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,

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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

Parameter	Values for Chlorpyrifos	Source
Chemical Name	O,O-diethyl o-(3,5,6-trichloro-2-pyridyl phosphorothioate	USEPA (2011b)
Chemical Abstracts Service (CAS) Registry Number	2921-88-2	
Empirical formula	$C_9H_{11}Cl_3NO_3PS$	
USEPA Pesticide Code (PC #)	59101	
Smiles notation	S=P(OC1=NC(=C(C=C1Cl)Cl)Cl)(OCC)OCC	
Molecular mass	350.6 g mol^{-1}	Mackay et al. (2014)
Vapor pressure (25 °C)	1.73×10^{-5} torr	
Water solubility (20 °C)	0.73 mg L^{-1}	
Henry's Law Constant	1.10×10^{-5} atm m^{-3} mol^{-1}	
Log K_{OW}	5.0	

Table 2 Environmental fate properties of chlorpyrifos

Parameter	Values	Source
Hydrolysis (t½)	pH 5: 73 d pH 7: 72 d pH 9: 16 d	USEPA (2011b)
Aqueous photolysis (t½)	29.6 d	
Aerobic soil metabolism (t½)	2–1,576 d, N = 68 (next highest value is 335 d)	See SI Table A-1
Aerobic aquatic metabolism (t½)	22–51 d, N = 3	See SI Table A-5
Anaerobic soil metabolism (t½)	15 and 58 d	USEPA (2011b)
Anaerobic aquatic metabolism (t½)	39 and 51 d	
Soil adsorption coefficient K_{OC}	973–31,000 mL g^{-1}, N = 33	See SI Table A-4
Terrestrial field dissipation (t½)	2–120 d, N = 58	See SI Table A-3

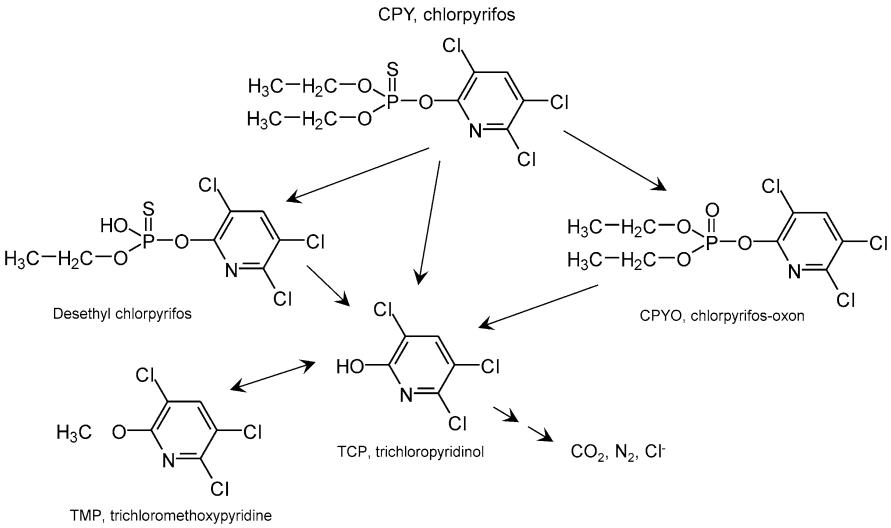

Fig. 1 Pathways for degradation of chlropyrifos in the environment (after Racke 1993)

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 CO_2. 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

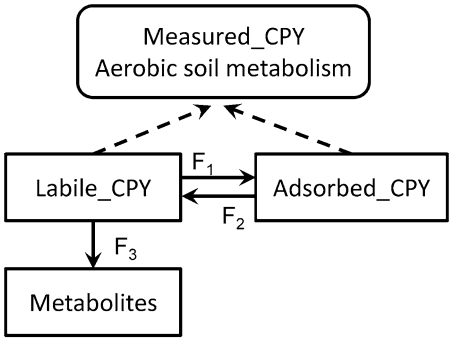

Fig. 2 Schematic diagram of a two–compartment kinetic model for chlorpyrifos (CPY) degradation

