-trichloro-2-pyridinyl phosphorothioate, CPY; CAS No. 2921-88-2) are the primary determinants that govern fate (movement, adsorption, degradation, and catabolism) in the environment and in biota. The uses of chlorpyrifos in locations of interest, such as the United States in the case of this paper, are the primary determinants of the entry of chlorpyrifos into the environment and its subsequent fate in the regions of use and beyond. The uses and manner of use are addressed in this paper.

The data on physical and chemical properties provided here were the basis for modeling long range transport and assessing bioaccumulation (Mackay et al. 2014), characterizing routes of exposure to chlorpyrifos in terrestrial systems such as soil,
foliage, and food items (Cutler et al. 2014; Moore et al. 2014), and in surface-water aquatic systems (Giddings et al. 2014; Williams et al. 2014). The currently-registered formulations of chlorpyrifos and their uses in the United States were the basis for the development of the scenarios of exposure and the conceptual models used in assessing risks to birds (Moore et al. 2014), pollinators (Cutler et al. 2014), and aquatic organisms (Williams et al. 2014). These data on use are based on the current labels and reflect changes in labels and use-patterns since the earlier assessments of risks to aquatic (Giesy et al. 1999) and terrestrial organisms (Solomon et al. 2001). Physical and chemical properties of chlorpyrifos were extensively reviewed by Racke (1993) and, rather than repeat all of this information, relevant values from Racke 1993 are included in this paper and supplemental material (SI) with updates as appropriate.

2 Physical and Chemical Properties of Chlorpyrifos

Fundamental to assessing and predicting the general fate of chlorpyrifos in the environment are having reliable data on physical chemical and reactivity properties that determine partitioning and persistence in the environment. In the following sections, some of the key properties are discussed in more detail.

2.1 Properties Affecting Fate in Air and Long-Range Transport

The fate of CPY and chlorpyrifos-oxon (CPYO; CAS No. 5598-15-2; CPY’s biologically active metabolite, degradate, and minor technical product component) in air, with respect to short- and long-distance transport are discussed in detail in a companion paper (Mackay et al. 2014). The physical and chemical properties specific to fate in air are presented in Tables 5–8 in Mackay et al. (2014) and are not repeated here except in the context of biological relevance and fate and movement in other matrices.

2.2 Properties Affecting Fate in Soil, Water, and Sediment

An extensive review of the data on half-lives of CPY in soils and has shown the high variability attributed to soil organic carbon content, moisture, application rate and microbial activity (Racke 1993). Fewer data are available for water and sediments, but processes related to soils and sediments have been summarized in a recent review (Gebremariam et al. 2012). The key physical and chemical properties of CPY are listed in Tables 1 and 2.

Chlorpyrifos has short to moderate persistence in the environment as a result of several dissipation pathways that might occur concurrently (Fig. 1). Primary mechanisms of dissipation include volatilization, photolysis, abiotic hydrolysis, and
Table 1 Physicochemical properties of chlorpyrifos

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values for Chlorpyrifos</th>
<th>Source</th>
</tr>
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<tbody>
<tr>
<td>Chemical Name</td>
<td>O,O-diethyl o-(3,5,6-trichloro-2-pyridyl phosphorothioate</td>
<td>USEPA (2011b)</td>
</tr>
<tr>
<td>Chemical Abstracts Service (CAS) Registry Number</td>
<td>2921-88-2</td>
<td></td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C₉H₁₁Cl₃NO₃PS</td>
<td></td>
</tr>
<tr>
<td>USEPA Pesticide Code (PC #)</td>
<td>59101</td>
<td></td>
</tr>
<tr>
<td>Smiles notation</td>
<td>S=P(OC1=NC(=C(C(=C1Cl)Cl)Cl)(OCC)OCC</td>
<td></td>
</tr>
<tr>
<td>Molecular mass</td>
<td>350.6 g mol⁻¹</td>
<td>Mackay et al. (2014)</td>
</tr>
<tr>
<td>Vapor pressure (25 °C)</td>
<td>1.73 × 10⁻⁵ torr</td>
<td></td>
</tr>
<tr>
<td>Water solubility (20 °C)</td>
<td>0.73 mg L⁻¹</td>
<td></td>
</tr>
<tr>
<td>Henry’s Law Constant</td>
<td>1.10 × 10⁻³ atm m⁻³ mol⁻¹</td>
<td></td>
</tr>
<tr>
<td>Log Kow</td>
<td>5.0</td>
<td></td>
</tr>
</tbody>
</table>

Table 2 Environmental fate properties of chlorpyrifos

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values</th>
<th>Source</th>
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</thead>
<tbody>
<tr>
<td>Hydrolysis (t½)</td>
<td>pH 5: 73 d</td>
<td>USEPA (2011b)</td>
</tr>
<tr>
<td>Aqueous photolysis (t½)</td>
<td>29.6 d</td>
<td></td>
</tr>
<tr>
<td>Aerobic soil metabolism (t½)</td>
<td>2–1,576 d, N = 68 (next highest value is 335 d)</td>
<td>See SI Table A-1</td>
</tr>
<tr>
<td>Aerobic aquatic metabolism (t½)</td>
<td>22–51 d, N = 3</td>
<td>See SI Table A-5</td>
</tr>
<tr>
<td>Anaerobic soil metabolism (t½)</td>
<td>15 and 58 d</td>
<td>USEPA (2011b)</td>
</tr>
<tr>
<td>Anaerobic aquatic metabolism (t½)</td>
<td>39 and 51 d</td>
<td></td>
</tr>
<tr>
<td>Soil adsorption coefficient KOC</td>
<td>973–31,000 mL g⁻¹, N = 33</td>
<td>See SI Table A-4</td>
</tr>
<tr>
<td>Terrestrial field dissipation (t½)</td>
<td>2–120 d, N = 58</td>
<td>See SI Table A-3</td>
</tr>
</tbody>
</table>

Fig. 1 Pathways for degradation of chlorpyrifos in the environment (after Racke 1993)
microbial degradation. Volatilization dominates dissipation from foliage in the initial 12 h after application, but decreases as the formulation adsorbs to foliage or soil (Mackay et al. 2014). In the days after application, CPY adsorbs more strongly to soil, and penetrates more deeply into the soil matrix, and becomes less available for volatilization; other degradation processes become important.

**Dissipation from soil.** Factors affecting degradation of CPY in soil have been reviewed by Racke (1993). The key values that affect soil dissipation have been updated and are presented in SI Table A-1. Photolysis and oxidation are known to form CPYO in air (Mackay et al. 2014) and on foliar surfaces. These routes are either insignificant in soil or CPYO degrades as quickly as it is formed, since CPYO has only been formed in undetectable or small amounts in studies that have used radiotracers to investigate degradation in soils in the laboratory (de Vette and Schoonmade 2001; Racke et al. 1988) or field (Chapman and Harris 1980; Rouchaud et al. 1989). The primary degradation pathway in soil involves hydrolysis to yield 3,5,6-trichloropyridinol (TCP, Fig. 1) from either CPY or CPYO. Results of several studies have shown that this step can be either abiotic or biotic, and the rate is 1.7- to 2-fold faster in biologically active soils. Both modes of hydrolysis can occur in aerobic and anaerobic soil. The rate of abiotic hydrolysis is faster at higher pH. Hydrolysis is also faster in the presence of catalysts such as certain types of clay (Racke 1993). Degradation of the intermediate, TCP, is dependent on biological activity in soil, and leads to formation of bound residues and reversible formation of 3,5,6-trichloro-2-methoxypyridinol (TMP; Fig. 1). Under aerobic conditions, the primary, terminal degradation product of CPY is CO₂. Since TCP and TMP are not considered to be residues of concern (USEPA 2011b), they were not included in characterizations of exposures presented here or the assessment of risk in the companion papers. Because of rapid degradation in soil (see above), CPYO (Fig. 1) was not included in the characterization of exposures via soil.

The half-life for degradation of CPY in soils, based on results of studies conducted under standardized laboratory conditions, ranged from 2 to 1,575 d (n=68, next highest value is 335 d; SI Table A-1). This range in rates of degradation was attributed to differences in soil organic carbon content, moisture, rate of application, and microbial activity in the reported studies (Racke 1993); however, quantitative relationships between these potential drivers and rates of degradation have not been developed. Greater rates of application resulted in slower degradation, possibly due to the concentration in soil-water reaching the solubility limit of approximately 1 mg L⁻¹, which affects bioavailability to microbiota. The formulation applied can affect results; dissipation from material applied as the granular product is slower (Racke 1993). Half-lives for dissipation from soils determined under field conditions have been reported to range from 2 to 120 d (N=58; SI Table A-2).

**Biphasic dissipation.** Results of studies of aerobic degradation of CPY in soils under laboratory conditions exhibit bi-phasic behavior in most soils. Initial rates of degradation are greater than overall degradation rates by factors of 1.1 to 2.9 (Racke 1993). This behavior of CPY is also variable and not as apparent for some of the soils studied, for which half-lives were calculated by using simple first-order
kinetics (de Vette and Schoonmade 2001). Nonetheless, some of the half-lives reported in SI Table A-2 that have been derived from 1st-order degradation kinetics might overestimate the persistence of CPY in the environment.

There have been several approaches to calculate rate constants of degradation for this biphasic degradation of CPY. The DT50 values reported by Bidlack were calculated using the Hamaker two-compartment kinetic model (Nash 1988), but details of the goodness of fit were not provided and the DT50 values do not correspond to degradation rate constants (Bidlack 1979). Also, bi-phasic degradation, described by use of the double first-order parallel (DFOP) model, best characterized the data from three dissipation studies performed in terrestrial environments (Yon 2011).

To obtain the biphasic rate constants for the available aerobic soil degradation results, a dissipation model was structured with two compartments for the parent compound; one adsorbed in such a manner that was not available for biological degradation or abiotic hydrolysis, and the other in which these processes can occur (Fig. 2). The initial thought was to consider these as adsorbed and dissolved compartments, respectively. However, it is known that partitioning of CPY between soil and soil pore water reaches equilibrium within hours (Racke 1993), whereas the biphasic degradation process observed for CPY occurs over a period of several days. The two compartments were identified as Labile CPY and Adsorbed CPY. Reversible movement of parent CPY between these compartments was represented as two simple first-order processes shown by arrows F1 and F2 in Fig. 2, with rate constants k_ads and k_des. This model has advantages over older two-compartment models in that simple first-order equations are used and the rate constants are not concentration-dependent as they are in the Hamaker kinetic equations (Nash 1988). Since the reported concentrations of CPY include both compartments, the model was configured so that measured values are entered as the sum of the amounts in these two compartments at each time point (Fig. 2). The sum of processes that degrade CPY was also described as a first-order kinetic process F3, but was non-reversible. The rate constant for this process was designated km. The resulting set of three first-order equations was integrated numerically using Model-Maker Version 4.0 software from Cherwell Scientific Software Ltd. UK. Metabolism data from 11 soils reported in two studies (Bidlack 1979; de Vette and Schoonmade 2001) were fit to this model. It was assumed that the CPY was entirely in the labile compartment at time-zero, and the rate of degradation was determined by km and the concentration
in this compartment. As CPY partitions into the adsorbed compartment, less is available for degradation, and the rate of desorption, described by the rate constant $k_{des}$, becomes the rate limiting step. This transition from $k_m$ to $k_{des}$ creates the biphasic behavior in the model. Further details on the equations used the model set-up and typical results are given in SI Appendix C.

The model results fit the data well (SI Appendix C; SI Table C-2) (Bidlack 1979). The resulting rate constant represents the entire data set for each soil, optimized simultaneously and represents a consistent model across all the soils considered. This provides a better representation of the half-life than the values in the original reports. As noted above, it is expected that the rate constants might be correlated with the physical and chemical properties of the soils such as % organic matter, etc. No significant correlation could be found among rate constants or half-lives with the KOC, or water-holding capacity. It has been suggested that there might be a correlation between the rate constant $k_m$ for degradation of CPY, and pH (Bidlack 1979). This is expected, given the dependence of the abiotic hydrolysis on pH, which contributes to this process, but the correlation is not simple. A graph of half-life vs. pH is shown (Fig. 3). It is possible to consider the data in two groups; one group of soils has half-lives >30 d, which were pH dependent; the other group had shorter half-lives with a much weaker correlation to pH.

The correlations for the two groups in the range from pH 5 to 8 are given in (1) and (2).

\[
\text{Group 1 half-life} = 93.5 - 10.86 \times pH \left( r^2 = 0.76 \right) \quad (1)
\]

\[
\text{Group 2 half-life} = 267 - 30.14 \times pH \left( r^2 = 0.92 \right) \quad (2)
\]

The mean half-life in the Group-1 was 17.6 d with a 90th centile of 25.9 d and for Group-2 was 77.7 d with a 90th centile of 97.7 d. The greatest half-life among the U.S. soils in each group was selected as a conservative value to represent the group in simulations with the PRZM/EXAMS model runs used to characterize concentrations in surface waters (Williams et al. 2014). These values were 96 d from the Stockton soil and 28 d from the Catlin soil (Table 3).
Adsorption to soil. Based on reported water-soil adsorption coefficients ($K_{OC}$) of 973 to 31,000 mL g$^{-1}$; mean 8,216 mL g$^{-1}$ (SI Table A-3), CPY has a large potential to adsorb to soil and would not likely be biologically available for uptake by roots of plants. Possible uptake by roots, translocation, and metabolism of CPY in plants also has been investigated (summarized in Racke 1993). In general, negligible amounts enter the plant via the roots. Thus, CPY is not systemic and this pathway of exposure need not be considered in exposure assessments for CPY.

Dissipation from plants. CPY rapidly dissipates from foliar surfaces of plants, primarily due to volatility and secondarily due to photolysis, with most reported dissipation half-lives on the order of several days (Racke 1993). In a field study performed in California that examined mass loss of CPY to air, maximum volatility fluxes occurred in the first 8 h after application to recently cut alfalfa (Rotondaro and Havens 2012). Total mass loss of CPY, based on the calculated fluxes, ranged between 15.8 and 16.5% of applied mass, as determined by the Aerodynamic (AD) and Integrated Horizontal Flux (IHF) methodologies, respectively. Data on dissipation of CPY from various crops are provided in SI Table A-4.

Dissipation in aquatic systems. In aquatic systems, abiotic degradation of CPY due to aqueous hydrolysis has been reported to occur with half-lives at 25 °C of 73, 72, and 16 d at pH 5, 7, and 9, respectively (summarized in Racke 1993). The U.S. EPA (2011a) used an aqueous hydrolysis half-life of 81 d at pH 7 in modeling to estimate concentrations of CPY in drinking water. Half-lives of 22–51 d have been
reported from metabolism studies conducted in aerobic aquatic systems (Kennard 1996; Reeves and Mackie 1993). A half-life of 30 d was reported in an aqueous photolysis study of CPY that was conducted under natural sunlight in sterile pH 7 phosphate buffered solution (Batzer et al. 1990). Data on the dissipation of CPY from aquatic systems are summarized in SI Table A-5.

