Fate in the Environment and Long-Range Atmospheric Transport of the Organophosphorus Insecticide, Chlorpyrifos and Its Oxon

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1 Introduction

The fate and movement of the organophosphorus insecticide chlorpyrifos (CPY; CAS No. 2921-88-2) and its principal transformation product of interest, chlorpyrifos-oxon (CPYO; CAS No. 5598-15-2), are primary determinants of exposures experienced by animals in terrestrial and aquatic environments. Dynamics of the movement of CPY and CPYO are determined by the interactions between chemical and physical properties (Solomon et al. 2013a) and environmental conditions. Together, these properties provide the basis for developing and refining models of exposure for assessing risks. An extensive review of the environmental fate of CPY was published in 1993 (Racke 1993). The following sections build on this review, with updates exploiting relevant data from new studies and other reviews in the literature as these pertain to the assessment of risks in the ecosystem. This report addresses processes that affect fates of CPY and CPYO in various compartments of the environment and how these affect exposures of ecological receptors (Fig. 1) as discussed in companion papers (Cutler et al. 2014; Moore et al. 2014; Williams et al. 2014). This paper serves as an update on the environmental dynamics and

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Fig. 1 Qualitative
diagrammatic representation
of the sequence of processes
influencing the fate of CPY
in various environmental
compartments after release
and their influence on
exposures to biota
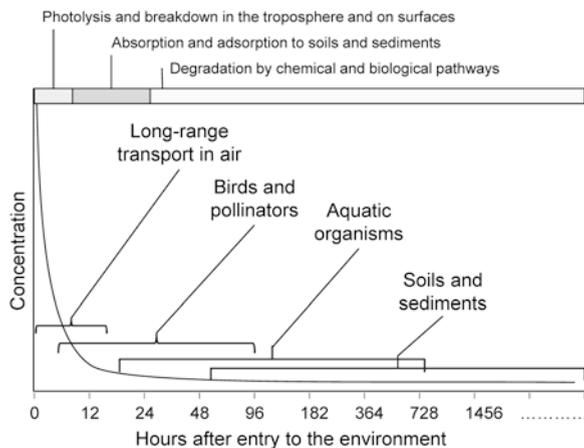
potential exposures to CPY that were presented previously (Giesy et al. 1999; Solomon et al. 2001) and includes additional information on environmental chemodynamics of CPY that have become available subsequent to those earlier publications. There have been and continue to be extensive studies on the presence of CPY and CPYO in environmental media near to and remote from sites of application. Many are prompted by concerns that these substances may have effects on distant sensitive organisms, such as amphibians and in remote food webs as have occurred with organo-chlorine pesticides.

2   Fate in the Atmosphere and Long-Range Transport

The potential for long-range transport (LRT) is a concern for synthetic chemicals of commerce, including pesticides. Concentrations of synthetic chemicals measured at locations distant from sources, in conjunction with mass-balance modeling, have combined to provide information on key contributing processes involved in LRT, especially for persistent organic pollutants (POPs) that have relatively long residence times in the atmosphere. A quantitative predictive capability has emerged in the form of simple mass-balance models such as TAPL3 and the OECD Tool (Beyer et al. 2000; Wegmann et al. 2009). These models have been used in regulatory contexts and characterize LRT as a Characteristic Travel Distance (CTD) over which some two-thirds of the mass of chemical transported from source regions is deposited or transformed to other chemicals, while the remaining third is transported greater distances through the atmosphere. The focus here is the organophosphate insecticide, CPY and its transformation product CPYO, in which the sulfur atom is replaced by oxygen (Giesy et al. 1999; Racke 1993).

Table 1 Reported concentrations of CPY in air in N America

Location and dates of sampling	Concentration (ng m⁻³)	Reference
CANCUP data for 8 sites in Canada 2004–2005, values range from areas of application to distant areas	0.08–22	Yao et al. (2008)
Passive air samples in Ontario 2003–2005	0.0003–0.06; median 0.007; 73% FOD[a]	Kurt-Karakus et al. (2011)
Iowa 2000–2002	Average 1.0, 19% FOD 1.4 at 1A—AM Site, 0.88 at Hills	Peck and Hornbuckle (2005)
Mississippi River Valley 1994	0.43	Majewski et al. (1998)
Chesapeake Bay 2000	0.015–0.670 Median 0.110 FOD 87%	Kuang et al. (2003)
Bratt's Lake (Saskatchewan) and Abbotsford (British Colombia)	Mostly 10–100 with 3 concentrations exceeding 100 and a maximum of 250 in Aug 2003 at Bratt's Lake near area of use but max only 1.38 in Jul 2005. Concentrations in Abbotsford, an area of lesser use all <0.26 in 2004 and 2005	Raina et al. (2010)
Mississippi River Valley	FOD 93, MS 35%, Iowa City 90%, Cedar Rapids 50%, Minneapolis 10%, Princeton MN 3%	Foreman et al. (2000)
Central Valley (CA) and Sierra Nevada	CPY up to 180 and CPYO up to 54, lesser concentrations in Sequoia NP	Aston and Seiber (1997)
CPY and CPYO in air in Sequoia NP	0.16–17.5	LeNoir et al. (1999)

[a]*FOD* = frequency of detection

2.1 Chlorpyrifos and Chlorpyrifos-Oxon

Evidence that CPY is subject to LRT is provided in reports of concentrations in air and other media at locations remote from sites where CYP is applied in agriculture (Tables 1, 2, 3 and 4). Notable are studies conducted in the intensely agricultural, Central Valley of California and adjacent National Parks. CTDs of several pesticides, including CPY have been estimated (Muir et al. 2004). Results of these modeling exercises have suggested a CTD of 280–300 km for CPY, the narrow range being the direct result of close similarities between the model equations. Monitoring observations of concentrations of CPY in air close to and carried downwind from application areas are in general accord with these distances. Also in accord are monitoring data reflecting deposition in foothill and mountainous terrain, especially in the Sierra Nevada of California.

Table 2 Reported concentrations of CPY in rain and snow and fluxes

Location and dates of sampling	Concentration in ng L^{-1}	Reference
Chesapeake Bay 2000	Rain; 0.97–29 average 4.8, FOD[a] 14% Wet flux, 190 ng m^{-2} event total 6,100 ng m^{-2}, 1.1 kg/yr	Kuang et al. (2003)
Svalbard Ice Cap 1979–1986	Ice, peak concentration 16.2 at ~15 m	Hermanson et al. (2005)
Delaware/Maryland April to Sept 2000–2003	Rain; 1.0–29 average 1.0 39% FOD Fluxes ~610–1750 average 1.0–4.5 ng m^{-2}	Goel et al. (2005)
7 US National Parks (NP) March–April 2003	Snow in Sequoia NP; 2.8, 1.3 Other NP ; 0.033 ~0.05 ~0.5 ~0.02 ~0.02 and 0.03 Deposition in Sequoia NP; 2,600 ng m^{-2} Other parks; 25, 65, 35, 30, 14, and 4 ng m^{-2} Correlations with altitude and distance, 75, 150, 300 km from sources	Hageman et al. (2006)

[a]*FOD* = frequency of detection

A comprehensive ecotoxicological risk assessment of CYP was developed for birds and mammals (Solomon et al. 2001) and aquatic environments (Giesy et al. 1999) that were near areas of application. The analysis of LRT of CPY and CPYO presented here extends those assessments to regions downwind of points of application. The approach taken in this study was to compile and evaluate data on concentrations of CPY and CPYO at locations both near to applications and remote from sources. This assessment of LRT thus goes beyond determination of CTD to include estimates of concentrations of CPY and CPYO in other environmental media such as rain, snow, and terrestrial phases as well as in the atmosphere at more remote locations, including high altitudes. This was accomplished by developing a relatively simple mass-balance model, predictions from which could be compared to available measured concentrations of CYP in air and other media. This can provide an order-of-magnitude test of the accuracy of the predictions of the model, and, in this way, make an indirect assessment of the relative importance of the included processes and parameters. The model can then serve as a semi-quantitative predictive framework that is consistent with observations. The equations included in the model enable examination of the effect of changes in parameters such as application rate, temperature, meteorology, distance from source and precipitation. Estimated concentrations in terrestrial and aquatic environments remote from areas of application can be used, in combination with toxicological data, to assess risk to organisms in those media and locations.

Monitoring data. Reports of concentrations of CPY in air at a variety of locations are presented in Table 1, with comments on other influencing factors such as altitude. Also included are reports of concentrations of toxicologically-relevant transformation products, such as CPYO, if and when such information was available. Reports of concentrations of CPY in precipitation (rain and snow) are given in Table 2, while Table 3 provides data for water bodies and other terrestrial media.