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 DT_{50} 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 DT_{50} 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 F_1 and F_2 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 F_3, 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 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 k_m and the concentration

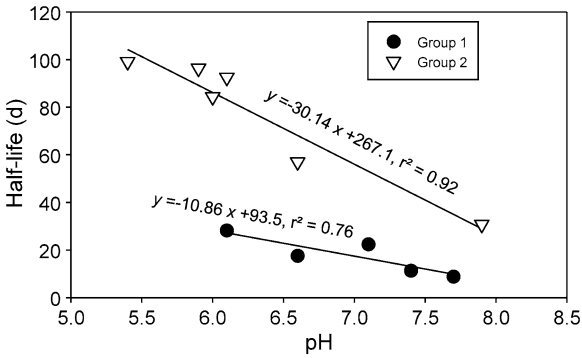

Fig. 3 Correlation of half-life of chlorpyrifos with pH of soil (data from Bidlack 1979; de Vette and Schoonmade 2001)

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 K_{OC}, 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).

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

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

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).

Table 3 Half-lives of chlorpyrifos in selected soils recalculated using a two-compartment model

Soil	Reported T½[a]	Calculated T½[1] from two-compartment model[b]	Group	Reference
Commerce, MI	11	11	2	Bidlack (1979)
Barnes, ND	22	22	2	Bidlack (1979)
Miami, IN	24	18	2	Bidlack (1979)
Caitlin, IL	34	28	2	Bidlack (1979)
Marcham, UK	43	9	2	de Vette and Schoonmade (2001)
Thessaloniki, GR	46	31	1	de Vette and Schoonmade (2001)
Charentilly, FR	95	93	1	de Vette and Schoonmade (2001)
Norfolk, VA	102	57	1	Bidlack (1979)
Stockton, CA	107	96	1	Bidlack (1979)
Cuckney, UK	111	84	1	de Vette and Schoonmade (2001)
German 2:3	141	99	1	Bidlack (1979)

[a]Rounded to nearest day
[b]For detailed derivation of the data, see SI Appendix B in (Williams et al. 2014)

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

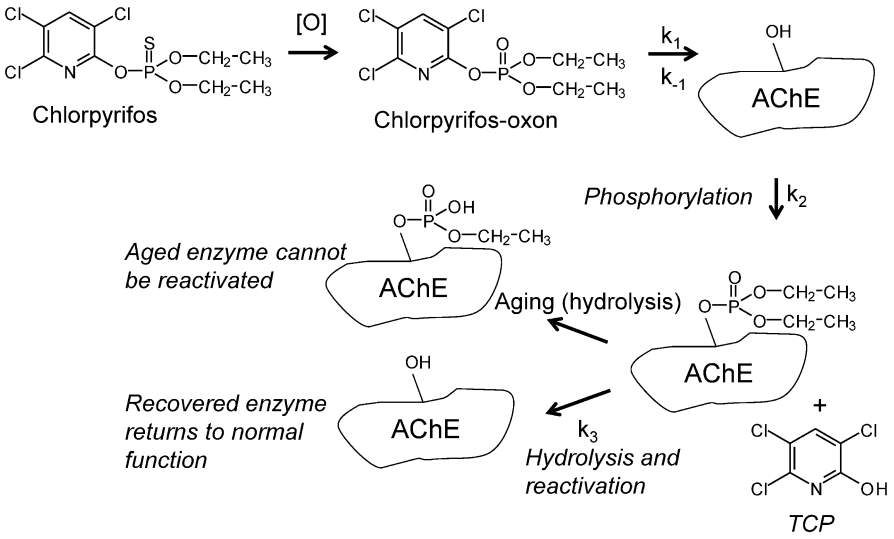

Fig. 4 Diagrammatic representation of the mechanism of action of chlorpyrifos in the nerve synapse

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

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 pre-plant, 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. (wtwt) (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, reservoirs, 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.