Field-scale analyses of runoff have demonstrated little potential for CPY to be transported with runoff water (Racke 1993). Chlorpyrifos has been extensively examined in field studies under varying conditions, including greater and lesser antecedent soil moisture, incomplete and full canopy development stages, 2 h to 7 d intervals between application and rainfall, maximum soil erosion conditions, different soils properties, and a range of rainfall events up to a 1-in-833 year return frequency (Cryer and Dixon-White 1995; McCall et al. 1984; Poletika and Robb 1994; Racke 1993). Resulting concentrations of CPY in runoff ranged from 0.003 to 4.4% of the amount applied (McCall et al. 1984; Poletika and Robb 1994). A field runoff study conducted in Mississippi indicated that the majority of chemical mass was transported in the dissolved chemical phase (Poletika and Robb 1994), while a study conducted in Iowa under record high rainfall conditions concluded that the majority of compound was transported attached to eroded sediment (Cryer and Dixon-White 1995).

### 3 Toxicity of CPY

The primary mode of action of organophosphorus insecticides, such as CPY, is well known and has been characterized in mammals (Testai et al. 2010) and in aquatic organisms, particularly fish (Giesy et al. 1999). Chlorpyrifos inhibits the enzyme acetylcholinesterase (AChE) in synaptic junctions of the nervous system. As a result of this inhibition, acetylcholine accumulated in the synapse causes repeated and uncontrolled stimulation of the post-synaptic axon. Disruption of the nervous system that results is the secondary effect that causes the death of the animal. The amino acid sequence of acetylcholinesterase is highly conserved in animals, with the result that CPY is toxic to most groups of animals, although differences in toxicokinetics (adsorption, distribution, metabolism, and excretion—ADME) account for differences in susceptibility among taxa (Timchalk 2010).

#### 3.1 Mechanism of Action

The mechanism of action (toxicodynamics) of CPY involves activation by biotic transformation to CPYO, followed by covalent binding to the serine-hydroxyl in the active site of the acetylcholinesterase molecule (Testai et al. 2010) (Fig. 4). While this can occur in the environment (Mackay et al. 2014), in animals this reaction is
catalyzed by multifunction oxidase enzymes (MFO) and is important in the mode of action of CPY. For example, inhibition of MFOs by the synergist piperonyl butoxide resulted in a decreased toxicity of CPY by up to sixfold in aquatic organisms (El-Merhibi et al. 2004). Chlorpyrifos itself is not a strong inhibitor of AChE, but when transformed to CPYO, the phosphorus atom in the molecule becomes more susceptible to nucleophilic attack by the serine hydroxyl in the active site of AChE. The initial association of CPYO with AChE is reversible (\(k_1, k_{-1}\); Fig. 4) and is modified by the tertiary structure of the enzyme and the inhibitor. During phosphorylation of the serine–OH (\(k_2\); Fig. 4), CPYO is hydrolyzed to release the leaving group TCP (Fig. 4), the reaction is no longer reversible, and AChE is inhibited for as long as it remains phosphorylated. The phosphonic acid moiety is covalently bound to the serine in AChE but the bond can be cleaved by hydrolysis, unless the phosphorylated enzyme ages. If the serine-O-P bond is hydrolyzed by water, AChE is reactivated and normal function returns. If aged via hydrolysis of one of ethyl-ester bonds (Fig. 4), the reactivity of the serine-O-P bond is greatly reduced, AChE cannot be reactivated, and recovery essentially requires the synthesis of new AChE.

The leaving group, TCP, is several orders of magnitude less toxic than CPY or CPYO (Giesy et al. 1999) and is not of toxicological significance (USEPA 2011a). The phosphonic acid released by reactivation of AChE is of low toxicity and is easily excreted from animals (Timchalk 2010). For this reason, the focus of the risk assessments in this series of papers (Cutler et al. 2014; Giddings et al. 2014; Moore et al. 2014) is only on CPY and CPYO. It should be noted that CPYO is the activated form of CPY and its formation in the animal is integral to the mode of action

![Fig. 4 Diagrammatic representation of the mechanism of action of chlorpyrifos in the nerve synapse](image)
of this insecticide, and thus, the toxicity of CPYO is implicitly considered when the toxicity of CPY is studied. As CPYO is also formed in the atmosphere (Mackay et al. 2014), it is considered in the risk assessments.

### 3.2 Interactions with Other Pesticides

Because conversion of CPY to CPYO is essential to the mode of action, compounds that induce multifunction oxidase activity in animals can influence the toxicity of CPY by increasing the rate of formation of CPYO. Atrazine, a herbicide with lesser toxicity than CPY and no activity on AChE, has been reported to synergize (increase or result in supra-additivity) the toxicity of CPY and some other organophosphorus pesticides in aquatic animals such as the midge, *Chironomus dilutus* (formerly *tentans*) (Belden and Lydy 2001). The mechanism of this synergism was via induction of multifunction oxidases by atrazine and the resulting increase in the formation of CPYO (Belden and Lydy 2000). Similar synergism has either not been observed or was observed only at small synergistic ratios (<2) in other invertebrates (Trimble and Lydy 2006) and vertebrates (Tyler Mehler et al. 2008; Wacksman et al. 2006). In addition, synergism was only observed at greater concentrations of atrazine and CPY, which rarely co-occur (Rodney et al. 2013). For this reason, synergistic interactions between CPY and other chemicals were not included in the assessment of the risks of CPY to aquatic organisms (Giddings et al. 2014).

Synergism of CPY by the sterol-inhibiting fungicide prochloraz was reported to occur in the red-legged partridge (Johnston et al. 1994), but this was only observed in birds pretreated at a large dose of 180 mg prochloraz kg$^{-1}$ (bwt), an extremely unlikely exposure in birds. The synergism was attributed to induction of multifunction oxidases and an increase in the formation of CPYO. As for aquatic organisms, interactions of this type were judged to be very unlikely to occur in terrestrial organisms and were not included in the risk assessment.

### 4 Use of Chlorpyrifos and Its Formulations

CPY is a widely used organophosphate pesticide with broad spectrum insecticidal activity. It is used against a broad array of insects and mites, primarily as a contact insecticide, although it does have some efficacy through ingestion. It provides control for many adult and larval forms of insects. Foliar pests for which CPY provides control include: aphids, beetles, caterpillars, leafhoppers, mites, and scale. CPY is also effective against many soil insects, including rootworms, cutworms, wireworms, and other grubs. Although it does not translocate readily, CPY can effectively control boring insects in corn, fruit, and other crops through contact exposure. It can also provide contact control of such insects as case-bearers, orange-worms, and other flies that damage fruits and nuts. The diversity of arthropod pests subject to control with CPY has made it one of most widely used insecticides.
4.1 Formulations of Chlorpyrifos

CPY is currently available as a granular formulation and as several spray formulations. CPY is widely effective against many different insects in various habitats that may attack crop throughout the year. Therefore, it has a wide variety of applications and may be applied to foliage, soil, or dormant trees. Application might occur preplant, at-plant, post-plant or during the dormant season using aerial equipment, chemigation systems, ground-boom sprayers, air-blast sprayers, tractor-drawn spreaders, and hand-held equipment. Dow AgroSciences (and its predecessors) originally developed CPY, but it is now also produced and/or marketed by other registrants of pesticides. The analysis of uses covered in this paper addresses only those CPY products that are registered by Dow AgroSciences, including Special Local Needs labels (SLNs, FIFRA section 24c) for specific States in the U.S. that are based upon these products.

*Lorsban 15G®* is a granular formulation that contains 15% (wt/wt) CPY (a.i.) in a solid matrix (Dow AgroSciences 2008). It is used primarily as a soil insecticide, although it can be applied into the whorls of corn to control European corn borer. Applications are in-furrow, banded, and broadcast. One “special local needs” label (FIFRA section 24c State label) was found for use on ginseng in Michigan.

*Lorsban 4E®* is an emulsifiable concentrate that contains 44.9% (wt/wt) a.i. (479 g L⁻¹ = 4 pounds of per gallon) (Dow AgroSciences 2004). It is used both directly on plants and as a soil treatment. Foliage and woody parts of plants can be treated. Treatments of soil are by broadcast, banded, side-dress, or, for onions and radishes, applied in-furrow. Chemigation is specified for some treatments. There are a few special local needs (24c) labels for the Lorsban 4E, but many old ones have expired and appear to have been replaced by similar labels for Lorsban Advanced®.

*Lorsban Advanced®* is a newer, low odor, water-based version of Lorsban 4E that contains 40.18% a.i. (wt/wt) (450 g L⁻¹ = 3.755 lb. a.i. per gallon) (Dow AgroSciences 2010). It is used in the same ways as the 4E formulation but contains smaller quantities of volatile solvents, thus reducing air pollution by VOCs. There are a number of special local needs (24c) labels for Lorsban Advanced that both modify application methods and rates and for several additional crops.

*Lorsban 75WG®* was registered by EPA late in 2011 (Gowan 2011), but is not yet listed among Dow AgroSciences products. It contains 75% a.i. (wt/wt) as water dispersible granules for use in many of the same crops as the Lorsban 4E and Lorsban Advanced formulations. One special local needs (24c) label for peppers in Florida was found that referenced Dow AgroSciences as the registrant, although Gowan Company was the distributor.

*Lorsban 50 W®* is a water soluble formulation that contains 50% a.i. (wt/wt) and is used for treating seeds in commercial establishments (Dow AgroSciences 2007). It is not permitted for such use on farms and other agricultural sites. It does, however, have a supplemental label for use on unspecified trees in the eastern U.S. The treatment is to trunks of trees at a rate of 3 lb a.i./100 gallons of spray, but no amount or limit per acre is specified. A similar use for Lorsban Advanced is only for apple trees in the eastern U.S., but the Lorsban 50 W label is not limited to any species of tree.
Rates and methods of application for Lorsban 15G are summarized in SI Table B-1. Flowable formulations of Lorsban Advanced, Lorsban 4E, and Lorsban 75WG are summarized (SI Tables B-2, B-3, and B-4). The crops, pests, methods, and rates are very similar for these three two flowable formulations. Because Lorsban 50 W does not have a federal label for application in agricultural settings, it was not included in the tabular information.

4.2 Environmental Precautions

All Lorsban products have the standard precautionary labeling involving risks to aquatic organisms, birds, small mammals, and bees. It is not to be applied to water or below the mean high tide level or when bees are visiting the area; dusk to dawn applications are allowed for many uses when bees are active during the day. Labels advise that drift and runoff might be hazardous in water adjacent to treated areas.

Lorsban 15G has a limitation on aerial application; rates >1.121 kg a.i. ha\(^{-1}\) (=1 lb. a.i. A\(^{-1}\)) are not permitted. Lorsban 4E, Lorsban Advanced, and Lorsban 75WG have mandatory buffers in their sections on drift-management: Setback buffers from aquatic habitats (“permanent bodies of water such as rivers natural ponds lakes, streams, reservoirms, marshes, estuaries and commercial fish ponds”) “must” be utilized: 7.6 m (25 ft) for ground application and chemigation, 15 m (50 ft) for orchard air blast, and 45 m (150 ft) for aerial applications. Aerial applications must follow nozzle and boom width requirements, and applications must neither be made more than 3 m (10 ft) above the height of the plants (unless required for aircraft safety), nor when wind speed exceeds 16 km h\(^{-1}\) (10 mph). The above buffers are mandatory. In addition, there are numerous additional recommendations on the label(s) meant to reduce drift. Lorsban Advanced, Lorsban 4E, and Lorsban 75WG may only be applied by ground spray equipment in Mississippi.

4.3 Use of Chlorpyrifos in U.S. Field Crops

Chlorpyrifos is one of the most widely used insecticides in the world. Estimates of annual use in the U.S. since 2008 range from 3.2 to 4.1 M kg y\(^{-1}\) (7 to 9 M lb a.i. per annum) (Gomez 2009; Grube et al. 2011). Because of withdrawal of domestic uses, changes in agricultural production, and the introduction of new insecticides, current use is less than 50% of estimated amounts used in the early 2000s (USEPA 2001). Although there are selected survey data from some states on certain crops, and quantitative usage data from California, there were no other recent applicable data on national usage. Estimates of use vary with the amounts of crops planted or harvested, with climate and pest pressure, and sometimes with recent or local occurrences of new or resistant pests.
Data on sales of granular and flowable CPY, presented as percent of total use across the U.S. from 2010 to 2011, are provided in Fig. 5 (developed from unpublished sales data from Dow AgroSciences). Regions with the highest percentage of total sales (depicted in blue), include Kern, Tulare, Santa Cruz, Fresno counties in central California; Lancaster County in southeastern Pennsylvania; and Calhoun, Decatur, and Mitchell counties in southeast Georgia.

Since purchases of CPY might not be made close to areas of use, data on sales might not accurately reflect use. Several agencies estimate pesticide use on crops but these estimates are derived from a variety of imprecise sources. Although California’s Pesticide Use Reporting (PUR) is based upon the actual amounts reported by pesticide users, all others are derived from sampling and statistical analyses. For specific crops, analysis of CPY use was undertaken by EPA (2008), Gomez (2009), and USDA’s National Agricultural Statistics Service (USDA 2012). Usage data for CPY are inclusive of all products from any manufacturer or registrant.

Data on amounts of pesticides used were collected differently by Gomez, USEPA, and USDA. EPA acquired their data from USDA/NASS from 2001 to 2006, proprietary market research data from 2001 to 2006, data from the CropLife Foundation’s National Pesticide Use Database, only when other data were not available, and California Pesticide Use Report (PUR) data from 2000 to 2005 when 95% of the crop was grown in California (USEPA 2008). EPA noted that their estimates included only data from states that were surveyed, rather than for the entire U.S. The reported figures were derived from an algorithm that covers many years but

Fig. 5 Geographical distribution of use of granular and liquid formulations of chlorpyrifos in the United States from 2010 to 2011 as % of total. Derived from unpublished sales data from Dow AgroSciences, Indianapolis, IN
gives more weight to recent data so as to give a “current” picture for the period over which the data were developed. Information is consistent across almost all crops and includes the total of active ingredient (a.i.) applied, likely average percent of crop treated and likely maximum percent of crop treated.

Gomez (2009) used proprietary data from 2003 to 2008 and California’s PUR data, when that State had more than 40% of the crop acreage. Gomez does not indicate if the reported usage covers all of the U.S.; it seems likely that the proprietary data would concentrate on states where the most acreage of specific crops was planted. Gomez reported estimated usage for all crops considered both for individual years and averages of 4–5 years. Although Gomez provided valuable data on the percentage of a crop treated, he used different methods of analysis based on proprietary data, which precluded comparisons with EPA and NASS data analyses. Gomez also used data that typically had 3–5 significant figures, while EPA used one significant figure in their estimates, or 2 significant figures for numbers of more than 1,000,000. Gomez calculated and presented the percent difference between his estimates and those of EPA. Although real differences existed between some numbers, many apparent differences resulted from averaging and different rounding methods.