Table 3 Reported concentrations of CPY in aquatic and terrestrial media

Location and dates of sampling	Concentration in ng g^{-1}dwt unless indicated otherwise	Reference
Sierra Nevada CA 2,785–3,375 m elevation 2004/2005 and Yosemite National Park	Water: all concentrations in water were <0.07 ng L^{-1} Sediment: 0.043–3.478 median 0.107 0.285–12.44 median 1.73 0.011–2.276 median 0.101 0.499–10.72 median 1.372 Tadpoles: 2.224–156, median 22.2 ng g^{-1} lipid 2.741–68.4, median 19.9 ng g^{-1} lipid	Bradford et al. (2010a) Bradford et al. (2013)
Lassen National Park, CA, 25 km from the San Joaquin Valley edge	Tadpoles of Pacific tree frog (*Hyla regilla*): 10–17 ng g^{-1}wwt	Datta et al. (1998)
Kaweah, Kings, and Kern Watersheds 43–85 km from the San Joaquin Valley edge	Tadpoles of Pacific tree frog (*Hyla regilla*): <0.6 ng g^{-1}wwt	Bradford et al. (2010b)
Thirty Canadian lakes 1999–2001	Lake water in application region: 0.28–1.0 mean 0.65 ng L^{-1} Lake water in remote regions: <0.017–2.9 mean 0.82 ng L^{-1} Lake water, subarctic: <0.017–<0.017 ng/L^{-1} in all samples Lake water, arctic: <0.017–1.6 mean 0.27 ng L^{-1}	Muir et al. (2004)
Ontario 2003/2005	Lake water: <0.002 to 0.5 ng L^{-1} median 0.02, 77% FOD Rain: <0.004 to 43 ng L^{-1} median 0.76, 80% FOD Zooplankton: <0.003–0.08, 0.004, 0.005 ng g^{-1}wwt (geometric means=GM) BAF in Zooplankton (GM) 70 (wwt), 3,300 (lipid wt)	Kurt-Karakus et al. (2011)
Chesapeake Bay, 2000	0.51–4.6	Kuang et al. (2003)
Lichen in Yosemite NP 2003–2005	0.92 ng g^{-1}, 1.7 ng g^{-1}	Mast et al. (2012)
Pine needles in Sequoia NP, 1994	10–125 ng g^{-1}dwt	Aston and Seiber (1997)
Sequoia NP, 1996–1997	Dry deposition: 0.2–24 ng m^{-2} d^{-1} Surface water: 0.2–122 ng L^{-1}	LeNoir et al. (1999)

A significant portion of these data are from the Sierra Nevada, including National Parks that are some 30–200 km and primarily downwind and up-gradient from the productive agricultural Central Valley of California, in which there is significant usage of CPY (Solomon et al. 2014).

The data in (Tables 1, 2, 3 and 4) confirm that measurable concentrations of CPY are found in air and other media remote from sources with a significant

Table 4 Numbers and approximate percentage distributions of reported concentration levels expressed as percentages of reported data

Phase	Air ng m^{-3}	Rain ng L^{-1}	Snow ng L^{-1}	Water ng L^{-1}	Sediment ng g^{-1}	Soil ng g^{-1}	Biota ng g^{-1}
Number and conc.	~100	15	18	30	8	2	10
% >10	15	20	11	0	0	0	0
% 1–10	14	40	17	46	20	0	10
% 0.1–1.0	36	20	11	27	40	100	10
% 0.01–0.1	27	20	61	10	40	0	80
% 0.001–0.01	8	0	0	17	0	0	0

Note that concentrations in air and rain appear similar numerically because the air-water partition coefficient of 0.00034 is similar to the 0.001 factor conversion from m^3 to L

frequency of detection. The key issue in this context is not one of presence/absence, because CPY and CPYO can be monitored in air at concentrations as little as 0.001 ng m^{-3}, which are much less than thresholds for adverse effects. Risk depends on the magnitude of concentrations, especially in media where organisms might be exposed and thus are potentially at risk. It can be difficult to assimilate ranges in concentrations in the atmosphere and the variety of concentration units of differing magnitudes in sampled media. Accordingly, here, the feasibility was assessed of compiling a more readily comprehendible depiction of multi-media environmental concentrations by expressing the concentrations as ranges and converting concentrations in various media to fugacities. Fugacity is essentially partial pressure and can be deduced for all media and compared directly, without difficulties introduced by the use of different concentration units for individual compartments of the environment. Using fugacity as a synoptic descriptor of concentrations in the ecosystem has been applied previously to multi-media concentrations of organochlorines in the Great Lakes (Clark et al. 1988). It is, of course, possible to calculate multi-media equilibrium concentrations using partition coefficients directly, rather than using fugacity as an intermediate, but the equilibrium status of two phases with units such as ng m^{-3} in air and mg kg^{-1} in vegetation may not be obvious.

Ideally, to demonstrate directly the trend of decreasing concentrations, the data should be plotted as a function of distance from source, but because sources are often uncertain and concentrations vary with time as a function of transformation of the material at the location of release, this is rarely possible. The approach adopted here was to compile a distribution of reported concentrations to gain perspective on the range in magnitude of concentrations at various distances from points of release, at least for ecosystems for which sufficient monitoring data have been compiled. Accordingly, Table 4 depicts the distribution of reported concentrations for air, rain, snow, water bodies, soils, sediments, and biota on a decade scale. In some cases, products of transformation are included and in others they were specifically excluded. Some of the data were reported graphically or as ranges, so numerical values were sometimes difficult to establish. Locations for which information was available varied geographically and often lacked information on current and recent meteorology such as wind speed, temperature, and precipitation. Some values reported for each concentration range are approximate because reports gave only

Table 5 Key physical-chemical properties of CPY

Property	Units	Value	Comments
Melting point (mp)	°C	42	
Molar mass	g/mol	350.6	
Fugacity ratio (FR)	–	0.68	Estimated from mp
Vapor pressure (VP) of solid	Pa	0.0023	EPA gives 0.00249
Vapor pressure of sub-cooled liquid	Pa	0.0034	Consistent with FR and solid VP
Solubility of solid in water	g m^{-3} or mg L^{-1}	0.73	EPA gives 1.43
Solubility of sub-cooled solid	g m^{-3}	1.07	Consistent with FR and solid solubility
Henry's Law constant	Pa m^{-3} mol^{-1}	1.11	VP/Solubility, EPA gives 0.628
Air-water partition coeff. K_{AW}	–	0.00045 Log is −3.35	Calculated from H/RT
Octanol-water partition coeff. K_{OW}	–	100,000 Log is 5.0	EPA gives 4.7
Octanol-air partition coeff. K_{OA}	–	2.2×10^8 Log is 8.34	Log is 8.34, $K_{OA} = K_{OW}/K_{AW}$
Organic carbon-water partition coeff. K_{OC}	L/kg	8,500 Log is 3.93	EPA gives 5,860, 4,960, 7,300

Data from Mackay et al. (1997); Muir et al. (2004); Racke (1993); USEPA (2011). Values are at 25 °C unless otherwise stated

minimum, maximum, and mean or median concentrations. Such results are reported as three points. Given these limitations, only an approximate distribution of observed values can be obtained.

Concentrations in air that exceed 20 ng CYP m^{-3} were generally near sources (areas of application), while those in the range 0.01–10 ng CYP m^{-3} were regarded as "regional", corresponding to distances of up to 100 km from sources. Concentrations less than 0.01 ng CYP m^{-3} were considered to be "remote". There is a possibility that lesser concentrations could have been measured close to sources if the prevailing wind direction is not from the source region. Approximately 70% of the data for concentrations in air were in the range of 0.01–1.0 ng CYP m^{-3}. For rain, the greatest frequency (40%) was in the range 1–10 ng CYP L^{-1}. The distribution of concentrations of CPY in snow exhibited similar patterns, but with more concentrations in the range 0.01–0.1 ng CYP L^{-1}.

Physical-chemical properties of chlorpyrifos and chlorpyrifos-oxon. The model developed here was designed to describe transport and fate of CPY from source to remote destinations and thus obtain a semi-quantitative assessment of its LRT characteristics and provide estimates of exposure concentrations at remote locations. Estimates can then be compared with measured concentrations from monitoring programs. The sensitivity of the results to uncertainty in the various input parameters can also be determined. Fundamental to assessing and predicting LRT of CPY and CPYO are reliable values for physical-chemical properties and rates of reaction by different processes that determine partitioning and persistence in the environment. Data from the literature were compiled and critically assessed to obtain consistent values of these physical-chemical properties (Tables 5, 6, and 7).