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

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

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

Crop	Ave. lbs.[a] a.i. applied (Gomez 2009) from Doane	Ave. lbs. a.i. applied (USEPA 2008)	Ave. % crop treated (USEPA 2008)	Ave. lbs. a.i. applied (NASS program states –latest year)[b] (USDA 2012)	Ave. % crop treated (NASS) (USDA 2012)
Alfalfa	374,750	400,000	5		
Almonds	341,991	500,000	30		
Asparagus	22,104	20,000	25	211,100	44
Apples	414,600	400,000	55		
Beans, green	4,119	3,000	<1		
Beans & peas, dry		4,000	<1		
Broccoli	60,385	90,000	45		
Brussels Sprouts		6,000	n/c		
Cabbage	7,055	10,000	10		
Carrots (SLN-WA[c])		1,000	<2.5		
Cauliflower	15,239	20,000	40		
Cherries, all	80,140	60,000	30	36,300	16–23
Christmas trees				26,600	16–20
Corn	2,617,432	3,000,000	5	478,000	1
Cotton	285,350	200,000	<1		
Cranberries		50,000	70		
Grapefruit	54,855	60,000	15	42,500	19
Grapes, wine	68,603			64,500	4
Grapes, table	60,428			40,000	12
Grapes, all		100,000	5		
Hazelnuts	7,286	7,000	15		
Lemons	47,033	90,000	35	22,800	12
Mint		50,000	25		
Nectarines		20,000	20	3,400	5
Onions, dry	68,805	60,000	35	51,100	30–32
Oranges	241,735	300,000	10	194,800	12
Peaches	69,853	70,000	30	8,900	7
Peanuts	119,213	200,000	5		
Pears	29,564	30,000	20	11,300	10
Peas, green		<500	<1		
Pecans	296,596	300,000	35		
Peppers (SLN-FL)		2,000	<1		
Plums & Prunes	18,674	40,000			
Plums			15	2,400	7
Prunes			10		
Sod/turf		2,000	n/c		
Sorghum		30,000	<1		

(continued)

Table 4 (continued)

Crop	Ave. lbs.[a] a.i. applied (Gomez 2009) from Doane	Ave. lbs. a.i. applied (USEPA 2008)	Ave. % crop treated (USEPA 2008)	Ave. lbs. a.i. applied (NASS program states –latest year)[b] (USDA 2012)	Ave. % crop treated (NASS) (USDA 2012)
Soybeans	1,017,953	700,000	<1		
Strawberries	10,043	9,000	15	7,700	15
Sugar Beets	138,020	100,000	10		
Sunflowers	34,857	20,000	<1		
Sweet Corn	120,881	100,000	10	36,500	13–23
Sweet potatoes		100,000	65		
Tangelos & tangerines		8,000	10	8,300	7–19
Tobacco	98,468	100,000	15		
Walnuts	195,505	400,000	45		
Wheat	288,751	300,000	<1	577,000	2–3
Total					

[a]To maintain consistency with uses and the labels of formulated products sold in the U.S., amounts of CPY applied are given in imperial units (pounds (lbs.))
[b]Generally this is 2011 for fruits and 2010 for other crop
[c]Special Label Needs

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)

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

(continued)

Table 5 (continued)