The NASS performed usage surveys of individual pesticides on certain crops in selected states (“program states”) where those crops were most important (http://www.nass.usda.gov/). These surveys are not performed every year. The frequency is dependent upon the crop and typically varies from 3 to 5 y. Methods used by NASS are publically available; but, because they are required to protect individual privacy, data are aggregated in ways that sometimes hides useful information. NASS maintains databases of known growers that are stratified in several ways. They typically send out questionnaires to selected samples of growers. Depending upon the nature of the survey, they might follow up by letter, telephone or computer. They analyze these data using standard statistical aggregation. Therefore, the collected data are representative rather than actual, and only apply to the selected states. As a result, the amounts presented as total pesticide applied nationally are likely to be underestimates, the magnitude of which depends upon how much of a particular crop is grown in the states selected for analysis. However, the percentage of crops treated and the amount applied by acre are likely to be comparable in non-selected states. NASS data are reliable for specific states, at least for years that are sampled. Although annual data might be skewed, the comparisons are fairly close among sources when averaged over several years.

A summary of data from the three national sources on the amount of CPY used on various crops is given in Table 4. EPA estimates usage from existing stocks on some crops that are no longer labeled, but these are not included in Table 4. NASS usage estimates are only given for the latest year, although the amount of CPY used will vary considerably from year to year, depending upon pest pressure.
Table 4  Summary of amount of chlorpyrifos used and percentage of crop treated for selected crop sites

<table>
<thead>
<tr>
<th>Crop</th>
<th>Ave. lbs. a.i. applied (Gomez 2009)</th>
<th>Ave. lbs. a.i. applied (USEPA 2008)</th>
<th>Ave. % crop treated (USEPA 2008)</th>
<th>Ave. lbs. a.i. applied (NASS program states –latest year) USDA 2012</th>
<th>Ave. % crop treated (NASS USDA 2012)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alfalfa</td>
<td>374,750</td>
<td>400,000</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Almonds</td>
<td>341,991</td>
<td>500,000</td>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Asparagus</td>
<td>22,104</td>
<td>20,000</td>
<td>25</td>
<td>211,100</td>
<td>44</td>
</tr>
<tr>
<td>Apples</td>
<td>414,600</td>
<td>400,000</td>
<td>55</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Beans, green</td>
<td>4,119</td>
<td>3,000</td>
<td>&lt;1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Beans &amp; peas, dry</td>
<td>4,000</td>
<td>4,000</td>
<td>&lt;1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Broccoli</td>
<td>60,385</td>
<td>90,000</td>
<td>45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brussels Sprouts</td>
<td>6,000</td>
<td>n/c</td>
<td>n/c</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cabbage</td>
<td>7,055</td>
<td>10,000</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carrots (SLN-WA)</td>
<td>1,000</td>
<td>&lt;2.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cauliflower</td>
<td>15,239</td>
<td>20,000</td>
<td>40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cherries, all</td>
<td>80,140</td>
<td>60,000</td>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Christmas trees</td>
<td>26,600</td>
<td>16–20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Corn</td>
<td>2,617,432</td>
<td>3,000,000</td>
<td>5</td>
<td>478,000</td>
<td>1</td>
</tr>
<tr>
<td>Cotton</td>
<td>285,350</td>
<td>200,000</td>
<td>&lt;1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cranberries</td>
<td>50,000</td>
<td>70</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Grapefruit</td>
<td>54,855</td>
<td>60,000</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Grapes, wine</td>
<td>68,603</td>
<td>64,500</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Grapes, table</td>
<td>60,428</td>
<td>40,000</td>
<td>12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Grapes, all</td>
<td>100,000</td>
<td>10</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hazelnuts</td>
<td>7,286</td>
<td>7,000</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lemons</td>
<td>47,033</td>
<td>90,000</td>
<td>35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mint</td>
<td>50,000</td>
<td>25</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nectarines</td>
<td>20,000</td>
<td>20</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Onions, dry</td>
<td>68,805</td>
<td>60,000</td>
<td>35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oranges</td>
<td>241,735</td>
<td>300,000</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peaches</td>
<td>69,853</td>
<td>70,000</td>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peanuts</td>
<td>119,213</td>
<td>200,000</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pears</td>
<td>29,564</td>
<td>30,000</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peas, green</td>
<td>&lt;500</td>
<td>&lt;1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pecans</td>
<td>296,596</td>
<td>300,000</td>
<td>35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peppers (SLN-FL)</td>
<td>2,000</td>
<td>&lt;1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plums &amp; Prunes</td>
<td>18,674</td>
<td>40,000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plums</td>
<td></td>
<td>15</td>
<td>2,400</td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>Prunes</td>
<td></td>
<td>10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sod/turf</td>
<td>2,000</td>
<td>n/c</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sorghum</td>
<td>30,000</td>
<td>&lt;1</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(continued)
4.4 Timing of the Use of Chlorpyrifos

CPY is normally applied to coincide with infestations of pests, which vary from one location to another. Timing of application of CPY in relation to local climatic conditions, rainfall, and patterns of weather might have significant effects on the degradation, potential for movement, and exposures of non-target organisms. To properly characterize timing of the use of CPY, we relied on the USDA publication “Usual Planting and Harvesting Dates for U.S. Field Crops” (USDA 2010) and other sources (i.e., mainly state extension services and the internet). These data are summarized in Table 5 for crops that are in the field year round, and in Table 6 for crops that are seasonal.

From these data, it is apparent that there is no strong seasonal use of CPY, although there is a somewhat greater usage in winter months for tree crops in California and greater use in summer for certain field crops (e.g., corn). These use patterns and how they affect scenarios for exposures are discussed in more detail in the companion papers of this volume (Moore et al. 2014; Williams et al. 2014).

5 Summary

Physical properties and use data provide the basis for estimating environmental exposures to chlorpyrifos (CPY) and for assessing its risks. The vapor pressure of CPY is low, solubility in water is <1 mg L⁻¹, and its log K_{ow} is 5. Chlorpyrifos has
Table 5  Timing of chlorpyrifos use for crops in the U.S. that are in the field all year (Jan to Dec)

<table>
<thead>
<tr>
<th>Crop and location</th>
<th>Months of the year in which CPY is applied</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>J</td>
</tr>
<tr>
<td>Alfalfa, warmer states (CA, AZ, etc.)</td>
<td></td>
</tr>
<tr>
<td>Cooler states</td>
<td></td>
</tr>
<tr>
<td>Southern MO</td>
<td></td>
</tr>
<tr>
<td>Northern MO</td>
<td></td>
</tr>
<tr>
<td>Apple tree trunks</td>
<td></td>
</tr>
<tr>
<td>Asparagus CA only Southern desert</td>
<td></td>
</tr>
<tr>
<td>Delta</td>
<td></td>
</tr>
<tr>
<td>Central coast</td>
<td></td>
</tr>
<tr>
<td>Other U.S.</td>
<td></td>
</tr>
<tr>
<td>Brassica (cole) leafy vegetables</td>
<td></td>
</tr>
<tr>
<td>Brussels sprouts</td>
<td></td>
</tr>
<tr>
<td>Carrots for seed OR &amp; WA</td>
<td></td>
</tr>
<tr>
<td>Christmas tree</td>
<td></td>
</tr>
<tr>
<td>Citrus orchard floors</td>
<td></td>
</tr>
<tr>
<td>Citrus fruits</td>
<td></td>
</tr>
<tr>
<td>Cranberry</td>
<td></td>
</tr>
<tr>
<td>Fig (CA only)</td>
<td></td>
</tr>
<tr>
<td>Ginseng (MI, WI-SLN*)</td>
<td></td>
</tr>
<tr>
<td>Grape (E of Continental Divide only)</td>
<td></td>
</tr>
<tr>
<td>Grapes (CA-SLN)</td>
<td></td>
</tr>
<tr>
<td>Grass and clover for seed (NV, ID, OR, WA-SLNs)</td>
<td></td>
</tr>
<tr>
<td>Legume vegetables (except soybeans)</td>
<td></td>
</tr>
<tr>
<td>Onion (dry bulb)</td>
<td></td>
</tr>
<tr>
<td>Pears (CA, OR, &amp; WA only)</td>
<td></td>
</tr>
<tr>
<td>Peppers (FL only – special local need)</td>
<td></td>
</tr>
<tr>
<td>Pineapple (HI only – special local need)</td>
<td></td>
</tr>
<tr>
<td>Pulpwood (cottonwood &amp; poplar, OR, WA-SLNs)</td>
<td></td>
</tr>
<tr>
<td>Strawberries</td>
<td></td>
</tr>
<tr>
<td>Tree fruits and nuts – all applications, almond</td>
<td></td>
</tr>
<tr>
<td>Apples (all U.S.)</td>
<td></td>
</tr>
<tr>
<td>Apples (eastern U.S.)</td>
<td></td>
</tr>
<tr>
<td>Cherry</td>
<td></td>
</tr>
<tr>
<td>Filbert</td>
<td></td>
</tr>
<tr>
<td>Nectarine</td>
<td></td>
</tr>
<tr>
<td>Peach</td>
<td></td>
</tr>
<tr>
<td>Pear</td>
<td></td>
</tr>
<tr>
<td>Pecan</td>
<td></td>
</tr>
<tr>
<td>Plum</td>
<td></td>
</tr>
<tr>
<td>Prune</td>
<td></td>
</tr>
<tr>
<td>Walnut</td>
<td></td>
</tr>
<tr>
<td>Turfgrass</td>
<td></td>
</tr>
<tr>
<td>Wheat (W of the Mississippi River)</td>
<td></td>
</tr>
</tbody>
</table>

(continued)
short to moderate persistence in the environment as a result of several dissipation pathways that may proceed concurrently. Primary mechanisms of dissipation include volatilization, photolysis, abiotic hydrolysis, and microbial degradation. Volatilization dominates dissipation from foliage in the initial 12 h after application, but decreases as CPY adsorbs to foliage or soil. In the days after application, CPY adsorbs more strongly to soil, and penetrates more deeply into the soil matrix, becoming less available for volatilization. After the first 12 h, other processes of degradation, such as chemical hydrolysis and catabolism by microbiota become important. The half-life of CPY in soils tested in the laboratory ranged from 2 to 1,575 d (N = 126) and is dependent on properties of the soil and rate of application. At application rates used historically for control of termites, the degradation rate is much slower than for agricultural uses. In agricultural soils under field conditions, half-lives are shorter (2 to 120 d, N = 58). The mean water-soil adsorption coefficient (KOC) of CPY is 8,216 mL g⁻¹; negligible amounts enter plants via the roots, and it is not translocated in plants.
Half-lives for hydrolysis in water are inversely dependent on pH, and range from 16 to 73 d. CPY is an inhibitor of acetylcholinesterase and is potentially toxic to most animals. Differences in susceptibility result from differences in rates of adsorption, distribution, metabolism, and excretion among species. CPY is an important tool in management of a large number of pests (mainly insects and mites) and is used on a wide range of crops in the U.S. Estimates of annual use in the U.S. from 2008 to 2012 range from 3.2 to 4.1 M kg y\(^{-1}\), which is about 50% less than the amount used prior to 2000. Applications to corn and soybeans accounts for 46–50% of CYP’s annual use in the U.S.

### Table 6: Timing of chlorpyrifos use for crops in the U.S. that are in the field part of the year

<table>
<thead>
<tr>
<th>Crop in field, location, and use of CPY</th>
<th>Months of the year in which CPY is applied</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>J</td>
</tr>
<tr>
<td>Corn, Southern states in field</td>
<td></td>
</tr>
<tr>
<td>Use of CPY</td>
<td></td>
</tr>
<tr>
<td>Northern states in field</td>
<td></td>
</tr>
<tr>
<td>Use of CPY</td>
<td></td>
</tr>
<tr>
<td>Cotton, Southern areas in field</td>
<td></td>
</tr>
<tr>
<td>Use of CPY</td>
<td></td>
</tr>
<tr>
<td>Northern areas + CA in field</td>
<td></td>
</tr>
<tr>
<td>Use of CPY</td>
<td></td>
</tr>
<tr>
<td>Peanuts, in field</td>
<td></td>
</tr>
<tr>
<td>Use of CPY</td>
<td></td>
</tr>
<tr>
<td>Peppermint and Spearmint, in field</td>
<td></td>
</tr>
<tr>
<td>Use of CPY</td>
<td></td>
</tr>
<tr>
<td>Sorghum, in field</td>
<td></td>
</tr>
<tr>
<td>Use of CPY</td>
<td></td>
</tr>
<tr>
<td>Soybeans, in field</td>
<td></td>
</tr>
<tr>
<td>Use of CPY</td>
<td></td>
</tr>
<tr>
<td>Sugarbeets, in field Imperial Valley, CA</td>
<td></td>
</tr>
<tr>
<td>Use of CPY</td>
<td></td>
</tr>
<tr>
<td>Other locations in field</td>
<td></td>
</tr>
<tr>
<td>Use of CPY</td>
<td></td>
</tr>
<tr>
<td>Sunflowers, in field CA</td>
<td></td>
</tr>
<tr>
<td>Use of CPY</td>
<td></td>
</tr>
<tr>
<td>TX &amp; OK in field</td>
<td></td>
</tr>
<tr>
<td>Use of CPY</td>
<td></td>
</tr>
<tr>
<td>Other states in field</td>
<td></td>
</tr>
<tr>
<td>Use of CPY</td>
<td></td>
</tr>
<tr>
<td>Sweet potato, in field</td>
<td></td>
</tr>
<tr>
<td>Use of CPY</td>
<td></td>
</tr>
<tr>
<td>Tobacco, in field New England &amp; PA</td>
<td></td>
</tr>
<tr>
<td>Use of CPY</td>
<td></td>
</tr>
<tr>
<td>Southern states in field</td>
<td></td>
</tr>
<tr>
<td>Use of CPY</td>
<td></td>
</tr>
</tbody>
</table>

Data from: (Chen et al. 2011; USDA 2010; Zheljazkov et al. 2010)
Acknowledgements The authors thank Kendall Price, Waterborne, and Larry Turner, Compliance Services International, for compiling information on the properties and use of chlorpyrifos. We thank the anonymous reviewers of this paper for their suggestions and constructive criticism. Prof. Giesy was supported by the Canada Research Chair program, a Visiting Distinguished Professorship in the Department of Biology and Chemistry and State Key Laboratory in Marine Pollution, City University of Hong Kong, the 2012 “High Level Foreign Experts” (#GDW20123200120) program, funded by the State Administration of Foreign Experts Affairs, the P.R. China to Nanjing University and the Einstein Professor Program of the Chinese Academy of Sciences. Funding for this study was provided by Dow AgroSciences.