Table 6 Estimated reaction half-lives of CPY in various media as used in the modeling of LRT

Medium	Value	Comment
•OH radical reaction in air	9.1×10^{-11} cm^3 molecules^{-1} s^{-1}	2nd order rate constant
Half-life in air	1.4 h	•OH radical conc. of 1.5×10^6 molecules cm^{-3}
	3.0 h	•OH radical conc. of 0.7×10^6 molecules cm^{-3}
Half-life in air	3 h	Conservative value assuming lesser concentration of •OH
Half-life in soil	7–30 d	168–720 h
Half-life in surface water	30–50 d	720–1,200 h
Half-life in sediment	50–150 d	1,200–3,600 h

Table 7 Estimated and measured physical-chemical properties of CPYO

Property	Value	Comment
Molar mass	334.6	
Vapor pressure	0.00088 Pa (USEPA 2011)	Goel et al. (2007) give 0.0000062
Solubility in water	26 mg L^{-1} (USEPA 2011)	
Octanol water partition coefficient K_{OW}	776 (USEPA 2011). Log is 2.89	Appears very low compared to K_{OW} for CPY
Half-life in air	11 h	•OH radical conc. of 1.5×10^6 molecules cm^{-3} (Aston and Seiber 1997)
	7.2 h	•OH radical conc. of 1.56×10^6 molecules cm^{-3}
Half-life in air	11 h	Conservative value assuming lesser concentration of •OH
Half-life in soil	9–30 d	
Half-life in water	13.2 d (USEPA 2011) 40 d, pH=4, 20 °C 4.7 d, pH=7, 20 °C 1.5 d, pH=9, 20 °C (Tunink 2010)	The more conservative value of 13.2 d was used in the modeling
Half-life in sediment	132 d	10× half-life in water assumed

Note that some of these values are only illustrative and are subject to considerable error

Selected values presented for CPY in Tables 5 and 6 are well established and judged to be accurate within a factor of approximately 2 but, in some cases, ranges are given to reflect the variability and uncertainty in values. Since CPYO has been less studied, the values presented in Table 7 are subject to more uncertainty than those for CPY and must be treated as tentative.

The vapor pressure and solubility were used only to estimate the air-water partition coefficient K_{AW} and the Henry's Law constant, H. The octanol-water partition coefficient (K_{OW}) was used only indirectly to estimate the organic carbon water partition coefficient (K_{OC}) in the TAPL3 LRT model but, since there are extensive empirical data on K_{OC}, these empirical values were used directly. The octanol-air

partition coefficient (K_{OA}) can be used to determine partitioning from air to aerosol particles. Its value is not used directly, but is estimated from the ratio K_{OW}/K_{AW}; however, its relatively low value proves to be less important because monitoring data confirm that CPY does not partition appreciably to aerosol particles in the environment (Yao et al. 2008) or indoors (Weschler and Nazaroff 2010).

From the perspective of LRT, the single most important parameter determining concentrations at any given location and the distance that a chemical can be transported, is transformation half-life in the atmosphere. Results of a study of the atmospheric chemistry of CPY and CPYO at the EUPHORE experimental facility in Spain have been reported showing that the principal process that transforms CPY in the atmosphere is reaction with •OH radicals, although there are also contributions from direct photolysis and reactions with ozone and nitrate radicals (Muñoz et al. 2012). In that study, a second-order rate constant for transformation of 9.1×10^{-11} cm^3 molecules^{-1} s^{-1} was determined. Combining that second order rate constant with a concentration of 1.5×10^6 •OH molecules cm^{-3} gives a first order rate constant of 13.6×10^{-5} s^{-1} which corresponds to a half-life of 1.4 h. Half-lives of CPY, thus depend directly on the assumed concentration of •OH. For CPYO, the corresponding rate constant is less certain ($0.8–2.4 \times 10^{-11}$ cm^3 molecules^{-1} s^{-1}) and was estimated to be a factor of approximately 5.5 slower. Experimental results indicated a 10–30% yield of CPYO from transformation of CPY, which is judged to be relatively small, given the absence of significant yields of other transformation products.

In their assessment of LRT, Muir et al. (2004) used the AOPWIN, structure activity (SAR) program to predict a second-order rate constant for CPY of 9.17×10^{-11} cm^3 molecules^{-1} s^{-1}, a value almost identical to that estimated by Muñoz et al. (2012). Muir et al. used a more conservative concentration of •OH that is tenfold less, which yielded an estimated half-life of 14 h (Muir et al. 2004). The lesser concentration of •OH was selected to account for concentrations of •OH likely to occur in more remote regions and at higher latitudes, for example in Canada. Global concentrations of •OH have been compiled and a concentration of 0.9×10^6 •OH molecules cm^{-3} was reported for April in the Central Valley of California and increasing to 1.46×10^6 in July and decreasing to 0.63×10^6 in October (Spivakovsky et al. 2000). At the latitude of Iowa, USA, concentrations of •OH in summer were approximately 80–85% of the concentrations observed in California. In the assessment of LRT reported here, atmospheric half-lives of 3 and 12 h were selected as being reasonable and conservative daily averages for CPY and CPYO, respectively. The actual half-lives of CPY could be a factor of two shorter, especially during midsummer daylight hours and polluted conditions when concentrations of •OH are greater. Monitoring data suggest that CPYO might have a shorter half-life. Half-lives, based on experimental data for CPY-methyl (CPY-methyl), have been reported to be in the range of 3.5 h for reactions between CPY-methyl and •OH, 15 h for direct photolysis, >8 d for reactions with ozone (O_3) and a half-life of 20 d for transformation of CPY-methyl through reactions with nitrate radicals (Munoz et al. 2011). Given the structural similarity between CPY and CPY-methyl, it is likely that similar proportions apply to both substances for reactions in the atmosphere, but not necessarily in other media such as rainwater and surface water where rates are pH-dependent.

Reported half-lives of CPY in soils vary considerably, which has been attributed to differences in soil organic carbon content, moisture, application rate and microbial activity (Racke 1993). Less data were available for water and sediments. From a critical review of the literature, the half-lives in Table 6 were selected. These are considerably shorter than those predicted by the EPIWIN program and used by Muir et al. (2004). Since these half-lives are uncertain, the selected values must be regarded as tentative, although they are not critical to the determination of potential for LRT because deposited CPY evaporates slowly. These half-lives are, however, important for assessing the extent and duration of exposures in distant water, soil, and sediment ecosystems.

Volatilization. For LRT in the atmosphere, one of the most important parameters is the rate of volatilization from surfaces of leaves and soils. Drift is also important but over shorter distances. The quantity of CPY entering the atmosphere following application is a function of several variables, including the physical-chemical properties of the formulation, whether it is applied as a liquid or granular formulation, the quantity applied, the area to which it is applied, the soil properties where applied, meteorological conditions, spray composition and related parameters and the resulting losses by spray drift. The early period after spraying and particularly 24–48 h after application is critical in determining the fraction of applied CPY that enters the atmosphere and becomes subject to LRT (Racke 1993). Relatively fast initial volatilization of applied CPY is observed in the first 12 h after application. The initial loss rate is hypothesized to result directly from volatilization of the "neat" formulated product. But, as the CPY sorbs to the substratum (e.g., foliage or soil), it becomes subject to photolysis, and the rate of volatilization decreases as a function of time. Photolysis of the formulation occurs on the surface of leaves and soils to form CPYO, which also volatilizes. These assertions are consistent with the results of the study by Zivan (2011), who demonstrated substantial rates of photolysis of CPY to CPYO on various surfaces. In the days subsequent to application, CPY adsorbs more strongly to soil, penetrates more deeply into the soil matrix, becomes less available for volatilization, and becomes subject to biological transformation processes.

The model developed here uses illustrative numerical values of quantities applied and characteristics of the environment to which it is applied. To simulate a desired application, these parameters can be varied to explore the effects of rates and conditions of application on volatilization. Results of pesticide dissipation studies that immediately followed application have been complied and reviewed by several authors (Majewski 1999; van Jaarsveld and van Pul 1999). Results of two experimental field studies are particularly applicable to this LRT study. In the first study, two techniques for direct flux measurement were applied to CPY and CPYO following application of 0.98 kg CPY(a.i.) ha^{-1} to recently cut alfalfa in the Central Valley of California (Rotondaro and Havens 2012). The Aerodynamic method gave a maximum flux of 0.657 μg m^{-2} s^{-1} (2,365 μg CPY m^{-2} h^{-1}) which decreased to 0.002 μg CPY m^{-2} s^{-1} (7.2 μg CPY m^{-2} h^{-1}) by 24 h. The Integrated Horizontal Flux method gave a maximum flux of 0.221 μg CPY m^{-2} s^{-1} (797 μg CPY m^{-2} h^{-1}), which

decreased to 0.002 μg CPY m^{-2} s^{-1} (7.2 μg CPY m^{-2} h^{-1}) by 24 h following application. Total loss of CPY mass in the 12–24 h after application ranged from 15.8 to 16.5%, but diurnal variability is expected. CPYO was also observed to evaporate but at a lesser rate of 0.0164 μg m^{-2} s^{-1} for the 3–8 h period after application, which corresponds to 0.85% of the CPY applied. These results confirm that some of the CPY was transformed to CPYO on the surface and/or in the atmosphere immediately above the surface and subsequently entered the atmosphere. The average initial flux was approximately 1,500 μg CPY m^{-2} h^{-1} and decreased by a factor of approximately 200–7.2 μg CPY m^{-2} h^{-1}. In an earlier study, the eddy correlation micro-meteorological technique was used to estimate evaporation fluxes for several pesticides including CPY in the days following application in California (Woodrow and Seiber 1997). For CPY, a flux of 92.3 μg m^{-2} h^{-1} was calculated following application of 1.5 kg CPY ha^{-1}, which is equivalent to 0.15 g CPY m^{-2}. Fluxes of other pesticides were directly correlated with vapor pressure (P, Pa) and inversely proportional to K_{OC} (L kg^{-1}) as well as solubility in water (S, mg L^{-1}). The parameter described by $\dfrac{P}{\left(K_{OC}S\right)}$ is essentially an air/soil partition coefficient analogous to an air/water partition coefficient, thus this correlation has a sound theoretical basis. This flux of 92.3 μg CPY m^{-2} h^{-1} from a site containing 0.15 gm^{-2} corresponds to a loss of a fraction of $92.3 \times 10^{-6}/0.15$ or 615×10^{-6} per hour, which is equivalent to 0.0615% per hour or 1.4% per day. The total flux from an area of 1 ha or 10^{4} m^{2} is thus predicted to be approximately 0.92 g CPY h^{-1}, with a possible error judged to be a factor of 3.