[a]Special Label Needs
Data from:
USDA (2010)
Missouri Extension Service: http://extension.missouri.edu/p/G4550
http://ohioline.osu.edu/b826/b826_14.html
http://www.pickyourown.org/FLcitrus.htm; http://www.pickyourown.org/CAharvest calendar. htm
Seasonal Patterns of Citrus Bloom, by William A. Simanton, Florida Agricultural Experiment Station Journal Series No. 3426. Florida State Horticultural Society, 1969, pp 96–98
http://en.wikipedia.org/wiki/Cranberry; http://www.wenatcheeworld.com/news/2011/oct/07/cranberry-harvest-under-way-on-wa-coastal-bogs/; http://www.capecodtravel.com/attractions/ nature/cranberries0900.shtml
Morton, J. 1987. Fig. p. 47–50. In: Fruits of warm climates. Julia F. Morton, Miami, FL. @ http://www.hort.purdue.edu/newcrop/morton/fig.html; also http://www.latimes.com/features/ la-fo-market16-2008jul16,0,4856462.story
http://en.wikipedia.org/wiki/Cranberry; http://www.wenatcheeworld.com/news/2011/oct/07/cranberry-harvest-under-way-on-wa-coastal-bogs/; http://www.capecodtravel.com/attractions/nature/cranberries0900.shtml\
Monitoring and Control Tactics for Grape Root Borer Vitacea polistiformis Harris (Lepidoptera: Sesiidae) in Florida Vineyards. By Scott Weihman. Master's Degree Thesis, University of Florida, 2005 @ http://etd.fcla.edu/UF/UFE0009182/weihman_s.pdf
The Grape Root Borer in Tennessee, by P. Parkman, D. Lockwood, and F. Hale, University of Tennessee Extension Service publication W171, 2007. @ https://utextension.tennessee.edu/publications/documents/W171.pdf www.nysipm.cornell.edu/factsheets/grapes/pests/gcb.pdf
http://www.calagquest.com/BloomTime.php
http://sacramentogardening.com/edible_gardening.html
http://wiki.answers.com/Q/What_time_of_year_do_you_grow_peas
Pest Management Strategic Plan for Dry Bulb Storage Onions in Colorado, Idaho, Oregon, Utah, and Washington. Summary of a workshop held on February 26–27, 2004. Boise, ID. @ http://www.ipmcenters.org/pmsp/pdf/WesternONION.pdf
http://aggie-horticulture.tamu.edu/archives/parsons/publications/onions/oniongro.html
http://edis.ifas.ufl.edu/mv112
http://www.ctahr.hawaii.edu/oc/freepubs/pdf/f_n-7.pdf
http://www.strawberry-recipes.com/plant-strawberries.html
http://strawberryplants.org/2010/05/strawberry-varieties/

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 (K_{OC}) of CPY is 8,216 mL g^{-1}; negligible amounts enter plants via the roots, and it is not translocated in plants.

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

Crop in field, location, and use of CPY	Months of the year in which CPY is applied											
	J	F	M	A	M	J	J	A	S	O	N	D
Corn, Southern states in field			■	■	■	■	■	■	■			
Use of CPY			▒	▒	▒	▒	▒	▒	▒			
Northern states in field					■	■	■	■	■	■	■	
Use of CPY					▒	▒	▒	▒	▒	▒	▒	
Cotton, Southern areas in field			■	■	■	■	■	■	■			
Use of CPY				▒	▒	▒	▒	▒	▒			
Northern areas + CA in field				■	■	■	■	■	■	■	■	
Use of CPY					▒	▒	▒	▒	▒	▒	▒	
Peanuts, in field				■	■	■	■	■	■	■		
Use of CPY				▒	▒	▒	▒	▒				
Peppermint and Spearmint, in field			■	■	■	■	■	■	■			
Use of CPY			▒	▒	▒	▒	▒	▒	▒			
Sorghum, in field			■	■	■	■	■	■	■	■	■	
Use of CPY			▒	▒	▒	▒	▒	▒	▒			
Soybeans, in field				■	■	■	■	■	■	■	■	
Use of CPY				▒	▒	▒	▒	▒	▒	▒		
Sugarbeets, in field Imperial Valley, CA	■	■	■	■	■	■	■		■	■	■	■
Use of CPY	▒	▒	▒	▒	▒				▒	▒	▒	▒
Other locations in field				■	■	■	■	■	■	■	■	
Use of CPY				▒	▒	▒	▒	▒	▒	▒		
Sunflowers, in field CA			■	■	■	■	■	■				
Use of CPY			▒	▒	▒	▒	▒					
TX & OK in field				■	■	■	■	■	■	■	■	
Use of CPY				▒	▒	▒	▒	▒	▒	▒		
Other states in field					■	■	■	■	■	■	■	
Use of CPY					▒	▒	▒	▒	▒	▒		
Sweet potato, in field			■	■	■	■	■	■	■			
Use of CPY			▒	▒								
Tobacco, in field New England & PA					■	■	■	■	■			
Use of CPY					▒	▒						
Southern states in field				■	■	■	■	■	■	■		
Use of CPY				▒	▒	▒						

Data from: (Chen et al. 2011; USDA 2010; Zheljazkov et al. 2010)

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.

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