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Poletika NN, Robb CK (1994) A field runoff study of chlorpyrifos in Mississippi delta cotton. Indianapolis, IN, DowElanco, Unpublished Report


### SI Table A-1  Studies on dissipation of chlorpyrifos from soil under aerobic laboratory conditions

<table>
<thead>
<tr>
<th>Location</th>
<th>Soil series or texture</th>
<th>O.C. (%)</th>
<th>pH</th>
<th>Temp (°C)</th>
<th>T½ (d)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commerce, Mississippi</td>
<td>Loam</td>
<td>0.68</td>
<td>7.4</td>
<td>25</td>
<td>11</td>
<td>Bidlack (1979)</td>
</tr>
<tr>
<td>Barnes, North Dakota</td>
<td>Loam</td>
<td>3.8</td>
<td>7.1</td>
<td>25</td>
<td>22</td>
<td>Bidlack (1979)</td>
</tr>
<tr>
<td>Norfolk, Virginia</td>
<td>Loam</td>
<td>0.29</td>
<td>6.8</td>
<td>25</td>
<td>102</td>
<td>Bidlack (1979)</td>
</tr>
<tr>
<td>Miami, Indiana</td>
<td>Silt loam</td>
<td>1.12</td>
<td>6.6</td>
<td>25</td>
<td>24</td>
<td>Bidlack (1979)</td>
</tr>
<tr>
<td>Caitlin, Illinois</td>
<td>Silty clay loam</td>
<td>2.01</td>
<td>6.5</td>
<td>25</td>
<td>34</td>
<td>Bidlack (1979)</td>
</tr>
<tr>
<td>Germany</td>
<td>2.3 Standard</td>
<td>1.01</td>
<td>5.4</td>
<td>25</td>
<td>141</td>
<td>Bidlack (1979)</td>
</tr>
<tr>
<td>Stockton, California</td>
<td>Clay Adobe</td>
<td>1.15</td>
<td>5.9</td>
<td>25</td>
<td>107</td>
<td>Bidlack (1979)</td>
</tr>
<tr>
<td>Marcham, UK</td>
<td>Sandy clay loam</td>
<td>1.7</td>
<td>7.7</td>
<td>20</td>
<td>43</td>
<td>(de Vette and Schoonmade 2001)</td>
</tr>
<tr>
<td>Charentilly, France</td>
<td>Silty clay loam</td>
<td>1</td>
<td>6.1</td>
<td>20</td>
<td>95</td>
<td>(de Vette and Schoonmade 2001)</td>
</tr>
<tr>
<td>Cuckney, UK</td>
<td>Sand</td>
<td>1.2</td>
<td>6</td>
<td>20</td>
<td>111</td>
<td>(de Vette and Schoonmade 2001)</td>
</tr>
<tr>
<td>Thessaloniki, Greece</td>
<td>Loam</td>
<td>0.8</td>
<td>7.9</td>
<td>20</td>
<td>46</td>
<td>(de Vette and Schoonmade 2001)</td>
</tr>
<tr>
<td>Catania, (south) Italy</td>
<td>Soil A 77% WHC</td>
<td>1.5</td>
<td>8.3</td>
<td>30</td>
<td>2</td>
<td>(Finocchiaro et al. 2004)</td>
</tr>
<tr>
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*Half-life rounded to the nearest day unless a range provided.

*Study referenced in (Racke 1993)

*WCH = Water Holding Capacity
### SI Table A.2. Studies on dissipation of chlorpyrifos from soil in terrestrial field environments

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*Half-life rounded to the nearest day.

Study referenced in (Racke 1993)
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<td>K_d</td>
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* Study referenced in (Racke 1993)

* Not calculated because of the small concentrations of carbon in the clays.
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<th>Conditions</th>
<th>Location</th>
<th>Initial Residue (mg kg⁻¹)</th>
<th>Racke¹</th>
<th>Reference</th>
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<tr>
<td>Bluegrass</td>
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<td>Field</td>
<td>New York</td>
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¹ Study referenced in (Racke 1993)
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<th>Clay</th>
<th>pH</th>
<th>Temp (°C)</th>
<th>T½ *</th>
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<td>Clay loam sediment from pond</td>
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<td>25.4</td>
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*T½ is for the combined sediment-water system.

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SI Appendix B. Use pattern for formulations of CPY
To maintain consistency with uses and the labels of formulated products sold in the USA, rates of application of CPY are given in imperial units.

**SI Table B-1 Use patterns for the application of Lorsban 15G** (granular chlorpyrifos Dow AgroSciences 2008a)

<table>
<thead>
<tr>
<th>Crop</th>
<th>Method of application</th>
<th>Maximum single application rate (lbs. a.i./A)</th>
<th>Maximum number of applications per season</th>
<th>Maximum seasonal application rate (lbs. a.i./A)</th>
<th>Minimum retreatment interval (d)</th>
<th>Timing</th>
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<tbody>
<tr>
<td>Alfalfa (Missouri only)</td>
<td>In-furrow (at-plant)</td>
<td>1</td>
<td>1</td>
<td>1</td>
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<td>At plant</td>
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<tr>
<td>Asparagus (California only)</td>
<td>Band (postplant); cover with soil the day of application</td>
<td>1.5</td>
<td>2</td>
<td>3</td>
<td>--</td>
<td>180-d PHI*</td>
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<tr>
<td>Citrus orchard floors</td>
<td>Broadcast uniformly to soil; no incorporation or covering with soil</td>
<td>1</td>
<td>3</td>
<td>3 (including foliar)</td>
<td>10</td>
<td>28-d PHI</td>
</tr>
<tr>
<td>Cole crop (Brassica) leafy vegetables*, rutabaga, and turnip</td>
<td>T-band (at-plant); shallow incorporation</td>
<td>2.25</td>
<td>1 (15 G); foliar as on foliar label</td>
<td>2.25</td>
<td>10 (foliar chlorpyrifos)</td>
<td>At plant</td>
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<tr>
<td>Corn (field corn and sweet corn, including corn grown for seed)*</td>
<td>T-band (at-plant) or in-furrow (at-plant); incorporate T-band ½-1 inch; split band on either side of row (postplant) and covered with soil, or aerial or ground broadcast (postplant) into whorls of ears</td>
<td>1.3 (ground); 1 (aerial)</td>
<td>2 (15G); (might apply 3 total chlorpyrifos)</td>
<td>2.3</td>
<td>10</td>
<td>At plant in furrow or T-band; unspecified for post-plant split band; broadcast (aerial or ground) when ear whorls have formed</td>
</tr>
</tbody>
</table>

* Pre-harvest Intervals (PHI) are intended for the protection of consumers and do not necessarily relate to ecological exposure and effects. However, they do provide information on when, during a crop cycle, chlorpyrifos might be applied ecological exposure and effects.

* Brassica leafy vegetables include bok choy, broccoli, broccoli raab, Brussels sprouts, cabbage, cauliflower, Chinese broccoli, Chinese cabbage, collards, kale, and kohlrabi.

* Aerial applications of Lorsban 15G to corn not permitted within 160 feet of water (rivers, natural ponds, lakes, etc.)
<table>
<thead>
<tr>
<th>Crop</th>
<th>Method of application</th>
<th>Maximum single application rate (lbs. a.i./A)</th>
<th>Maximum number of applications per season</th>
<th>Maximum seasonal application rate (lbs. a.i./A)</th>
<th>Minimum retreatment interval (d)</th>
<th>Timing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ginseng (24c MI, WI)</td>
<td>Broadcast with incorporation (pre-plant); Bed-directed (prior to seeding); Broadcast with overhead watering (postemergence bed-directed)</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>--</td>
<td>Preplant or post-emergent; 365-d PHI</td>
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<tr>
<td>Onion (dry bulb)</td>
<td>In-furrow (at-plant); or (in CO, ID, WA, OR only) in 5-7 inch band with shallow incorporation</td>
<td>1</td>
<td>1 (of any formulation)</td>
<td>1</td>
<td>--</td>
<td>At plant</td>
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<tr>
<td>Peanut</td>
<td>6-12 inch Band (at-plant, postplant preventative) 10-18 inch band (postplant rescue) Incorporate at plant band 1 inch</td>
<td>4</td>
<td>2 (15 G)</td>
<td>4 (all chlorpyrifos)</td>
<td>10</td>
<td>21-d PHI</td>
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<td>Radish</td>
<td>In-furrow (at-plant)</td>
<td>2.75</td>
<td>1</td>
<td>2.75</td>
<td>--</td>
<td>At plant</td>
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<tr>
<td>Sorghum - grain sorghum (milo)</td>
<td>6-6 inch T-band (at-plant); incorporate ½ to 1 inch (&quot;absolutely necessary&quot;)</td>
<td>1.5</td>
<td>1 (15 G)</td>
<td>1.5 (no label limits on other formulations)</td>
<td>10 d before application of liquid chlorpyrifos</td>
<td>At plant</td>
</tr>
<tr>
<td>Soybean</td>
<td>4-10 inch T-band (at-plant, postplant); incorporate ½ to 1 inch</td>
<td>2 (at-plant); 1 (postplant)</td>
<td>1 (15G); 3 (all chlorpyrifos)</td>
<td>2</td>
<td>10 d before application of liquid chlorpyrifos</td>
<td>At plant; postplant not specified; 28-d PHI</td>
</tr>
<tr>
<td>Sugarbeet</td>
<td>Band (at-plant or postemergence); incorporate ½ to 1 inch</td>
<td>2</td>
<td>1 (15G); 3 (all chlorpyrifos)</td>
<td>2 (maximum 3 lb. a.i. total chlorpyrifos)</td>
<td>10 d before application of liquid chlorpyrifos</td>
<td>At plant or before 4-leaf stage</td>
</tr>
<tr>
<td>Sunflower</td>
<td>7 inch T-band (at-plant); incorporate 1 inch</td>
<td>1.3</td>
<td>1 (15G); 3 (all chlorpyrifos)</td>
<td>2 (maximum 3 lb. a.i. total chlorpyrifos)</td>
<td>10 d before application of liquid chlorpyrifos</td>
<td>At plant</td>
</tr>
<tr>
<td>Crop</td>
<td>Method of application</td>
<td>Maximum single application rate (lbs. a.i./A)</td>
<td>Maximum number of applications per season</td>
<td>Maximum seasonal application rate (lbs. a.i./A)</td>
<td>Minimum retreatment interval (d)</td>
<td>Timing</td>
</tr>
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<td>-------------------------------------------</td>
</tr>
<tr>
<td>Sweet potato</td>
<td>Broadcast with 4-6 inch incorporation (pre-plant)</td>
<td>2</td>
<td>1 (of any chlorpyrifos formulation)</td>
<td>2</td>
<td>–</td>
<td>1-14 d pre-plant; 150 d PHI</td>
</tr>
<tr>
<td>Tobacco</td>
<td>Broadcast with 2-4 inch incorporation (pre-plant)</td>
<td>2</td>
<td>1 (of any chlorpyrifos formulation)</td>
<td>2</td>
<td>–</td>
<td>1 week before transplanting; 7 d PHI</td>
</tr>
<tr>
<td>Crop</td>
<td>Method of application</td>
<td>Maximum single application rate (lbs. a.i./A)</td>
<td>Maximum number of applications per season</td>
<td>Maximum seasonal application rate (lbs. a.i./A)</td>
<td>Minimum retreatment interval (d)</td>
<td>Timing</td>
</tr>
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<td>----------------------------</td>
</tr>
<tr>
<td>Alfalfa (not for use in MS)</td>
<td>Broadcast aerial or ground spray, or sprinkler chemigation (foliar application)</td>
<td>0.94</td>
<td>4 (but maximum of 1 app /cutting)</td>
<td>3.75 (of any chloryrifos product)</td>
<td>10</td>
<td>7-21-d PHI</td>
</tr>
<tr>
<td>Almond orchard floor (24c CA)</td>
<td>Individual mound treatment</td>
<td>4</td>
<td>2</td>
<td>8</td>
<td>14</td>
<td>14-d PHI</td>
</tr>
<tr>
<td>Apple tree trunk (east of Rockies only)(not for use in MS)</td>
<td>One application per year directed to lower 4 feet of apple tree trunk from a distance of no more than 4 feet away. No rate per acre given, but 2.82 lbs. a.i./100 gal of spray. Not to contact foliage or fruit.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Asparagus²</td>
<td>Broadcast foliar spray by ground</td>
<td>0.94</td>
<td>3</td>
<td>2.82</td>
<td>10</td>
<td>1-d PHI</td>
</tr>
<tr>
<td>Bok Choy, broccoli raab, Chinese broccoli (24c CA)</td>
<td>Broadcast spray to soil by ground only</td>
<td>2.11</td>
<td>1</td>
<td>2.11</td>
<td>--</td>
<td>30-d PHI</td>
</tr>
<tr>
<td>Brassica (cole) leafy vegetables and radish, rutabaga, and turnip (Section 3 federal label including 24 c label for CA)³</td>
<td>Pre-plant broadcast spray to soil with 2-4 inch incorporation (pre-plant)</td>
<td>1.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Four-inch banded soil application at plant or directed spray to base of plant after transplant; or postemergent sidedress for broccoli &amp; cabbage</td>
<td>Broccoli, Brussels sprouts, leafy brassica, turnip, rutabaga: 2.1</td>
<td>1 soil of any kind</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Apply as drench in seed furrow at planting</td>
<td>Radish: 2.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

² For use on asparagus only in Arizona, California, Idaho, Illinois, Indiana, Iowa, Kansas, Michigan, Minnesota, Missouri, Nebraska, North Dakota, Ohio, Oregon, South Dakota, Washington and Wisconsin.
³ California has a 24 c label that has the same provisions for this as the federal label, except that it allows two treatments 10 d apart for cauliflower broccoli and Brussels sprouts, but the total maximum soil application rate for the year is the same. This 24c label has slightly different directions also for rutabaga and cabbage which do not alter the exposure potential.
⁴ On the federal label, crops include broccoli, broccoli raab, Brussels sprouts, cabbage, cauliflower, Chinese cabbage, collards, kale, kohlrabi, mizuni, mustard greens, and rape greens.
<table>
<thead>
<tr>
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<th>Maximum single application rate (lbs. a.i./A)</th>
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<th>Minimum retreatment interval (d)</th>
<th>Timing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brussels sprout</td>
<td>Four-inch banded soil application at plant or directed spray to base of plant after transplant; or foliar application</td>
<td>0.94</td>
<td>3</td>
<td>2.82</td>
<td>10</td>
<td>21-d PHI</td>
</tr>
<tr>
<td>Carrots for seed (24c OR, WA)</td>
<td>Foliar broadcast</td>
<td>0.94</td>
<td>1</td>
<td>0.94</td>
<td>--</td>
<td>As needed</td>
</tr>
<tr>
<td>Christmas trees (plantations) (not for use in MS)</td>
<td>Foliar ground broadcast; power spray (postplant); cut stump drench</td>
<td>0.94</td>
<td>3</td>
<td>2.82</td>
<td>7</td>
<td>As needed</td>
</tr>
<tr>
<td>Christmas trees (plantations) (24c WA)</td>
<td>Broadcast foliar spray (aerial)</td>
<td>0.94</td>
<td>3</td>
<td>2.82</td>
<td>7</td>
<td>As needed</td>
</tr>
<tr>
<td>Christmas trees (plantations) (24c OR)</td>
<td>Broadcast foliar spray (aerial-helicopter only)</td>
<td>0.94</td>
<td>3</td>
<td>2.82</td>
<td>7</td>
<td>As needed</td>
</tr>
<tr>
<td>Citrus fruits(^a) (not for use in MS)</td>
<td>Foliar broadcast; directions imply air-blast but aerial not precluded</td>
<td>3.3 except CA &amp; AZ</td>
<td></td>
<td>5.6 in AZ &amp; Fresno, Tulare, Kern, Kings and Madera Counties, CA</td>
<td>2 (not including orchard floor)</td>
<td>7.04</td>
</tr>
<tr>
<td>Citrus (red scale only) (24c CA)</td>
<td>Foliar broadcast spray with ground equipment</td>
<td>5.64</td>
<td>2</td>
<td>7.04</td>
<td>30</td>
<td>35-d PHI; &quot;To avoid excessive ridging, do not apply Lorsban 4-E to citrus fruit from December 1 up to the initiation of bloom&quot;</td>
</tr>
</tbody>
</table>