In summary, it is suggested that, in the 12 h following application of the liquid formulation to the surface, approximately 10–20% of the applied material volatilizes, but variability is expected diurnally, with temperature, rainfall and soil moisture content. Sorption then "immobilizes" the CPY and subsequent volatilization is slower, with a rate of approximately 1% per day that decreases steadily to perhaps 0.1% per day in the subsequent weeks. During these periods on the surface and in the atmosphere, there is direct photolysis of CPY to CPYO. A detailed characterization of the initial 12 h period is given by Rotondaro and Havens (2012), while studies by Woodrow et al. (Woodrow and Seiber 1997; Woodrow et al. 2001) characterized average volatilization during the day or 2 following application. In the context of modeling volatilization losses, the simplest approach is to determine the total applied quantity and area treated, assume an immediate volatilization loss of 10–20% followed by a period of slower volatilization at an approximate initial rate of 1% per day decreasing with a half-life of approximately 3 d to 0.1% after 10 d. Rain and temperature will affect these rates. For illustrative modeling purposes, it was assumed that a typical rate of application is 1.5 kg CPY ha^{-1}, which corresponds to 0.15 g CPY m^{-2} (Woodrow and Seiber 1997) to an illustrative area of 1.0 ha (10^{4} m^{2}).

Concentrations in air. Of primary interest here are concentrations of CPY in the atmosphere following application. A maximum concentration is dictated by the saturation vapor pressure of solid CPY of 0.0023 Pa, which corresponds to

approximately 0.00033 g m^{-3} or 330,000 ng m^{-3} in an enclosed ecosystem. It is inconceivable that this concentration could be achieved in the field because of dilution in formulations and mass transfer limitations during evaporation. Concentrations of CPY in air above a potato field in the Netherlands at noon in midsummer ranged from 14,550 to 7,930 ng m^{-3} at 1 and 1.9 m above the crop 2 h after application (Leistra et al. 2005). These declined to a range of 2,950 to 1.84 ng m^{-3} after 8 h and to 26 to 15 ng m^{-3} in the 6 d following application. The initial flux was large (5–9 mg m^{-2} h^{-1}), possibly because of the large surface area of the leaves of this crop. As CPY is not registered for use on potatoes in the U.S., these data were not used in this assessment. Similarly high concentrations of CPY in air following an application of 4.5 kg ha^{-1} to turf were in the range of 1,000–20,000 ng m^{-3} (Vaccaro 1993). This might be a "worst case" in terms of concentrations and represents ~10% of the saturation concentration in air, i.e., the vapor pressure/RT, where RT is the gas constant-absolute temperature group. Immediately after application, concentrations of CPY of approximately 10,000 ng CPY m^{-3} (~3% of saturation) were measured at a height of 1.5 m above an alfalfa crop (Rotondaro and Havens 2012). Concentrations then decreased to approximately 100 ng m^{-3} after the initial more rapid evaporation. The USEPA conducted a modeling study to assess potential exposures of bystanders close to the site of application (USEPA 2013), but these values are not directly relevant to larger distances, in which concentrations would be much smaller because of dilution.

Concentrations of pesticides in air downwind of the site of application can, in principle, be calculated from an estimated flux by assuming a wind-speed, a mixing height, an atmospheric stability class and dimensions of the site. This is most rigorously done by using air dispersion models, such as SCREEN3 (Turner 1994; USEPA 1995). Detailed estimation of near-source concentrations in the atmosphere are beyond the scope of the simulation utilized here, which was focused on transport over distances up to 100s of km. Such estimates are nonetheless useful to estimate the order of magnitude of these "source" concentrations when monitoring data have been obtained in the vicinity of sources. The SCREEN3 model has been used to estimate concentrations in air at ground-level (1.5 m) immediately downwind, such as 10–30 m, from treated crops (Woodrow and Seiber 1997). Measured concentrations of five pesticides were of similar magnitude to predicted concentrations (μg m^{-3}) and similar in magnitude to estimated fluxes (μg m^{-2} s^{-1}), a result that is consistent with the ratio of these two parameters being approximately 1 m s^{-1}. This ratio of flux to concentration can be regarded as an effective wind-speed or mass transfer coefficient into which the evaporated chemical is diluted and is similar to the actual wind-speed of a few meter per second. Measured and simulated concentrations of pesticides in air were in good agreement. Accordingly, using this simple estimation method, ground-level concentrations in air at the site studied by Woodrow et al. are expected to be approximately 92 μg m^{-2} h^{-1} divided by a typical wind-speed of 3,600 m h^{-1}, giving 0.025 μg m^{-3}, which is 25 ng m^{-3}. This result is consistent with the above estimate. Volatilization rates of approximately 1,500 μg CPY m^{-2} h^{-1} (Rotondaro and Havens 2012) yielded a concentration of approximately 500 ng CPY m^{-3}. Concentrations would be expected to be less downwind because

of dissipation by vertical and lateral atmospheric dispersion. Concentrations in the range of 100 ng CPY m^{-3} ± a factor of 10 are regarded as typical of areas immediately downwind (~1 km) of application sites, but large variability is expected from differences in rates of application, nature of the crops treated, site area and meteorological conditions, especially temperature and wind-speed.

In support of these concentration ranges, Raina et al. (2010) have reported CPY concentrations at the Canadian agricultural field site at Bratt's Lake SK in 2003 and 2005. Over a 4-d sampling period, concentrations were 1–100 ng CPY m^{-3} with some values as high as 250 ng CPY m^{-3}. These are similar to measured concentrations in the range 4–180 ng CPY m^{-3} adjacent to a citrus orchard at the Lindcove Field Station in California (Aston and Seiber 1997). Concentrations of a variety of pesticides, including CPY, have been measured at locations across Canada (Yao et al. 2008). In the intensive fruit and vegetable growing area of Vineland, Ontario, the greatest concentrations of CPY were 21.9 ng CPY m^{-3} in 2004 and 20.6 ng CPY m^{-3} in 2005. These concentrations suggest that sampling was at a site within a few km of treated areas and possibly during or shortly after application. It has been confirmed that the samples were taken immediately adjacent to the application and were timed to coincide with the application (Personal communication, Dr. T. Harner).

Volatilization from water. It is possible that some CPY enters nearby ponds or streams as a result of spray drift and run-off and subsequently evaporates from these water bodies or flows downstream. To assess the significance of this process a simple kinetic analysis was conducted using the two-resistance or two-film model. If typical water and air mass transfer coefficients (MTCs) for water to air exchange are assumed of 0.05 and 5 m h^{-1} and K_{AW} is 4.5×10^{-4}, respectively, then the water and air phase resistances are $\dfrac{1}{0.05}$ and $\dfrac{1}{5 \times 4.5 \times 10^{-4}}$ h m^{-1}, respectively, i.e., 20 and 444 h m^{-1} and the overall water phase MTC would be 0.0021 m h^{-1} as follows (1):

$$\frac{1}{(20 + 444)} = 0.0021 \, \text{m h}^{-1} \tag{1}$$

The primary resistance to transport thus lies in the air phase. For a water depth of 1 m, the rate constant for evaporation would be 0.0021 h^{-1} and the half-life would be 322 h, which is 13 d. This is similar to the half-lives estimated for transformation of CPY in water, which suggests that both volatilization and transformation are significant pathways of dissipation of CPY in such bodies of water. Partitioning to suspended solids and deposition to bottom sediments are also likely to remove some CPY from solution (Gebremariam et al. 2012) and reduce the volatilization rate. CPY reaching water bodies will thus be subject to other loss processes and relatively slow and delayed evaporation over a period of weeks. It is concluded that secondary volatilization from water bodies is unlikely to be significant compared with the primary volatilization immediately following application.

2.2   Model of Long Range Transport and Characteristic Travel Distance

Estimation of mass loss by transformation and deposition. As a parcel of air containing 100 ng CPY m^{-3} is conveyed downwind, the total mass and concentrations of CPY decrease. The mass decreases as a result of transformation processes, primarily reaction with •OH radicals and net deposition. Oxidation primarily results in the formation of CPYO. The rate of the overall process can be represented (2) as follows:

$$V \times C \times k_R \text{ or } 0.693 \times V \times C/t \tag{2}$$

Where: V is volume, C is concentration and k_R and t are the first-order rate constant (0.23 h^{-1}) and half-life (3 h), respectively. There is also loss of mass of CPY by transport from air to the ground, specifically due to deposition in rain or snow, sorption to aerosol particles that subsequently are deposited by wet and dry deposition, and direct sorption to terrestrial and aquatic surfaces as shown by Aston and Seiber (1997), LeNoir et al. (1999) and Bradford et al. (2013). Estimates of these process rates can be made and the overall results can be compared to measured concentrations of CPY. Rates of these processes can be combined into a chemical-specific net mass transfer coefficient or velocity k_M m h^{-1}. The rate of deposition is described in (3):

$$C \times k_M \text{ g m}^{-2}\text{h}^{-1} \tag{3}$$

and the loss of mass is described by (4):

$$A \times C \times k_M \text{ g h}^{-1} \tag{4}$$

Where: A is the area and is equivalent to the volume (V) divided by the parcel height (H, expressed in m). Thus, the rate of loss of mass of CPY is described (5) as:

$$\frac{V \times C \times k_M}{H} \text{ g h}^{-1} \tag{5}$$

The parameter $\dfrac{k_M}{H}$ can be regarded as a rate constant. The TAPL3 model, which is discussed later, suggests that this rate constant is approximately 0.0016 h^{-1} for an atmospheric height H of 1,000 m, which is a factor of 144 slower than transformation. For deposition from a lesser atmospheric height such as 100 m, the rate constant is correspondingly greater by a factor of 10, thus there will be greater deposition from a near-ground level plume of higher concentration. The total rate of loss of mass by reaction and deposition is then described (6) as:

$$V \times C \times k_R + \frac{V \times C \times k_M}{H} \text{ g h}^{-1} \tag{6}$$

The rate of change of mass M in the parcel is given by the following relationships (7):

$$\frac{dV \times C}{dt} = -\left(V \times C \times k_R + \frac{V \times C \times k_M}{H} \right) = \frac{dM}{dt} \tag{7}$$

Integration from an initial mass M_0 gives the relationship (8):

$$M = M_0^{-\left(\left(k_R + \frac{k_M}{H} \right) \times t \right)} \tag{8}$$

If a constant wind velocity U m h^{-1} is assumed, t can be replaced by $\frac{L}{U}$, where L is distance in m. The CTD (m) is defined as L when the group in the exponent is -1.0, i.e., CTD is:

$$\frac{U}{\left(k_R + \frac{k_M}{H} \right)} \tag{9}$$

The corresponding characteristic travel time (CTT, expressed in h) is:

$$\frac{1}{\left(k_R + \frac{k_M}{H} \right)} \tag{10}$$

This time has the advantage that it applies regardless of the assumed wind velocity. When L equals CTD or CTT equals:

$$\frac{1}{\left(k_R + \frac{k_M}{H} \right)}, \text{ and } \frac{C}{C_0} \text{ is } e^{-1} \tag{11}$$

or 0.368 and 63.2% of the mass is lost by transformation and net deposition. A complication arises when describing the behavior of CPY in that some of the deposited CPY re-evaporates. The actual CTD is thus somewhat longer than that calculated, but, for CPY, this is a relatively small quantity. In practice, this complication is readily addressed by calculating the CTD by an alternative, but equivalent method, which has become standard in LRT calculations. This is done by use of a multimedia, mass balance model to calculate the steady-state mass of chemical in the atmosphere of an evaluative environment which contains water and soil compartments. The only emission is to air and no advective losses from air are included; thus, the only losses from air are degrading reactions and net deposition processes, i.e., deposition and absorption less volatilization. Since the rate of input to air is
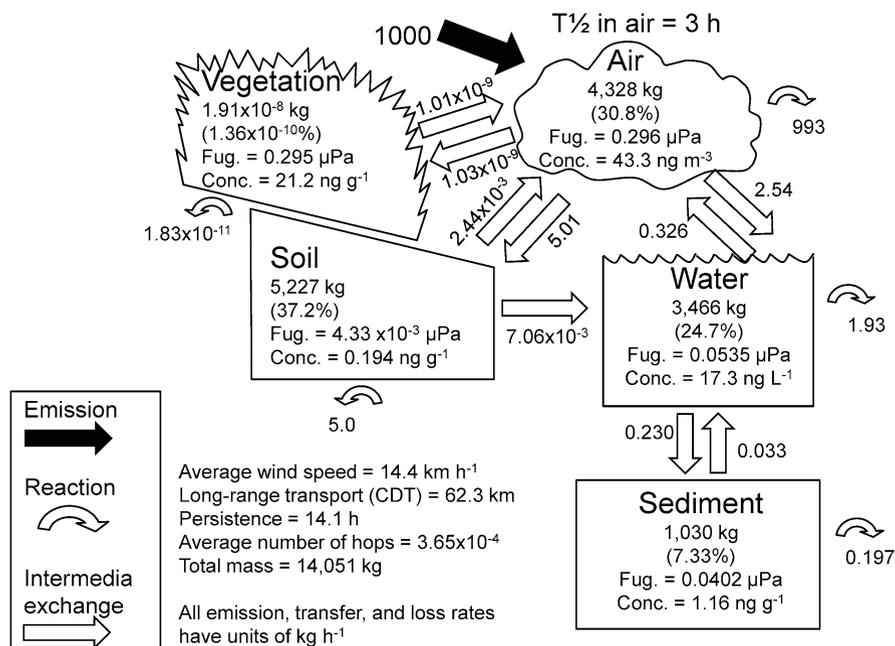
Fig. 2 Mass balance output from the TAPL3 LRT model. A 3 h half life is assumed for atmospheric degradation. The CTD is 62 km. Other parameters are as specified in Tables 5 and 6 and include the upper range (conservative) of half lives in water, soil and sediment in Table 6. The model can be downloaded from www.trentu.ca/cemc

known, that rate must equal the net rate of loss from air. Dividing the calculated mass in air by this rate gives the characteristic time defined above and this can be converted to a distance by multiplying by the wind velocity U, which is conventionally assumed to be 14.4 km h^{-1} or 4 m s^{-1}. Alternatively, the residence time or characteristic travel time (CTT) in air can be calculated as the mass in air divided by the rate of emission. This approach is used in the TAPL3 model (Beyer et al. 2000) and in the similar OECD Tool described by Wegmann et al. (2009)

The output of the TAPL3 simulation model is given diagrammatically for the selected half-life in air of 3.0 h (Fig. 2) and includes the conservative (long) half lives in other media (Table 7). The mass in air is 4,328 kg and the emission rate to air is 1,000 kg/h, thus, the residence time in air and the CTT is 4.3 h and the corresponding rate constant for total loss is 0.231 h^{-1}. The CTD is approximately 62 km, which is the product of 4.3 h and the wind velocity of 14.4 km h^{-1}. The rate of transformation is 993 kg h^{-1} and the net losses by deposition to water, vegetation, and soil total about 7 kg CPY h^{-1}, which corresponds to a rate constant of 0.0016 h^{-1}, and is less than 1% of the rate of degradation. The critical determinant of potential for LRT is the rate of transformation from reactions with •OH radicals
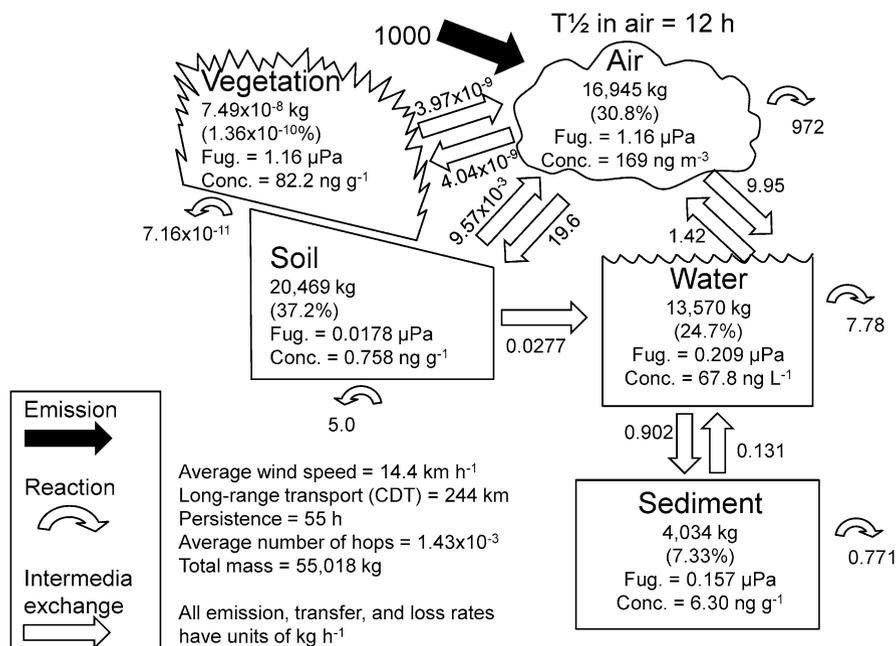
Fig. 3 Mass balance output from the TAPL3 LRT model. A 12 h (conservative) half life is assumed for atmospheric degradation. The CTD is 244 km. Other parameters are as specified in Tables 5 and 6 and include the upper range (conservative) of half lives in water, soil and sediment in Table 6. The model can be downloaded from www.trentu.ca/cemc

in air. If the half-life is increased by an arbitrary factor of 4–12 h as in Fig. 3, the CTD increases to 244 km.