\(^a\) Citrus fruits on label include calamondin, chironja, citrus citron, citrus hybrids, grapefruit, kumquat, lemon, lime, mandarin (tangerine), pomelo, Satsuma mandarin, sour orange, sweet orange, tangelo, tanger
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<tr>
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<th>Minimum retreatment interval (d)</th>
<th>Timing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Citrus (Argentine ants, fuller rose beetle (24c CA))</td>
<td>Broadcast spray to soil at base of trees (ants only)</td>
<td>1.0</td>
<td>3</td>
<td>Not specified</td>
<td>10</td>
<td>28-d PHI</td>
</tr>
<tr>
<td></td>
<td>Apply to fiberglass band of insulation wrapped around tree trunk (beetle and ants)</td>
<td>2.5</td>
<td>7.5</td>
<td>Not specified</td>
<td>Not specified</td>
<td>28-d PHI</td>
</tr>
<tr>
<td>Citrus orchard floors (not for use in MS)</td>
<td>Broadcast spray to orchard floor or sprinkler chemigation to soil around trees</td>
<td>1</td>
<td>3</td>
<td>2.82</td>
<td>10</td>
<td>28-d PHI</td>
</tr>
<tr>
<td>Clover for seed (24c OR — expires Dec 2012)</td>
<td>Broadcast spray to soil with 2-4 inch incorporation (pre-plant); Broadcast foliar spray (postplant)</td>
<td>1.88</td>
<td>1</td>
<td>1.88</td>
<td>--</td>
<td>Not specified</td>
</tr>
<tr>
<td>Corn (field, sweet, seed)</td>
<td>Broadcast spray to ground surface in &quot;Conservation Tillage&quot; (pre-plant, pre-emergence, at-plant); foliar spray by air (except MS) or ground (postplant)</td>
<td>1</td>
<td>3 (any chlorpyrifos)</td>
<td>3</td>
<td>10</td>
<td>21-d PHI</td>
</tr>
<tr>
<td>Corn (sweet) (24c CO, FL)</td>
<td>Foliar broadcast spray by air, ground, or chemigation</td>
<td>0.5</td>
<td>3 (folliar) + 1 preplant soil</td>
<td>10 CO 5 FL</td>
<td>7-d PHI</td>
<td></td>
</tr>
<tr>
<td>Cotton (not for use in MS)</td>
<td>Foliar broadcast spray by air, ground, or chemigation</td>
<td>0.94</td>
<td>3</td>
<td>2.82</td>
<td>10</td>
<td>14-d PHI</td>
</tr>
<tr>
<td>Cottonwood, poplar trees for pulp (24c OR — expires Dec 2011 &amp; WA-expires Dec 2012)</td>
<td>Foliar or dormant/delayed dormant spray by ground or air</td>
<td>1.88</td>
<td>3</td>
<td>5.64</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>Cranberry (not for)</td>
<td>Broadcast foliar or</td>
<td>1.41</td>
<td>2 (any)</td>
<td>2.82</td>
<td>10</td>
<td>60-d PHI; do not</td>
</tr>
<tr>
<td>Crop</td>
<td>Method of application</td>
<td>Maximum single application rate (lbs. a.i/A)</td>
<td>Maximum number of applications per season</td>
<td>Maximum seasonal application rate (lbs. a.i/A)</td>
<td>Minimum retreatment interval (d)</td>
<td>Timing</td>
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</tr>
<tr>
<td>use in MS</td>
<td>sprinkler irrigation (postplant)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>apply until winter flood water has been removed, nor when bags are flooded</td>
</tr>
<tr>
<td>Fig (CA only)</td>
<td>Broadcast spray to soil surface with three inch incorporation (dormant)</td>
<td>1.88</td>
<td>1</td>
<td>1.88</td>
<td></td>
<td>217-d PHI; apply late winter</td>
</tr>
<tr>
<td>Grape (east of the continental divide only) (not for use in MS)</td>
<td>Soil surface spray (4 ft. circle around base of vine), or spray drench to soil (prebloom)</td>
<td>Soil surface 2.12/100 gal to treat 3000 sq ft; Prebloom 0.94</td>
<td>1</td>
<td>Soil surface 2.12; Prebloom 0.94</td>
<td></td>
<td>35-d PHI; apply prior to bloom</td>
</tr>
<tr>
<td>Grape (mealybugs) (24c CA)</td>
<td>Broadcast spray to all above ground parts of plant</td>
<td>1.88</td>
<td>2</td>
<td>1.88 (all chlorpyrifos)</td>
<td></td>
<td>Not specified but 1 before budbreak and 1 after harvest</td>
</tr>
<tr>
<td>Grape (mealybug, cutworms) (24c WA, ID, CO)</td>
<td>Band at base of vine (cutworms);</td>
<td>0.94</td>
<td>2</td>
<td>1.88</td>
<td></td>
<td>35-d PHI; do not apply between budbreak and harvest</td>
</tr>
<tr>
<td>Grape (Argentine ants) (24c CA)</td>
<td>Broadcast spray to all above ground parts of plant</td>
<td>1.88</td>
<td>2</td>
<td>1.88</td>
<td></td>
<td>35-d PHI; do not apply after bloom stage</td>
</tr>
<tr>
<td>Grass for seed (perennial) (24c OR, WA, ID, NV)</td>
<td>Spray basal one-foot of vines and surrounding soil</td>
<td>0.94</td>
<td>3</td>
<td>2.88</td>
<td></td>
<td>Not specified</td>
</tr>
<tr>
<td></td>
<td>Foliar broadcast spray by ground (all states), or by air (WA, ID) or by chemigation (OR)</td>
<td>0.94</td>
<td>3</td>
<td>WA 2.5; OR, ID, NV 2.82</td>
<td></td>
<td>Apply early April (bilbugs), spring &amp; fall (cutworms), as colonies form before grass seed heading (aphids), or for webworms in OR only - September</td>
</tr>
<tr>
<td>Crop</td>
<td>Method of application</td>
<td>Maximum single application rate (lbs. a.i./A)</td>
<td>Maximum number of applications per season</td>
<td>Maximum seasonal application rate (lbs. a.i./A)</td>
<td>Minimum retreatment interval (d)</td>
<td>Timing</td>
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</tr>
<tr>
<td>Legume vegetables* (succulent or dried), all except soybean (not for use in MS)</td>
<td>Broadcast spray to soil with 1-3 inch incorporation (pre-plant); or 3-5 inch T-band with ¼-1 inch incorporation recommended (at-plant)</td>
<td>0.94</td>
<td>1</td>
<td>0.94</td>
<td>--</td>
<td>Preplant or at plant.</td>
</tr>
<tr>
<td>Onion (dry bulb)</td>
<td>Soil drench in 2-4 inch band with shallow incorporation at-plant; directed spray to seeding base postplant</td>
<td>0.94</td>
<td>2 (at-plant plus postplant)</td>
<td>1.88</td>
<td>At plant to seedling stage</td>
<td>60-d PHI; apply at or before seedling stage</td>
</tr>
<tr>
<td>Peanut</td>
<td>Aerial (except MS) or ground broadcast spray to soil with 3-4 inch incorporation (pre-plant)</td>
<td>1.88</td>
<td>1</td>
<td>4.0 (all chlorpyrifos products)</td>
<td>--</td>
<td>21-d PHI; preplant</td>
</tr>
<tr>
<td>Pear (California, Oregon and Washington only)</td>
<td>Airblast spray postharvest</td>
<td>1.88</td>
<td>1</td>
<td>1.88</td>
<td>--</td>
<td>After harvest</td>
</tr>
<tr>
<td>Peppermint and spearmint (not for use in MS)</td>
<td>Foliar ground broadcast spray or sprinkler irrigation; or pre-plant soil spray with 2-4 incorporation; or postharvest soil spray, watered-in or via chemigation</td>
<td>1.88</td>
<td>Apparently 3 (1 during growing season; 1 preplant; 1 postharvest)</td>
<td>5.64</td>
<td>Specified as stages of crop</td>
<td>90-d PHI; preplant for symphyans; Might-June for cutworms, postharvest for borers</td>
</tr>
<tr>
<td>Pineapple (nonbearing) (24c HI)</td>
<td>Foliar broadcast spray with ground equipment</td>
<td>1.88</td>
<td>3</td>
<td>5.64</td>
<td>30</td>
<td>365-d PHI; apply only within 3 months of planting</td>
</tr>
<tr>
<td>Radish for seed (24c)</td>
<td>Foliar broadcast spray</td>
<td>0.94</td>
<td>1</td>
<td>0.94</td>
<td>--</td>
<td>Apply in spring</td>
</tr>
</tbody>
</table>

* Legume vegetables on label include adzuki bean, asparagus bean, bean, blackeyed pea, broad bean (dry and succulent), cajfian, chickpea, Chinese longbean, cowpea, crowder pea, dwarf pea, edible pod pea, English pea, fava bean, field bean, field pea, garbanzo bean, garden pea, grain lupin, green pea, guar, hyacinth bean, jackbean, kidney bean, lablab bean, lentil, lime bean, moth bean, mung bean, navy bean, pea, pigeon pea, pinto bean, rice bean, runner bean, snap bean, snow pea, southern pea, sugar snap pea, sweet lupin, sword bean, tepary bean, urd bean, wax bean, white lupin, white sweet lupin, yardlong bean.
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<th>Minimum retreatment interval (d)</th>
<th>Timing</th>
</tr>
</thead>
<tbody>
<tr>
<td>OR</td>
<td>Broadcast foliar spray, aerial (except MS) or ground, or sprinkler irrigation</td>
<td>0.94</td>
<td>3</td>
<td>1.41</td>
<td>10</td>
<td>30-60-d PHI</td>
</tr>
<tr>
<td>Sorghum – grain sorghum (milo)</td>
<td>Soil spray at plant in 4-6 inch band; postemergent spray in 6-12 inch band over or 9-12 inch band at the side of the base, depending upon plant size; or foliar spray by ground, air, or sprinkler chemigation</td>
<td>0.94</td>
<td>3</td>
<td>2.82</td>
<td>14</td>
<td>28-d PHI; soil applications pre-to-early post plant; foliar as needed including after pod set</td>
</tr>
<tr>
<td>Soybean (not for use in MS)</td>
<td>Preplant broadcast spray to soil with incorporation (depth not specified); broadcast foliar spray at budbreak; or directed spray to crown postharvest</td>
<td>Preplant: 1.88 foliar; postharvest: 0.94</td>
<td>3 total (Preplant: 1 foliar + postharvest: 2)</td>
<td>3.76</td>
<td>Foliar: 10 Postharvest: 14</td>
<td>21-d PHI; do not apply when berries are forming or present</td>
</tr>
<tr>
<td>Strawberry (not for use in MS)</td>
<td>Banded soil application with 1-2 inch incorporation at or before planting; aerial broadcast or at-plant soil application in 10 inch band; or postemergent banded or broadcast foliar spray by air or ground or via chemigation</td>
<td>0.94</td>
<td>3</td>
<td>2.82</td>
<td>10</td>
<td>30-d PHI; treatment throughout season</td>
</tr>
<tr>
<td>Sugarbeet (not for use in MS)</td>
<td>Ground broadcast spray to soil with unspecified incorporation in fall after harvest</td>
<td>1.68</td>
<td>1</td>
<td>2.82 (to include basic label applications)</td>
<td>--</td>
<td>Apply in fall after harvest</td>
</tr>
</tbody>
</table>

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<th>Maximum seasonal application rate (lbs. a.i./A)</th>
<th>Minimum retreatment interval (d)</th>
<th>Timing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sugarbeets for seed and table beets for seed, (24c OR)</td>
<td>Broadcast spray to soil with 2-4 inch incorporation (pre-plant); banded spray with 2+ inch incorporation (at-plant)</td>
<td>1.88</td>
<td>1</td>
<td>1.88</td>
<td>--</td>
<td>Prior to or at planting</td>
</tr>
<tr>
<td>Sunflower (not for use in MS)</td>
<td>Ground broadcast spray with 2-4 inch incorporation (pre-plant); aerial or ground foliar broadcast (postemergence)</td>
<td>Pre-plant soil incorporated: 1.88 Postemergent foliar: 0.94</td>
<td>3 (any chlorpyrifos)</td>
<td>2.82</td>
<td>10</td>
<td>42-d PHI</td>
</tr>
<tr>
<td>Sweet potato</td>
<td>Aerial (except MS) or ground broadcast spray to soil with 4-6 inch incorporation (pre-plant)</td>
<td>1.88</td>
<td>1</td>
<td>1.88</td>
<td>--</td>
<td>125-d PHI; apply up to 14 d before planting</td>
</tr>
<tr>
<td>Sweet potato (24c NC, MS, LA)</td>
<td>Same as above except 60-d PHI</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tobacco</td>
<td>Aerial (except MS) or ground broadcast spray to soil with 2-4 inch incorporation (pre-plant)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>--</td>
<td>Apply 24-48 h before bedding or transplanting</td>
</tr>
<tr>
<td>Tobacco (24c KY, VA, GA, NC)</td>
<td>Broadcast spray to soil with 2-4 inch incorporation (pre-plant)</td>
<td>1.88</td>
<td>1</td>
<td>1.88</td>
<td>--</td>
<td>Apply 24-48 h before bedding or transplanting</td>
</tr>
<tr>
<td>Crop</td>
<td>Method of application</td>
<td>Maximum single application rate (lbs. a.l/A)</td>
<td>Maximum number of applications per season</td>
<td>Maximum seasonal application rate (lbs. a.l/A)</td>
<td>Minimum retreatment interval (d)</td>
<td>Timing</td>
</tr>
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</tr>
<tr>
<td>Tree fruits (apple, cherry, nectarine, peach, pear, plum, prune), almond and walnut (dormant/delayed dormant sprays) (not for use in MS)</td>
<td>Broadcast spray (air blast implied, but aerial not precluded) to cover “foliage”</td>
<td>1.88</td>
<td>1 of any chlorpyrifos for apples; 1 dormant/delayed dormant for others</td>
<td>1.88 as dormant/delayed dormant</td>
<td>10 d to any foliar</td>
<td>After winter rains and before budbreak</td>
</tr>
<tr>
<td>Tree fruits (cherry, nectarine, peach) and almond (trunk spray) (not for use in MS)</td>
<td>Apply to tree trunks and lower branches with coarse spray</td>
<td>1.41</td>
<td>Peaches, nectarines 1; almonds not specified</td>
<td>1.41</td>
<td>–</td>
<td>14-d PHI</td>
</tr>
<tr>
<td>Cherry</td>
<td>4.23</td>
<td>14 d for 2nd application, post harvest for 3rd</td>
<td>21-d PHI</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tree nuts (foliar sprays) (almond, filbert, pecan, walnut)</td>
<td>Aerial (except MS) or ground foliar broadcast spray</td>
<td>1.88</td>
<td>Almonds, filberts, pecans 3, walnuts 2</td>
<td>3.76 as foliar spray</td>
<td>10</td>
<td>28-d PHI for pecans; 14-d PHI for others</td>
</tr>
<tr>
<td>Tree nuts (almond, pecan, walnut) orchard floors (not for use in MS)</td>
<td>Ground broadcast spray to soil or sprinkler irrigation, not to contact foliage</td>
<td>Pecans: 1.88</td>
<td></td>
<td>2</td>
<td>3.76</td>
<td>10</td>
</tr>
<tr>
<td>Turfgrass grown for sod (not for use in MS)</td>
<td>Broadcast spray</td>
<td>3.76</td>
<td>Not specified – apparently 1, except 2 applications indicated, as needed, for two specific pests</td>
<td>Apparently 3.76</td>
<td>7</td>
<td>Any time depending upon pest</td>
</tr>
<tr>
<td>Wheat</td>
<td>Aerial or ground foliar</td>
<td>0.47</td>
<td>2</td>
<td>0.94</td>
<td>Not specified</td>
<td>14-d PHI</td>
</tr>
</tbody>
</table>