In a similar study, Muir et al. (2004) estimated the CTD of CPY by using two models (TAPL3 and ELPOS) and obtained values of 290 and 283 km for conditions in which the concentration of •OH radicals was smaller, thus yielding a half-life of 14 h. Introducing intermittent rather than continuous precipitation had a negligible effect on predicted concentrations. Their longer CTDs are entirely attributable to their assumed longer half-life, which is a factor of 4.7 greater and is regarded as very conservative, but might be more appropriate for conditions at higher latitudes and during winter. Since the CTD is the distance over which the mass of chemical decreases by a factor of e (2.718), at a distance of two CTDs, the mass would be reduced by a factor of 7.4 and at three CTDs this factor is 20. Under the conditions simulated for CPY, 5% of the initial mass would remain in air at a distance of approximately 180 km if the half-life is assumed to be 3 h. If the half-life is increased to 12 h, the fraction remaining at that distance increases to 47%.

Decreases in concentration caused by dispersion/dilution. In addition to the decrease in concentration corresponding to loss of mass, there is a decrease in concentration attributable to expansion of the volume of the parcel of air in horizontal

and vertical dimensions. This is difficult to quantify because it depends on terrain and local and recent meteorology. It is especially difficult if part of the parcel of air is subject to fast upward convective transport (thermals) or during a storm. This mass of air could be conveyed to higher altitudes and into a region of lesser concentrations of •OH, faster transport, and lower temperatures, which could enable the associated CPY to travel thousands of km. It is thus not surprising that small but detectable concentrations can be found in remote locations such as Svalbard (Hermanson et al. 2005; Muir et al. 2004). The largest concentration of 16 ng CPY L^{-1} was found in ice from Svalbard in the 1980s, but concentrations measured more recently are generally <1 ng CPY L^{-1}. Although CPY is unlikely to be used for agricultural purposes in such near-polar locations, there is a possibility that it was used locally for other purposes, such as for control of biting insects.

A simple but approximate approach to estimate concentrations of CPY at distances from sources is to use a dispersion model to estimate concentrations at ground level from a ground level source using standard air dispersion parameters (Turner 1994). To estimate concentrations at ground level downwind of applications, a simplified and approximate version of the Gaussian air dispersion model for a ground level source can be used, which can be described mathematically (12) as:

$$C = \frac{Q}{\left(\pi \times U \times \rho_y \times \rho_z \right)} \tag{12}$$

In (12), C is concentration (g m^{-3}), Q is emission rate (g h^{-1}), π is the mathematical constant that is the ratio of the circumference of a circle to its diameter, U is wind velocity (m h^{-1}) and ρ_y and ρ_z are respectively the horizontal (crosswind) and vertical Pasquill-Gifford dispersion parameters (m) that depend on downwind distance (km) and atmospheric stability class. This equation must be applied with caution because of variation of U as a function of height and topography, but it is used here to suggest the form of an appropriate correlation. Q can be estimated from the total quantity applied and an assumed fraction volatilized during a specified time period. Plots of ρ_y and ρ_z(m) versus downwind distance x (km) have been given (Turner 1994), and can be expressed as correlations for stability class C (13):

$$\rho_y = 100 \times x^{0.91} \text{ and } \rho_z = 61 \times x^{0.91} \tag{13}$$

For example, at 1.0, 10 and 100 km (the maximum distance) ρ_y is 100, 776 and 6,026 m, respectively and corresponding values of ρ_z are 61, 496 and 4,030 m. For an evaporation rate of 1.0 g h^{-1} into a wind of 1 m s^{-1}, the concentrations are 14 ng CPY m^{-3} at 1 km, 0.23 ng CPY m^{-3} at 10 km and 0.0037 ng CPY m^{-3} at 100 km. There is approximately an 8-fold increase in plume width and height from 1 to 10 km, and thus, there is about a 64-fold decrease in concentration. At 100 km, there is a further 61-fold decrease in concentration. For larger areas of application, concentrations of CPY would be correspondingly greater. Under other conditions of moderate atmospheric stability, e.g., categories D or B, the dispersion parameters

are smaller or larger respectively by factors such as 1.5–2.0 that can be estimated from the dispersion parameter plots. If the area of application is larger by a factor such as 100, i.e., 1 km², then local concentrations downwind of sources would probably be greater. Horizontal dispersion then merely mixes this air and most dilution is by vertical dispersion and the dilution factor discussed above would be of the order of 10 rather than 60. There will also be contributions from evaporation from other soils in the locality that have been subject to prior applications.

Due to uncertainty in calculating concentrations from the volatilization rate Q, it is more convenient and probably more accurate to calculate downwind concentrations from an assumed concentration at, for instance, 1 km from the source i.e., $C_{1\,km}$. By applying the equation for C at 1 km and at x km and taking the ratio, the concentration at a distance x km can be shown to be $\dfrac{C_{1km}}{x^{1.82}}$. The quantity $x^{1.82}$ can be regarded as a dilution factor. The wind speed cancels when the ratio of concentrations is deduced. In practice, the exponent of x can be lesser, but this gives a reasonable form of the dilution equation. When applied to monitoring data it was determined that an exponent of 1.5 is more appropriate.

Combining the mass loss and the volume expansion gives the concentration downwind as a function of $U, L,$ and the CTT, which is represented by (14):

$$C = \frac{Q}{\left(\pi \times U \times \rho_y \times \rho_z\right)} \times e^{-\left(k_R + \frac{k_M}{H}\right) \times \frac{L}{U}} \text{ or } C = \frac{Q}{\left(\pi \times U \times \rho_y \times \rho_z\right)} \times e^{-\left(k_R + \frac{k_M}{H}\right) \times CTT} \qquad (14)$$

Or, more conveniently, by (15):

$$\frac{C_{1km}}{x^{1.82}} \times e^{-\left(k_R + \frac{k_M}{H}\right) \times \frac{L}{U}} \text{ or } \frac{C_{1km}}{x^{1.82}} \times e^{-\left(k_R + \frac{k_M}{H}\right) \times CTT} \qquad (15)$$

It is these calculated concentrations (that do not include deposition) that can be compared with monitoring results.

Limitations in predicting concentrations downwind of a source are caused by the uncertainties inherent in the dispersion parameters, $Q, U,$ and $L,$ as well as the possibility that a remote region has experienced CPY transport from multiple sources. Equation (15) does, however, provide a basis for estimating concentrations of CPY in air at more remote locations as far as 100 km from the source. If desired, conservative assumptions can be applied. The effect of wind velocity can also be evaluated. Lesser wind speeds cause an increase in the initial concentration, because as the quotient $\dfrac{Q}{U}$ increases and transit times $\dfrac{L}{U}$ increase, the volatilized pesticide is more concentrated in the region of application, there is more transformation locally, and the impact of LRT would be reduced. The equation also enables the relative roles of transformation and dilution by dispersion to be assessed. For example, at relatively short distances downwind, dispersion dominates because the transit time is short relative to the half-life for transformation. At greater distances and

longer transit times, transformation is more influential. The equation can also be used to estimate the fraction of the volatilized mass of CPY that will travel a given distance, or be deposited, or the fraction of the applied mass that can reach a specified distance. The quantity of transformation products can also be estimated. Results of the model can also be used to design more targeted monitoring. The model equation for C as a function of $C_{1\,km}$, distance and time is applied later to test agreement with monitoring data.

2.3   Formation and Fate of Chlorpyrifos-Oxon

Despite uncertainties in partitioning and reactivity of CPYO, it is possible to estimate CPYO's rate of formation and concentrations in distant atmospheres relative to CPY. These estimates can also be compared with monitoring data. It is assumed for illustrative purposes here, that CPY reacts with •OH to form CPYO in air or on surfaces with a molar yield of 30%; CPYO also reacts by the same mechanism. Half-lives are assumed to be 3 and 12 h for the reactions of CPY and CPYO, respectively. In the later evaluation, we assume a more conservative yield of 70%.

A parcel of air containing M_0 mol of CPY will change in composition with time and distance, forming CPYO, which in turn is degraded. This decay series is analogous to a radioactive decay series. The quantity of CPY (M_1) will follow first order kinetics, which can be described as (16):

$$\frac{dM_1}{dt} = -M_1 \times k_1 \tag{16}$$

This can be integrated to give (17):

$$M_1 = M_0^{(-k_1 \times t)} \tag{17}$$

Where: k_1 is the first order rate constant. The corresponding differential equation for CPYO (M_2) is given by (18):

$$\frac{dM_2}{dt} = Y \times k_1 \times M_1 - k_2 \times M_2 \tag{18}$$

Where: Y is the upper reported molar yield of 0.3, i.e., 30% and k_2 is the transformation rate constant of CPYO. It is likely that Y is larger than is stated above because other transformation products are at lesser yields. Integration of this function gives (19):

$$M_2 = \frac{Y \times k_1}{k_2 - k_1} \times M_0 \times \left(e^{-k_1 \times t} - e^{-k_2 \times t} \right) \tag{19}$$

When $k_1 < k_2$, a "secular" or "transient" equilibrium is established with an approximately constant ratio of the two species. In this case, $k_1 > k_2$ and a "no

equilibrium" condition prevails in which the ratio M_2/M_1 increases monotonically with time.

Using the above relationships, half-lives, and yields, the following are the approximate quantities for an initial value of M_0 of 100 mol. After 0.46 h, when 10% of the initial CPY has degraded, 3 mol of CPYO are formed and the ratio CPYO/CPY is 0.033 (3/90). After 3 h, 50% of the initial CPY would have degraded, 14 mol of CPYO would be formed and the ratio CPYO/CPY would increase to 0.28. After 7 h, 80% of the CPY would have reacted and both M_2 and M_1 are 20 and their ratio would reach 1.0. After 10 h, M_1 is 10 and M_2 would reach its maximum value of 21, their ratio becoming 2.1. At longer times, the ratio would continue to increase, because, although M_1 and M_2 would both be decreasing, M_1 would be decreasing faster. For example, at 12 h, the ratio would be 3.2. This behavior results in the possibility that the CPYO/CPY ratio can provide insights into the approximate "age" of the air parcel, although this ratio may be influenced by conversion during sampling and prior to analysis. This ratio was observed to be approximately 1.0 in the summer of 1994 at Lindcove near Fresno CA, which suggests a transit time of ~5 h (Aston and Seiber 1997). A test using SF_6 as a tracer gave comparable transit times. At a more distant location, Ash Mountain in Sequoia National Park, the ratio increased to 7–30, corresponding to a longer transit time. At the even more distant location of Kaweah Canyon (elevation 1,920 m) the CPYO/CPY ratio was 2.7 in June to early July 1994 but later the CPY was less than the LOQ for much of the summer and only CPYO was measurable. Generally, similar results were obtained by LeNoir et al. (1999). The similar concentrations of CPY and CPYO observed in air at Lindcove were also observed in pine needles from the same location. In surface waters in the same region, concentrations of CPY exceeded those of CPYO, possibly because of faster hydrolysis of CPYO or differences in deposition rates and hydrology (LeNoir et al. 1999).

From knowledge of the kinetics or transformation, local meteorology, transit times, and atmospheric deposition characteristics, these results indicate that it is feasible to predict formation and fate of CPYO, and thus, to estimate concentrations in air and other media at distant locations. An implication is that, whereas CPY is the substance of greatest exposure and concern in areas of application, its transformation product CPYO might be of most concern in more distant locations subject to LRT. The absolute quantities of CPY transported to and retained in terrestrial media are small and the concentrations and exposures to aquatic organisms are relatively small, and much smaller than concentrations sufficient to cause toxicity (Aston and Seiber 1997; LeNoir et al. 1999). However, to quantify the risk of impacts on distant terrestrial and aquatic ecosystems, improved information is needed on the properties of CPYO and the parameters required by the simulation models. Seasonally stratified monitoring is also desirable. Concentrations of pesticides in surface water at altitudes greater than 2,040 m in the Sierra Nevada were below detection limits. This result suggests that, because of meteorological constraints, there is less effective transport to higher elevations (LeNoir et al. 1999). Concentrations also become lower because of faster wind speeds at high altitudes. The postulated "cold-condensation" effect, in which low temperatures associated with high elevations cause high deposition rates

Table 8 Estimated Z values of CPY at 25 °C used in fugacity calculations

Environmental phase	Formula	Value (mol m^{-3} Pa)	Comment
Air	1/RT	$Z_A = 4.03 \times 10^{-4}$	R is 8.314
Water	1/H	$Z_W = 0.90$	H = 1.11
Octanol and lipids	$Z_O = K_{OW}/H$	$Z_O = 90,000$	$K_{OW} = 10^5$
Organic carbon	$Z_{OC} = K_{OC}Z_W\rho oc$	$Z_{OC} = 7,730$	$K_{OC} = 8,500 \; \rho_{OC} = 1.01$ (density kg L^{-1})
Soils solids of 2% OC	$Z_S = \rho s Z_{OC} f_{OC}$	$Z_S = 371$	ρs 2.4 kg L^{-1}, $f_{OC} = 0.02$
Sediment solids of 10% OC	$Z_S = \rho s Z_{OC} f_{OC}$	$Z_S = 1,855$	$\rho s = 2.4$ kg L^{-1}, $f_{OC} = 0.10$
Aerosol particles	$Z_P = 0.1 \; Z_O$	$Z_P = 9,000$	Assumes 10% octanol equivalent
Snow Z_N	$Z_N = 15 \; Z_W$	$Z_N = 13.5$	Assuming factor of 15 lesser Henry's Law constant at 0 °C
Biota of 100% lipid equivalent	$Z_B = Z_O$	$= 90,000$	i.e., 100% octanol
Biota of 10% lipid equivalent	$Z_B = 0.1 \; Z_O$	$= 9,010$	i.e., 10% octanol, 90% water

and greater concentrations in terrestrial and aquatic systems, does not apparently apply to transport of CPY into the Sierra Nevada mountains.

The relationship between CPY and CPYO and their transport in the atmosphere is summarized as follows: Shortly after application, a fraction of the applied CPY volatilizes to the atmosphere where it is dispersed by atmospheric turbulence to lower concentrations estimated to be of the order of 100 ng m^{-3} at a distance of 1 km. It is also subject to transformation to CPYO, which is also subject to dispersion and transport for moderate or long distances. Some CPY will be transported from the plume back to neighboring soils and vegetation by direct gas absorption; however, the resulting concentrations in soils and vegetation will be small and many orders of magnitude less than those in the application area. The vapor pressure and K_{OW} of CPYO are smaller than those of CPY and its solubility in water is greater, thus it has a smaller K_{AW}. As a result, it is subject to faster deposition and there will be enhanced partitioning into water droplets in the air. CPYO is also subject to some gaseous deposition but it is likely to be further degraded in other compartments such as water and moist solid surfaces. Once in water, hydrolysis is rapid (Table 7). This process also explains the very infrequent detection of CPYO in surface waters (Williams et al. 2014). During heavy rainfall immediately following application, local deposition will be maximized. The rates could be estimated but will be speculative and will be difficult to confirm because most locally deposited CPY will result from spray drift and it will be difficult to discriminate between gaseous deposition and spray drift.

Interpretation of measured concentrations of chlorpyrifos in media by use of fugacity. There is an incentive to exploit all the available measured concentrations of CPY for all sampled media, rather than just air. This is feasible by converting all concentrations of CPY to the "common currency" of fugacity as outlined in Tables 8 and 9 (Mackay 2001). Fugacity is the escaping tendency for chemicals to move

Table 9 Concentration-fugacity conversion factors for CPY

Environmental phase	Conversion
Air	$1 \text{ ng m}^{-3} = 1 \times 10^{-9}/(350 \times 4.03 \times 10^{-4}) = 7.1 \times 10^{-9} \text{ Pa} = 7.1 \text{ nPa}$
Water and rain	$1 \text{ ng L}^{-1} = 1 \times 10^{-9} \times 1{,}000/(350 \times 0.9) = 3.2 \times 10^{-9} \text{ Pa} = 3.2 \text{ nPa}$
Snow	$1 \text{ ng g}^{-1} = 1 \times 10^{-9} \times 1{,}000/(350 \times 0.9 \times 15) = 0.21 \times 10^{-9} \text{ Pa} = 0.21 \text{ nPa}$
Organic carbon	$1 \text{ ng/g} = 1.01 \times 10^{6}/(350 \times 7{,}727) = 0.37 \text{ nPa}$
Sediment and soil solids 2% OC	$1 \text{ ng g}^{-1} = 2.4 \times 10^{6}/(350 \times 371) = 18.4 \text{ nPa}$
Sediment and soil solids 10% OC	$1 \text{ ng g}^{-1} = 2.4 \times 10^{6}/(350 \times 1{,}854) = 3.7 \text{ nPa}$
Biota concentrations on a lipid weight basis	$1 \text{ ng g}^{-1} = 10^{6}/(350 \times 90{,}000) = 0.032 \text{ nPa}$
Biota of 10% lipid or octanol equivalent	$1 \text{ ng g}^{-1} = 10^{6}/(350 \times 9{,}010) = 0.32 \text{ nPa}$

from one environmental compartment to another and has the units of pressure. At equilibrium, fugacities of a chemical in all compartments are equal. The relative concentrations in compartments do not change and are defined by the equilibrium partition coefficients, even though individual molecules are still moving between compartments. This conversion requires first that all concentrations (C) be converted to units of mol m^{-3}, which requires that the molar mass and possibly the phase density are known. This concentration is then divided by the appropriate Z value for the medium in which CPY is partitioned. Values of Z, which have units of mol m^{-3} Pa^{-1}, are deduced from partition coefficients. This yields the fugacity, f, as C/Z, of CPY in that medium, thus enabling fugacities in a variety of phases to be compared directly. Essentially, this analysis leads to a characterization of the equilibrium status of CPY in the entire ecosystem.