1 Not for use on almonds in Butte, Colusa, Glenn, Solano, Sutter, Tehama, Yolo, and Yuba counties, California
2 Might also be used as dip for peach and nectarine trees prior to planting (no exposure).
3 For use on wheat only in Arizona, California, Colorado, Idaho, Kansas, Minnesota, Montana, Nebraska, New Mexico, Nevada, North Dakota, Oklahoma, Oregon, South Dakota, Texas, Utah, Washington and Wyoming.
<table>
<thead>
<tr>
<th>Crop</th>
<th>Method of application</th>
<th>Maximum single application rate (lbs. a.i./A)</th>
<th>Maximum number of applications per season</th>
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<th>Minimum retreatment interval (d)</th>
<th>Timing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>broadcast spray or chemigation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crop</td>
<td>Method of application</td>
<td>Maximum single application rate (lbs. a.i./A)</td>
<td>Maximum number of applications per season</td>
<td>Maximum seasonal application rate (lbs. a.i./A)</td>
<td>Minimum retreatment interval (d)</td>
<td>Timing</td>
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<td>-------------------------------------------</td>
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<td>---------------------------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>Alfalfa (not for use in MS)</td>
<td>Broadcast aerial or ground spray, or sprinkler chemigation (foliar application)</td>
<td>1.0</td>
<td>4 (but maximum of 1 app /cutting)</td>
<td>4 (of any chlorpyrifos product)</td>
<td>10</td>
<td>7-21-d PHI</td>
</tr>
<tr>
<td>Asparagus</td>
<td>Ground broadcast foliar spray</td>
<td>1.0</td>
<td>3 (1 preharvest; 2 postharvest)</td>
<td>3</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Christmas trees (plantations) (not for use in MS)</td>
<td>Ground broadcast foliar spray (can also be applied as cut stump drench; lower rate calculated based on spray volume)</td>
<td>1.0</td>
<td>3</td>
<td>3.0</td>
<td>7</td>
<td>When needed</td>
</tr>
<tr>
<td>Citrus fruits (not for use in MS)</td>
<td>Broadcast foliar spray; air blast recommended, but aerial not precluded</td>
<td>3.5 except 6.0 in AZ &amp; Fresno, Tulare, Kern, Kings and Modere Counties, CA; 4.0 in the rest of CA</td>
<td>2 of any chlorpyrifos product (not including orchard floor applications)</td>
<td>7.5</td>
<td>30</td>
<td>21 to 35-d PHI</td>
</tr>
<tr>
<td>Citrus orchard floors (fire ant &amp; other ant control) (Not for use in MS)</td>
<td>Ground broadcast spray directed to floor of orchard or sprinkler chemigation around base of tree (do not contact foliage or fruit)</td>
<td>2.0</td>
<td>3</td>
<td>3.0</td>
<td>10 (including foliar apps)</td>
<td>None specified</td>
</tr>
</tbody>
</table>

1 Lorsban 4E can only be used in Mississippi in accordance with a 24c SLN label for corn (all), onions (dry bulb), peanuts, pecans, sorghum, tobacco, sweet potatoes, and vegetables (all Brassica). Directions in this table apply except that only ground applications are allowed. Aerial and chemigation applications are prohibited.

* For use on asparagus only in the Midwest (not defined) and Pacific Northwest states.
<table>
<thead>
<tr>
<th>Crop</th>
<th>Method of application</th>
<th>Maximum single application rate (lbs. a.i./A)</th>
<th>Maximum number of applications per season</th>
<th>Maximum seasonal application rate (lbs. a.i./A)</th>
<th>Minimum retreatment interval (d)</th>
<th>Timing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corn (field, sweet, seed)</td>
<td>Ground broadcast spray with 2-4 inch incorporation (pre-plant, pre-emergence, at-plant); aerial (except MS) or ground follar broadcast spray or sprinkler chemigation (postemergent)</td>
<td>3.0 preplant, preemergent or at plant; 1.0 postemergent</td>
<td>3 (4E)</td>
<td>3.0 (all chlorpyrifos)</td>
<td>10</td>
<td>35-d PHI</td>
</tr>
<tr>
<td>Cotton (not for use in MS)</td>
<td>Broadcast foliar spray, aerial or ground (except AZ &amp; CA) or sprinkler irrigation (postplant)</td>
<td>1.0</td>
<td>3</td>
<td>3.0</td>
<td>10</td>
<td>Foliar; 14-d PHI</td>
</tr>
<tr>
<td>Cranberry (Not for use in MS)</td>
<td>Broadcast foliar or sprinkler irrigation (postplant)</td>
<td>1.5</td>
<td>2</td>
<td>--</td>
<td>10</td>
<td>Do not apply when fields are flooded to avoid contamination of flood water. 50-d PHI</td>
</tr>
<tr>
<td>Fig (CA only)</td>
<td>Broadcast spray to soil surface with three inch incorporation (dormant)</td>
<td>2.0</td>
<td>1</td>
<td>--</td>
<td>--</td>
<td>Dormant season, 7-month PHI</td>
</tr>
<tr>
<td>Grape (east of the continental divide only) (not for use in MS)</td>
<td>Soil surface spray (4 ft. circle around base of vine); Soil drench (prebloom)</td>
<td>Soil surface 2.25/100 gal to treat 3000 sq ft; Prebloom 1.0</td>
<td>1</td>
<td>Soil surface 2.25/100 gal to treat 3000 sq ft; Prebloom 1.0</td>
<td>--</td>
<td>Prior to bloom; 35-d PHI</td>
</tr>
<tr>
<td>Grape (mealybug, cutworms) (24c, ID, CO)</td>
<td>Ground broadcast to soil; prebloom or dormant</td>
<td>1.0 prebloom; 2.0 dormant</td>
<td>2</td>
<td>2.0</td>
<td>--</td>
<td>90-d PHI ID; 35-d PHI CO</td>
</tr>
<tr>
<td>Grape (cutworms) (24c, OR)</td>
<td>Aerial or ground broadcast spray</td>
<td>1.0</td>
<td>1</td>
<td>1.0</td>
<td>--</td>
<td>Do not harvest in the year of application</td>
</tr>
<tr>
<td>Grass for seed (perennial) (24c, ID, NV)</td>
<td>Ground (ID, NV) or aerial (NV) broadcast spray</td>
<td>1.04</td>
<td>3 (ID), not specified (NV)</td>
<td>3.0 (on ID label only)</td>
<td>Not specified</td>
<td>Do not harvest grass seed in year of application</td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th>Crop¹</th>
<th>Method of application</th>
<th>Maximum single application rate (lbs. a.i./A)</th>
<th>Maximum number of applications per season</th>
<th>Maximum seasonal application rate (lbs. a.i./A)</th>
<th>Minimum retreatment interval (d)</th>
<th>Timing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mint (not for use in MS)</td>
<td>Foliar ground broadcast spray or sprinkler irrigation; or pre-plant soil spray with 2-4 incorporation; or postharvest soil spray, watered-in or via chemigation</td>
<td>2.0</td>
<td>1 (of any kind)</td>
<td>2.0</td>
<td>--</td>
<td>Preplant, foliar, or postharvest; 90-d PHI</td>
</tr>
<tr>
<td>Onion (dry bulb)</td>
<td>In-furrow drench at plant (incorporate 1-2 inches); directed soil drench to base of seedlings or transplants</td>
<td>1.0</td>
<td>2 (at-plant plus postplant)</td>
<td>2.0–</td>
<td>Not specified (but 1ˢᵗ is preplant and 2ⁿᵈ is to seedlings)–</td>
<td>Preplant and early season; 60-d PHI</td>
</tr>
<tr>
<td>Peanut</td>
<td>Broadcast spray to soil with 3-4 inch incorporation (pre-plant)</td>
<td>2.0 (4E)</td>
<td>1 (4E)</td>
<td>4 (pre-plant and postplant, all chlorpyrifos products)</td>
<td>--</td>
<td>Preplant (21-d PHI)</td>
</tr>
<tr>
<td>Sorghum – grain sorghum (milo)</td>
<td>Broadcast spray, aerial (except MS) or ground; or sprinkler irrigation; foliar or directed at base of young plants</td>
<td>1.0</td>
<td>3</td>
<td>1.5</td>
<td>10</td>
<td>Post-emergent; 30-d PHI</td>
</tr>
<tr>
<td>Soybean (not for use in MS)</td>
<td>Soil spray at plant in 4-6 inch band; postemergent spray in 6-12 band over or at the side of the base, depending upon plant size; or foliar spray by ground, air, or sprinkler chemigation</td>
<td>1.0</td>
<td>3</td>
<td>3.0</td>
<td>10</td>
<td>From at plant to 28-d PHI</td>
</tr>
</tbody>
</table>

¹Si Solomon et al. 2014 RECT 231 Page 25 of 43
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<tr>
<th>Crop</th>
<th>Method of application</th>
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<th>Maximum seasonal application rate (lbs. a.i./A)</th>
<th>Minimum retreatment interval (d)</th>
<th>Timing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strawberry (Not for use in MS)</td>
<td>Preplant broadcast spray to soil with incorporation (depth not specified); broadcast follar spray at budbreak; or directed spray to crown postharvest</td>
<td>Preplant: 2.0 Follar; postharvest: 1.0</td>
<td>Preplant: 1 Follar; postharvest: 2; Total 3</td>
<td>3.0</td>
<td>Foliar: 10 Postharvest: 14</td>
<td>Do not apply when berries are present; 21-d PHI</td>
</tr>
<tr>
<td>Sugarbeet (not for use in MS)</td>
<td>Preplant soil application with 1-2 inch incorporation or at-plant soil application in 10 inch band; postemergent banded or broadcast follar spray by air or ground</td>
<td>1.0</td>
<td>3</td>
<td>3.0</td>
<td>10</td>
<td>30-d PHI</td>
</tr>
<tr>
<td>Sugarbeet for seed (24c ID)</td>
<td>Ground broadcast spray with incorporation (pre-plant)</td>
<td>2.0</td>
<td>1</td>
<td>2.0</td>
<td>--</td>
<td>Preplant in fall (after harvest)</td>
</tr>
<tr>
<td>Sunflower (not for use in MS)</td>
<td>Ground broadcast spray with 2-4 inch incorporation (pre-plant); aerial or ground follar broadcast (postemergence)</td>
<td>Pre-plant: 2.0 Postemergence: 1.0 (in table, but specific use restrictions indicate maximum single application of 1.5)</td>
<td>3</td>
<td>3.0</td>
<td>10</td>
<td>42-d PHI</td>
</tr>
<tr>
<td>Sweet potato</td>
<td>Broadcast spray to soil with 4-6 inch incorporation (pre-plant)</td>
<td>2.0</td>
<td>1</td>
<td>2.0</td>
<td>--</td>
<td>125-d PHI</td>
</tr>
<tr>
<td>Table beets for seed, sugarbeets for seed (24c OR)</td>
<td>Broadcast spray to soil with 2-4 inch incorporation (pre-plant); or banded spray to soil with incorporation at least 2 inches (at-plant)</td>
<td>2.0 broadcast or 1.0 band</td>
<td>1</td>
<td>2.0</td>
<td>--</td>
<td>Apply in fall for protection the following year</td>
</tr>
<tr>
<td>Tobacco</td>
<td>Broadcast spray to soil with 2-4 inch incorporation (pre-plant)</td>
<td>2.0</td>
<td>1</td>
<td>2.0 (all chloropyrifos)</td>
<td>--</td>
<td>Preplant</td>
</tr>
<tr>
<td>Crop</td>
<td>Method of application</td>
<td>Maximum single application rate (lbs. a.i/A)</td>
<td>Maximum number of applications per season</td>
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<td>-----------------------------</td>
</tr>
<tr>
<td>Tree fruits and nuts (apple, almond, cherry, nectarine, peach, pear plum, and prune) (dormant/delayed dormant sprays) (not for use in MS)</td>
<td>Broadcast spray with air blast implied but aerial not precluded (not for almond use in Butte, Colusa, Glenn, Solano, Sutter, Yolo, and Yuba counties, CA)</td>
<td>2.0</td>
<td>1 as dormant</td>
<td>2.0 for dormant (additional foliar OK)</td>
<td>--</td>
<td>Preplant (or pretransplant)</td>
</tr>
<tr>
<td>Tree nuts (foliar sprays) (almonds, filberts, pecans, walnuts)</td>
<td>Aerial (except MS) or ground foliar spray</td>
<td>2.0</td>
<td>3, except for walnuts which has a limit of 2 applications</td>
<td>4.0 for foliar; (one additional dormant OK)</td>
<td>10</td>
<td>14-d PHI, except 28-d PHI for pecans</td>
</tr>
<tr>
<td>Tree nuts (almonds, pecans, walnuts) orchard floors (for fire and other pests) (Not for use in MS)</td>
<td>Ground broadcast spray to soil or sprinkler irrigation, not to contact foliage</td>
<td>4.0</td>
<td>2 (to orchard floor; other OK)</td>
<td>4.0</td>
<td>10</td>
<td>14-d PHI</td>
</tr>
<tr>
<td>Vegetables (broccoli, cabbage, Chinese cabbage, collard, kale, kohlrabi, rutabaga, turnip)</td>
<td>Four-inch banded soil application at plant or directed spray to base of plant after transplant; or postemergent sidedress for broccoli &amp; cabbage</td>
<td>2.25</td>
<td>1 soil appl/crop</td>
<td>2.25 of 4E</td>
<td>10</td>
<td>30-d PHI</td>
</tr>
<tr>
<td>Vegetables (Brussels sprouts)</td>
<td>Four-inch banded soil application at plant or directed spray to base of plant after transplant; or foliar application</td>
<td>2.25</td>
<td>1 soil or 3 total/crop (of any chlorpyrifos)</td>
<td>2.25 soil</td>
<td>10 (for any chlorpyrifos product)</td>
<td>30-d PHI ground; 21-d PHI for foliar</td>
</tr>
<tr>
<td>Vegetables (cauliflower)</td>
<td>Four-inch banded soil application at plant or directed spray to base of plant after transplant</td>
<td>2.0</td>
<td>1 soil appl/crop</td>
<td>2.0 of 4E</td>
<td>10 (for foliar chlorpyrifos products)</td>
<td></td>
</tr>
<tr>
<td>Vegetables (radish)</td>
<td>In furrow drench application at plant</td>
<td>2.75</td>
<td>1 soil appl/crop</td>
<td>2.75 of 4E</td>
<td>10 (for foliar chlorpyrifos products)</td>
<td></td>
</tr>
<tr>
<td>Crop</td>
<td>Method of application</td>
<td>Maximum single application rate (lbs. a.i./A)</td>
<td>Maximum number of applications per season</td>
<td>Maximum seasonal application rate (lbs. a.i./A)</td>
<td>Minimum retreatment interval (d)</td>
<td>Timing</td>
</tr>
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<td>---------------------------------</td>
<td>--------------</td>
</tr>
<tr>
<td>Wheat</td>
<td>Foliar broadcast spray - aerial, ground, or sprinkler irrigation</td>
<td>0.5</td>
<td>2</td>
<td>1.0</td>
<td>–</td>
<td>14-d PHI</td>
</tr>
</tbody>
</table>

\(^1\) For use on wheat only in Arizona, California, Colorado, Idaho, Kansas, Minnesota, Montana, Nebraska, New Mexico, Nevada, North Dakota, Oklahoma, Oregon, South Dakota, Texas, Utah, Washington and Wyoming.
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<th>Crop</th>
<th>Method of application</th>
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<th>Minimum retreatment interval (d)</th>
<th>Timing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alfalfa (not for use in MS)</td>
<td>Broadcast foliar spray by air, ground, or chemigation</td>
<td>1.0</td>
<td>4 (but maximum of 1 app /cutting)</td>
<td>4.0 (of any chlorpyrifos product)</td>
<td>10</td>
<td>7-21-d PHI</td>
</tr>
<tr>
<td>Apple tree trunk, (east of Rockies only) (not for use in MS)</td>
<td>One application per year directed to lower 4 feet of apple tree trunk from a distance of no more than 4 feet away. No rate per acre given, but 1.5 lbs a.i./100 gal of spray. Not to contact foliage or fruit.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Post bloom; 28-d PHI</td>
</tr>
<tr>
<td>Asparagus*</td>
<td>Broadcast foliar spray by ground</td>
<td>1.0</td>
<td>3</td>
<td>3.0</td>
<td>10</td>
<td>1-d PHI; 1 application preharvest; 2 applications post harvest</td>
</tr>
<tr>
<td>Brassica (cole) leafy vegetables and radish, rutabaga, and turnip*</td>
<td>Broadcast with 2-4 inch incorporation (pre-plant)</td>
<td>Cauliflower: 2.0</td>
<td></td>
<td>Broccoli, Brussels sprouts, leafy brassica, turnip, rutabaga: 2.25</td>
<td>10 (for other chlorpyrifos follower)</td>
<td>30-d PHI; preplant or after establishment</td>
</tr>
<tr>
<td></td>
<td>Spray to soil in band over seed row at planting time</td>
<td>Broccoli, Brussels sprouts, leafy brassica, turnip, rutabaga: 2.25</td>
<td>1 soil</td>
<td>Broccoli, Brussels sprouts, leafy brassica, turnip, rutabaga: 2.25</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Apply as drench in seed furrow at planting</td>
<td>Radish: 2.75</td>
<td></td>
<td>Radish: 2.75</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brassica (cole) leafy vegetables only</td>
<td>Foliar broadcast spray by air or ground</td>
<td>1.0</td>
<td>3</td>
<td>3.0</td>
<td>10</td>
<td>21-d PHI</td>
</tr>
<tr>
<td>Christmas trees (plantations) (not for use in MS)</td>
<td>Foliar ground broadcast power spray (postplant); cut stump drench</td>
<td>1.0</td>
<td>3</td>
<td>3.0</td>
<td>7</td>
<td>As needed</td>
</tr>
</tbody>
</table>

* For use on asparagus only in Arizona, California, Idaho, Illinois, Indiana, Iowa, Kansas, Michigan, Minnesota, Missouri, Nebraska, North Dakota, Ohio, Oregon, South Dakota, Washington and Wisconsin.

* Labeled crops include broccoli, broccolli raab, Brussels sprouts, cabbage, cauliflower, cavalo broccoli, Chinese broccolli, Chinese cabbage, collards, kale, kohlrabi, mizuna, mustard greens, mustard spinach, and rape greens.
<table>
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<th>Minimum retreatment interval (d)</th>
<th>Timing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Citrus fruits&lt;sup&gt;a&lt;/sup&gt; (not for use in MS)</td>
<td>Foliar broadcast; directions imply air-blast but aerial not precluded</td>
<td>3.5 except CA &amp; AZ, 6.0 in AZ &amp; Fresno, Tulare, Kern, Kings and Madera Counties, CA 4.0 in other CA counties</td>
<td>2 (not including orchard floor)</td>
<td>7.5</td>
<td>30 (any foliar)</td>
<td>21 to 35-d PHI; “To avoid excessive ridging, do not apply Lorsban 4-E to citrus fruit from December up to the initiation of bloom”</td>
</tr>
<tr>
<td>Citrus orchard floors (not for use in MS)</td>
<td>Broadcast spray to orchard floor or sprinkler irrigation to soil around trees</td>
<td>1</td>
<td>3</td>
<td>3.0</td>
<td>10</td>
<td>28-d PHI</td>
</tr>
<tr>
<td>Corn (field, sweet, seed)</td>
<td>Broadcast to surface in &quot;Conservation Tillage&quot;&lt;sup&gt;b&lt;/sup&gt; (pre-plant, pre-emergence, at-plant); foliar spray by air (except MS) or ground (postplant)</td>
<td>1</td>
<td>3 (any chlorpyrifos)</td>
<td>3.0</td>
<td>10</td>
<td>21-d PHI</td>
</tr>
<tr>
<td>Cotton (not for use in MS)</td>
<td>Foliar broadcast by air, ground, or chemigation</td>
<td>1.0</td>
<td>3</td>
<td>3.0</td>
<td>10</td>
<td>14-d PHI</td>
</tr>
<tr>
<td>Cranberry (not for use in MS)</td>
<td>Foliar broadcast spray or chemigation</td>
<td>1.5</td>
<td>2 (any chlorpyrifos)</td>
<td>3.0</td>
<td>10</td>
<td>60-d PHI; do not apply until winter flood water has been removed, nor when bogs are flooded</td>
</tr>
<tr>
<td>Fig (CA only)</td>
<td>Dormant ground spray with 3 inch incorporation</td>
<td>2.0</td>
<td>1</td>
<td>2.0</td>
<td>--</td>
<td>217-d PHI; apply late winter</td>
</tr>
</tbody>
</table>

<sup>a</sup> Citrus fruits on label include calamondin, chinonja, citrus citron, citrus hybrids, grapefruit, kumquat, lemon, lime, mandarin (tangerine), pummel, Satsuma mandarin, sour orange, sweet orange, tangelo, tanger
<table>
<thead>
<tr>
<th>Crop</th>
<th>Method of application</th>
<th>Maximum single application rate (lbs a.i./A)</th>
<th>Maximum number of applications per season</th>
<th>Maximum seasonal application rate (lbs a.i./A)</th>
<th>Minimum retreatment interval (d)</th>
<th>Timing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grape (east of the continental divide only) (not for use in MS)</td>
<td>Soil surface spray (4 ft. circle around base of vine); or spray drench to soil (prebloom)</td>
<td>Soil surface 2.25; prebloom 1.0</td>
<td>1</td>
<td>2.25</td>
<td>--</td>
<td>35-d PHI; apply prior to bloom</td>
</tr>
<tr>
<td>Legume vegetables (succulent or dried), all except soybean (not for use in MS)</td>
<td>Broadcast spray to soil with 1-3 inch incorporation (pre-plant); or 3-5 inch T-band with ½-1 inch incorporation recommended (at-plant)</td>
<td>1.0</td>
<td>1</td>
<td>1.0</td>
<td>--</td>
<td>Preplant or at plant.</td>
</tr>
<tr>
<td>Onion (dry bulb)</td>
<td>Soil drench in 2-4 inch band with shallow incorporation at-plant; directed spray to seedling base postplant</td>
<td>1.0</td>
<td>2 (at-plant plus postplant)</td>
<td>2.0</td>
<td>At plant to seedling stage</td>
<td>60-d PHI; apply at or before seedling stage</td>
</tr>
<tr>
<td>Peanut</td>
<td>Aerial (except MS) or ground broadcast to soil with 3-4 inch incorporation (pre-plant)</td>
<td>2.0</td>
<td>1</td>
<td>4.0 (all chlorpyrifos products)</td>
<td>--</td>
<td>21-d PHI; preplant</td>
</tr>
<tr>
<td>Pear (California, Oregon and Washington only)</td>
<td>Airblast spray postharvest</td>
<td>2.0</td>
<td>1</td>
<td>--</td>
<td>--</td>
<td>After harvest</td>
</tr>
<tr>
<td>Peppermint and spearmint (not for use in MS)</td>
<td>Ground broadcast to soil with 2-4 inch incorporation (pre-plant) or watered in (postharvest); or foliar spray/chemigation (postplant)</td>
<td>2.0</td>
<td>Apparently 3 (1 “during growing season”; 1 preplant; 1 postharvest)</td>
<td>6.0</td>
<td>Specified as stages of crop to 90-d PHI; preplant for symphyllans; Might-June for cutworms; postharvest for borers</td>
<td></td>
</tr>
</tbody>
</table>

Legume vegetables on label include adzuki bean, asparagus bean, bean, blackeyed pea, broad bean (dry and succulent), catjang, chickpea, Chinese longbean, cowpea, cowpea, edamame, edible pod pea, English pea, fava bean, field bean, field pea, garbanzo bean, garden pea, grain lupin, green pea, guar, hyacinth bean, jack bean, kidney bean, lablab bean, lentil, lima bean, mung bean, navy bean, pea, pigeon pea, pinto bean, rice bean, runner bean, snap bean, snow pea, southern pea, sugar snap pea, sweet lupin, sword bean, tepary bean, urd bean, wax bean, white lupin, white sweet lupin, yardlong bean.
<table>
<thead>
<tr>
<th>Crop</th>
<th>Method of application</th>
<th>Maximum single application rate (lbs a.i./A)</th>
<th>Maximum number of applications per season</th>
<th>Maximum seasonal application rate (lbs a.i./A)</th>
<th>Minimum retreatment interval (d)</th>
<th>Timing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peppers (unspecified) 24c FL</td>
<td>Broadcast foliar spray with power-operated ground equipment</td>
<td>1.0</td>
<td>8</td>
<td>8.0</td>
<td>10 (any chlorpyrifos)</td>
<td>7-d PHI</td>
</tr>
<tr>
<td>Sorghum – grain sorghum (milo)</td>
<td>Aerial (except MS) or ground foliar spray or chemigation (postemergence)</td>
<td>1.0</td>
<td>3</td>
<td>1.5</td>
<td>10</td>
<td>30-60-d PHI</td>
</tr>
<tr>
<td>Sour cherry and tree fruits (almond, filbert, pecan, walnut) foliar sprays* (not for use in MS, except on cherries)</td>
<td>Apply as a foliar spray by air blast (preferable) or aerial (except no aerial in MS) to cover foliage and crop</td>
<td>2.0</td>
<td>2 (walnuts); 3 (almonds, pecans, filberts); 8 (cherries)</td>
<td>4.0 (walnuts); 6.0 (almonds, pecans, filberts); 12.0 (cherries)</td>
<td>10</td>
<td>14-d PHI (almonds, filberts, sour cherry) or 28-d PHI (pecans)</td>
</tr>
<tr>
<td>Soybean (not for use in MS)</td>
<td>Ground broadcast to soil or band at plant with light incorporation; postemergent directed spray in 9-12 inch band to base of plant; foliar spray or chemigation for foliar pests</td>
<td>1.0</td>
<td>3</td>
<td>3.0</td>
<td>14</td>
<td>28-d PHI; soil applications pre-to early post plant; foliar as needed including after pod set</td>
</tr>
<tr>
<td>Strawberry (not for use in MS)</td>
<td>Broadcast with unspecified incorporation (pre-plant); broadcast foliar when buds appear; directed spray to crown after harvest</td>
<td>Preplant: 2.0; foliar, postharvest: 1.0</td>
<td>3 total (Preplant: 1; foliar + postharvest: 2)</td>
<td>4.0</td>
<td>Foliar: 10 Postharvest: 14</td>
<td>21-d PHI; do not apply when berries are forming or present</td>
</tr>
</tbody>
</table>

* Might also be used as dip for peach and nectarine trees prior to planting (no exposure).
<table>
<thead>
<tr>
<th>Crop</th>
<th>Method of application</th>
<th>Maximum single application rate (lbs a.i./A)</th>
<th>Maximum number of applications per season</th>
<th>Maximum seasonal application rate (lbs a.i./A)</th>
<th>Minimum retreatment interval (d)</th>
<th>Timing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sugarbeet (not for use in MS)</td>
<td>Banded soil application with 1.2 inch incorporation at or before planting; aerial broadcast or banded foliar spray or chemigation after emergence</td>
<td>1.0</td>
<td>3</td>
<td>3.0</td>
<td>10</td>
<td>30-d PHI; treatment throughout season</td>
</tr>
<tr>
<td>Sunflower (not for use in MS)</td>
<td>Broadcast spray to soil with 2-4 inch incorporation (pre-plant); foliar broadcast aerial or ground spray (postemergence)</td>
<td>Pre-plant soil incorporated: 2.0; Postemergent foliar: 1.0</td>
<td>3 (any chlorpyrifos)</td>
<td>3.0</td>
<td>10</td>
<td>42-d PHI</td>
</tr>
<tr>
<td>Sweet potato</td>
<td>Aerial (except MS) or ground broadcast spray to soil with 4-6 inch incorporation (pre-plant)</td>
<td>2.0</td>
<td>1</td>
<td>2.0</td>
<td>--</td>
<td>125-d PHI; apply up to 14 d before planting</td>
</tr>
<tr>
<td>Tobacco</td>
<td>Aerial (except MS) or ground broadcast spray to soil with 2-4 inch incorporation (pre-plant)</td>
<td>1.0</td>
<td>1</td>
<td>1.0</td>
<td>--</td>
<td>Apply 24-48 hours before bedding or transplant</td>
</tr>
<tr>
<td>Tree fruits (apple, cherry, nectarine, peach, pear, plum, prune), almond and walnut (dormant/delayed dormant sprays) (not for use in MS)</td>
<td>Broadcast spray to completely cover &quot;foliage&quot;</td>
<td>2.0</td>
<td>1 of any chlorpyrifos for apple tree trunks/entire year; 1 dormant/delayed dormant for others</td>
<td>2.0 as dormant/delayed dormant</td>
<td>10 d to any foliar</td>
<td>After winter rains and before budbreak</td>
</tr>
</tbody>
</table>

1 Not for use on almonds in Butte, Colusa, Glenn, Solano, Sutter, Tehama, Yolo, and Yuba counties, California

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<table>
<thead>
<tr>
<th>Crop</th>
<th>Method of application</th>
<th>Maximum single application rate (lbs a.i./A)</th>
<th>Maximum number of applications per season</th>
<th>Maximum seasonal application rate (lbs a.i./A)</th>
<th>Minimum retreatment interval (d)</th>
<th>Timing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tree fruits (cherry, nectarine, peach)* and almond (not for use in MS)</td>
<td>Apply to tree trunks and lower branches with coarse spray</td>
<td>3.0 lb a.i./100 gal of spray; no acreage-related limit</td>
<td>Peaches, nectarines 1; cherries 3; almonds not specified</td>
<td>No acreage-related limit</td>
<td>–</td>
<td>14-d PHI</td>
</tr>
<tr>
<td>Tree nuts (almond, pecan, walnut) orchard floors (not for use in MS)</td>
<td>Ground broadcast spray uniformly to soil</td>
<td>Pecans: 2.0</td>
<td></td>
<td>Almonds and walnuts: 4.0</td>
<td>4.0</td>
<td>10</td>
</tr>
<tr>
<td>Wheat*</td>
<td>Aerial or ground foliar broadcast spray or chemigation</td>
<td>0.5</td>
<td>2</td>
<td>1.0</td>
<td>Not specified</td>
<td>14-d PHI</td>
</tr>
</tbody>
</table>

* Might also be used as dip for peach and nectarine trees prior to planting.

* For use on wheat only in Arizona, California, Colorado, Idaho, Kansas, Minnesota, Montana, Nebraska, New Mexico, Nevada, North Dakota, Oklahoma, Oregon, South Dakota, Texas, Utah, Washington and Wyoming.

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SI Appendix C. Derivation of Chemical Input Parameter Values for Dissipation of CPY in Soil

Background
As noted in the discussion of the environmental fate of chlorpyrifos, the aerobic laboratory soil degradation study results show a clearly defined bi-phasic behavior in most soils. The DT50 values reported by Bidlack were calculated using a two compartment kinetic model, but the goodness of fit details were not provided in the report (Bidlack 1979). The graph of log concentration vs. time shows two linear sections, a faster initial degradation followed by a slower phase. An example of this behavior, prepared using the data from the Barnes soil (Bidlack 1979) is shown in (SI Fig. C1). The Initial phase rate constant was 0.0245 and the half-life was 25.3 days. The second phase rate constant 0.0045 and half-life 154 days.

Regression Correlation coefficients R² were 0.9979 and 0.9869 respectively. This biphasic behavior is not as apparent for the soils in the report by de Vette and Schoonmade, in which the half-lives were calculated using simple first order kinetics (de Vette and Schoonmade 2001).

A hypothetical dissipation model was set up with two compartments for the parent compound: one adsorbed in such a manner that is not available for biological degradation or abiotic hydrolysis; and the other in which these processes can occur (SI Fig. C2). It is known that CPY partitions between soil and soil pore water and that this reaches equilibrium within hours (Racke 1993), whereas the biphasic degradation process observed for CPY occurs over a period of several days (SI Fig. C1). The two compartments were identified as Labile_CPY and Adsorbed_CPY. This model has advantages over older two-compartment models in that all available data are used, simple first order equations are used and the rate constants are not concentration-dependent (Nash 1988)

Reversible movement of parent CPY between these compartments was represented as two simple first order processes shown by arrows F1 and F2 in SI Fig. C2, with rate constants $k_{ads}$ and $k_{des}$. Since the reported concentrations of CPY in the soil include nearly all the radiolabelled CPY residue present, these data represents the sum of the amounts in these two compartments at each time point as shown in SI Fig. C1. The sum
of processes that degrade CPY was also set up as a first order kinetic process F3, but was non reversible. The rate constant for this process was designated $k_m$. The resulting set of three first order equations was integrated numerically using Model-Maker Version 4.0 software from Cherwell Scientific Software Ltd. UK. Metabolism study data from 11 soils reported in two studies (Bidlack 1979; de Vette and Schoonmade 2001) were fit to this model.

When the model is set with 100% of the residue in the labile compartment at time zero, the degradation rate is initially controlled by $k_m$. When a significant proportion of the parent compound partitions into the adsorbed compartment, the rate limiting step in the degradation process shifts to $k_{des}$, and this represents the biphasic behavior. Note that when $k_{des}$ is rapid relative to $k_m$, the model approaches a simple first order degradation model. While the ratio of $k_{ads}$ and $k_{des}$ appears to be related to the adsorption coefficient, these rate constants include other factors such as uptake by microorganisms and depuration rates and represent an entirely different time scale as noted above.

**Setup of the model**

The Model-Maker software requires an initial approximation of the values of the rate constants, and initial values for the concentration in each compartment. The Adsorbed_CPY and the metabolites compartments were set to zero and the Labile_CPY compartment was set to the initial measured value except for the Charentilly and Cuckney soils, for which the intercept of the simple first order regression, 96.9 and 98.2% respectively were used. The first and second phase rate constants in the biphasic degradation curve were used as initial approximate values for $k_m$ and $k_{des}$. The initial value of $k_{ads}$ was set slightly higher than $k_{des}$. In some cases these values were adjusted to obtain a closer visual fit to the data so that the regression process would converge on an optimum set of rate constants. An example of the set-up used for each soil type is shown in SI SI Table C-1. This includes the differential equations used. The time-0 values are entered and the experimental data into a data table. When the model is run, the software first integrates the set of differential equations. Five integration methods (Euler, Mid-Point, Runge-Kutta, Bulirsch-Stoer and Gear's method) are available in the software. The default Runge-Kutta method was used for all sites. After integration, a least squares optimization process was run to
obtain the values of $k_{ads}$, $k_{des}$ and $k_m$ that best fit the data, and these values were output along with the goodness of fit statistics. The Marquardt Method with ordinary least squares optimization was used for all soils except the Catlin soil, which required the weighted least squares procedure.

---

### SI Table C-1 Example ModelMaker software set-up for Barnes soil

<table>
<thead>
<tr>
<th>compartment: Adsorbed_CPY Unconditional Universal</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d\text{Adsorbed_CPY}/dt = +F1-F2$</td>
</tr>
<tr>
<td>Initial Value = 0.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>compartment: Dissolved_CPY Unconditional Universal</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d\text{Dissolved_CPY}/dt = -F1+F2-F3$</td>
</tr>
<tr>
<td>Initial Value = 96.8</td>
</tr>
</tbody>
</table>

flow: F1 Unconditional Universal
Flow from Dissolved_CPY to Adsorbed_CPY

$F1 = k_{ads} \times \text{Dissolved\_CPY}$

flow: F2 Unconditional
Flow from Adsorbed_CPY to Dissolved_CPY

$F2 = k_{des} \times \text{Adsorbed\_CPY}$

flow: F3 Unconditional
Flow from Dissolved_CPY to Metabolites

$F3 = k_m \times \text{Dissolved\_CPY}$

variable: Measured_CPY Unconditional

Commerce Soil

$\text{Measured\_CPY} = \text{Adsorbed\_CPY} + \text{Dissolved\_CPY}$

<table>
<thead>
<tr>
<th>compartment: Metabolites Unconditional Universal</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d\text{Metabolites}/dt = +F3$</td>
</tr>
<tr>
<td>Initial Value = 0.0</td>
</tr>
</tbody>
</table>

---

### Results of the model

The results of the linear regression optimization of the rate constants are listed in SI Table C-2 and an example of the model output graph is shown in SI Fig. C-3. The resulting rate constant represent the entire data set optimized simultaneously and provide a better representation of the half-life than the values in the original reports for most soils and represent a consistent model across all the soils. It is possible to consider the data in two groups; one group of soils has half-lives >30 d, which are pH dependent and the other group has shorter half-lives with much weaker correlation to pH. The correlation to pH in the range from pH 5 to 8 is given by Equation SI C-1 for Group 1 and SI C-2 for Group 2.
<table>
<thead>
<tr>
<th>Soil</th>
<th>Optimized parameters</th>
<th>Optimization statistics</th>
<th>Group</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Parameter</td>
<td>Optimized value</td>
<td>Half-life (d)</td>
</tr>
<tr>
<td>German 2:3</td>
<td>k&lt;sub&gt;ads&lt;/sub&gt;</td>
<td>0.0124</td>
<td>56.9</td>
</tr>
<tr>
<td></td>
<td>k&lt;sub&gt;des&lt;/sub&gt;</td>
<td>0.0211</td>
<td>32.9</td>
</tr>
<tr>
<td></td>
<td>k&lt;sub&gt;m&lt;/sub&gt;</td>
<td>0.0070</td>
<td>99.1</td>
</tr>
<tr>
<td></td>
<td>k reported</td>
<td>141</td>
<td></td>
</tr>
<tr>
<td>Stockton</td>
<td>k&lt;sub&gt;ads&lt;/sub&gt;</td>
<td>0.0031</td>
<td>227.3</td>
</tr>
<tr>
<td></td>
<td>k&lt;sub&gt;des&lt;/sub&gt;</td>
<td>0.0021</td>
<td>338.1</td>
</tr>
<tr>
<td></td>
<td>k&lt;sub&gt;m&lt;/sub&gt;</td>
<td>0.0072</td>
<td>96.3</td>
</tr>
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<td>k reported</td>
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<tr>
<td>Charentilly</td>
<td>k&lt;sub&gt;ads&lt;/sub&gt;</td>
<td>0.0125</td>
<td>56.5</td>
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<tr>
<td></td>
<td>k&lt;sub&gt;des&lt;/sub&gt;</td>
<td>0.287</td>
<td>2.4</td>
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<tr>
<td></td>
<td>k&lt;sub&gt;m&lt;/sub&gt;</td>
<td>0.00749</td>
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<tr>
<td></td>
<td>k reported</td>
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<tr>
<td>Cuckney</td>
<td>k&lt;sub&gt;ads&lt;/sub&gt;</td>
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<tr>
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<tr>
<td></td>
<td>k reported</td>
<td>111.1</td>
<td></td>
</tr>
<tr>
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<td>k&lt;sub&gt;ads&lt;/sub&gt;</td>
<td>0.0129</td>
<td>53.7</td>
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<td></td>
<td>k&lt;sub&gt;des&lt;/sub&gt;</td>
<td>0.0125</td>
<td>55.5</td>
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<td></td>
<td>k&lt;sub&gt;m&lt;/sub&gt;</td>
<td>0.0122</td>
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<td>Thessaloniki</td>
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<td></td>
<td>k&lt;sub&gt;m&lt;/sub&gt;</td>
<td>0.02256</td>
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<td>0.00245</td>
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<td>0.01805</td>
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<td></td>
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<td>0.0312</td>
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Group 1 half-life = 267 - 30.14 X pH ($r^2 = 0.92$)  
(SI C-1)

Group 2 half-life = 93.5 - 10.86 X pH ($r^2 = 0.76$)  
(SI C-2)

The mean half-life in the Group-1 was 17.6 d with a 90th centile of 25.9 d and for Group-2 was 77.7 d with a 90th centile of 97.7 d.
There were only two US soils in the Group-2, and it was considered less common. The highest half-life among the US soils in each group was selected as a conservative value to represent the group in the PRZM/EXAMS model runs. These values were 96 d from the Stockton soil and 28 d from the Catlin soil (SI SI Table C-2).

The placement of the soils into these groups does not appear to be based on the physical properties of the soil. It is more likely to be related to the biological activity of the soil during the study, and the relative importance of abiotic and metabolic hydrolysis in the degradation. The group of soils with the longer half-lives has a greater contribution from abiotic hydrolysis, which is pH-dependent.

The two compartment model used for this analysis successfully described the behavior of chlorpyrifos in soil, but unfortunately there is no measured soil parameter that would allow the selection of a rate constant from the two groups for a particular soil. Therefore the PRZM/EXAMS modeling was carried out using the US soils with the longest half-
lives in each of the 2 groups: These were Stockton, from California and Catlin, from Illinois, with half-lives of 96 and 28 days respectively (Williams et al. 2013). No attempt was made to run the two compartment model described above on available field study data, but this can be done either within the growing season or by using the appropriate corrections for soil moisture and temperature.

The movement of material between the two compartments in the typical two compartment kinetic model has been considered to be a kind of pseudo-partition coefficient (Nash 1988), but this assumes an equilibrium. As noted previously, the adsorption/desorption equilibrium is established within hours, whereas the transition from the rapid degradation to slower degradation governed by \( k_{ads} \) and \( k_{des} \) occurs over many days and the system may not be at equilibrium. Moreover, the ratio does not predict the proportion of the residue that is available for leaching movement; both compartments of the two compartment model are fixed on the soil. These parameters are variable among soil types but neither the individual values nor the ratio of \( k_{ads} \) to \( k_{des} \) is related to the soil adsorption coefficient, \( K_d \) or \( K_{oc} \), or to other soil physical properties. It is likely that the labile phase is comprised of the biologically active component of the soil organic matter. This living component consists of a complex and variable collection of many different species, present as both biofilm and individual cells (Burmelle et al. 2007). Since the standard measures of microbial viability, e.g., evolution of CO\(_2\) do not correlate to the ability of a soil to metabolically transform a compound such as chlorpyrifos, there is no readily available measure for applying the model to a soil other than the ones tested. The adsorbed compartment is likely to be comprised of the soil particle surface, vacuoles, cell membranes and other micro-environments, which are not accessible to degradation enzymes or have a lower pH than the bulk soil. In any case the model compartments have a physical form in the soil, and the release of CPY from the adsorbed phase becomes the rate limiting step in the degradation in the second phase of the biphasic degradation process.

The following conclusions can be drawn from the DT50s and soil properties listed in SI Table C-2 from these two studies:

1. The half-life was significantly longer at 10°C or near the wilting point at 10% filed moisture capacity (FMC) compared to the same soil at 20°C and 40% FMC. This shows that temperature is a significant factor and that moisture can by limiting under extremely dry conditions.

2. Sterile conditions reduced the production of CO\(_2\) in the Marchand soil from the de Vette study, but the sterile conditions did not reduce the degradation rate of parent CPY. This shows that abiotic hydrolysis can be a major degradation pathway in soil.
3. The model results gave a good fit to the data. The resulting rate constants were not correlated to soil properties, but could be divided into two groups, one in which the metabolic half-life was >30 d and was correlated with the soil pH and the other in which the correlation to pH was much weaker and the half-life was <30 d. Otherwise the rate constants found do not appear to be predictable based upon the physical properties of the soil.

4. It is likely that the rate constants $k_{ads}$, $k_{des}$ and $k_m$ are related to the movement between biologically active and inert environments in the soil. At present there is no independent measure of the movement of material between these compartments. However, it may be that the soils that show a faster hydrolysis rate are those with a microbiome capable of biologically accelerated hydrolysis.

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