In many cases, phase fugacities in multi-media environments are similar in magnitude, e.g., water, sediments and small fish might exist at comparable fugacities. An additional advantage of incorporating rain, snow, and terrestrial components in the model is that concentrations of CPY are generally greater in solid and liquid media and can be analyzed more accurately. Concentrations are generally more stable as a function of time. It is with this perspective that considerable effort has been devoted to measuring concentrations of CPY in rain, snow, terrestrial, and aquatic systems in regions of interest. Insights into likely differences in fugacity between air and other media can be obtained by examining ratios of fugacities as predicted by models such as TAPL3. For example, in Fig. 2, the fugacity of CPY in surface water is 12% of that in air, largely because the rate of transformation in water is fast relative to the rate of deposition from air. Z-values and conversion factors are given in Table 6.

Since effects of mixing, transport, and transformation generally cause a decrease in fugacity of CPY as it travels from source to destination, it is expected that measured concentrations and fugacities of CPY will display this trend. In this case, the most convenient units for fugacity are nano Pascals (nPa) i.e., 10^{-9} Pa. The fugacity of liquid CPY as applied is limited by the vapor pressure of 0.002 Pa, $(2 \times 10^{6} \text{ nPa})$,

but it is likely to be smaller because of dilution in carrier fluids or granules. Incorporation of 0.15 g m^{-2} into solid phases of soils to a depth 2.5 cm or 0.025 m gives a bulk soil concentration of 0.017 mol m^{-3} and the corresponding fugacity is 46,000 nPa, a factor of 43 less than that of the applied chemical and is attributable to sorption and dilution.

A concentration of 100 ng m^{-3} in air close to a site of release corresponds to 0.286×10^{-9} mol m^{-3} and the fugacity would be 710 nPa. This is a factor of 64 less than the fugacity of the chemical in soil and is from dilution that occurs during evaporation. The total decrease in fugacities of CPY from the point of application is, thus, approximately 64×43 or 2,750. Most measured concentrations of CPY were in the range 0.01–1.0 ng m^{-3}, which corresponds to a range of fugacities of 0.07–7 nPa, a factor of 100–10,000-foldless than that of the initial concentrations of 100 ng m^{-3}. Therefore, CPY undergoes high dilution in the hundreds of km downwind of the source.

The concentration of CPY in rain of approximately 0.4 ng CPY L^{-1} or 400 ng m^{-3} that was reported by Mast et al. (2012) corresponds to approximately 1.1×10^{-9} mol m^{-3} and a fugacity of 1.32 nPa. The corresponding equilibrium concentration in air is 0.18 ng m^{-3} which is typical of concentrations in air in the Sierra Nevada. Fugacities of CPY in air and rain thus appear to be of a similar order of magnitude, which lends support to the use of fugacity as a method of combining and comparing measured concentrations among media.

Conversion of concentrations of CPY in snow to fugacities is more problematic because the Z value for snow is uncertain. This is because the low temperatures and the variable sorption to ice surfaces as distinct from partitioning to liquid water. There might also be greater deposition of aerosols in snow at lower temperatures. Concentrations of CPY in snow were reported to be approximately tenfold greater in snow than in rain (Mast et al. 2012). This result is consistent with the greater Z value, which is due to the lesser Henry's Constant and vapor pressure of CPY. The enthalpy of vaporization, which has been reported to be 73 kJ mol^{-1} for CPY (Goel et al. 2007) corresponds to a 15-fold decrease in vapor pressure from 25 to 0 °C. The value of Z for snow appears to be a factor of 10–20-fold greater than that of water. For this reason, rates of deposition of CPY associated with snow are expected to be greater than those in rain from a similar atmospheric concentration. Snow concentrates and integrates CPY more than does rain and can be useful for monitoring the presence of CPY, but using this information quantitatively is problematic because of uncertainties in translating concentrations of CPY in air to those in snow, especially for more intense snow-fall events when extensive scavenging of chemicals from the atmosphere occurs.

Concentrations in biota such as zooplankton, tadpoles, lichen, and pine needles can also be converted to fugacities by assuming a content of lipid, or more correctly an equivalent content of octanol. If data are reported on a lipid weight basis, conversion to fugacity involves division by the Z value of lipid or octanol. The average CPY lipid-based concentration in tadpoles from the Sierra Nevada in 2008–2009 has been reported to be 22.2 ng CPY g^{-1} (Mast et al. 2012). The corresponding fugacity of CPY is 0.7 nPa, which is similar in magnitude to the fugacities of air and rain.

Concentrations of pesticides were measured in frogs at 7 high elevation sites in the Sierra Nevada in 2009 and 2010 (Smalling et al. 2013). Although CPY was one of the most heavily used pesticides in the area, it was not detected in frog tissues above the LOD of 0.5 ng g^{-1}. In comparison, p,p'-DDE was widely detected with a 75th centile of 40 ng g^{-1} and the fungicide, tebuconazole was detected with a 75th centile of 120 ng g^{-1}. Concentrations of CPY in zooplankton in lakes in Ontario, expressed on a wet weight basis, have been reported to be 0.004 ng CPY g^{-1}wwt, but concentrations as great as 0.08 ng CPY g^{-1} can occur (Kurt-Karakus et al. 2011). Corresponding concentrations, normalized to the fraction of lipid (2%) in zooplankton results in a range of concentrations of 0.2 and to 4 ng CPY g^{-1} lipid in lakes distant from points of application of CPY. Corresponding fugacities for this range of concentrations are 0.0064 and 0.13 nPa. Bioconcentration factors (BCF) are considerably smaller than would be predicted from the octanol-water partition coefficient (K_{OW}) or from estimations based on simulation models such as BCFWIN. These lesser values for site-specific BCF calculated from measured concentrations are likely attributable to biotransformation. Aston and Seiber (1997) obtained pine needle/air bioconcentration factors of 9,800 of CPY that might be a function of the octanol/air partition coefficient and the quantity of lipid-like material in the cuticle. In summary, fugacity can act as a bridge between monitored concentrations in biota, air, and precipitation in regions subject to LRT in the atmosphere. The corollary is that estimated concentrations in air can be used to estimate concentrations in biota and possibly contribute to assessments of risk of adverse effects.

2.4   Long-Range Atmospheric Transport of Chlorpyrifos and Its Oxon

It is useful to present a perspective on the relevant distances in regions of the U.S. that have been monitored for CPY and CPYO. Much of the available data have been collected from the Central Valley of CA and adjacent National Parks in the Sierra Nevada. The Parks are 50–100 km from the areas of application in the Central Valley and have altitudes from 600 to 4,000 m. The region is approximately 50 km west of the border between California and Nevada, but the meteorology at higher elevations is complex and simple estimates of concentration versus distance are impossible. In Eastern and Midwest regions of the U.S., distances relative to application areas are less defined and are probably several hundreds of km. For example, the distance from central Iowa to the U.S. East Coast is approximately 1,000 km.

An example of monitored concentrations along a transect from source to destination is the work of Aston and Seiber (1997), who measured concentrations of CPY in June 1994 over a transect from Lindcove, CA (elevation 114 m) to Ash Mountain 22 km distant (elevation 533 m) and to Kaweah a further 10 km distant (elevation 1,920 m). Concentrations decreased from approximately 100 ng CPY m^{-3} at Lindcove to 0.1–0.5 ng CPY m^{-3} at Ash Mountain and to 0.1–0.3 ng CPY m^{-3} at Kaweah.

Those authors also present tracer data for SF_6 that suggest a dilution factor of 100 from a source 9 km SW of Lindcove to Ash Mountain, i.e., a distance of approximately 31 km. It is monitoring data of this type that can provide quantitative information on LRT and assist in calibrating models.

A semi-quantitative interpretation of measured concentrations of CPY and CPYO, assisted by use of the fate and transport model developed in this study is provided here including the effects of transformation, transport, and dispersion/dilution processes on downwind concentrations. A half-life of CPY of 3 h in air (Table 6) is assumed, but to test the sensitivity of the results to this half-life, the effect of a value of 12 h is also used. A wind speed of 15 km h^{-1} (4.16 m s^{-1}) is assumed for estimating the CTD. In the model, the concentration at a distance downwind C_L and distance x km can be estimated from the concentration $C_{1 km}$ at 1 km by (20) to give C_L as:

$$\frac{C_{1km}}{x^N} \times e^{-\left(k_R + \frac{k_M}{H}\right) \times \frac{L}{U}} \text{ or } \frac{C_{1km}}{x^N} \times e^{-\left(k_R + \frac{k_M}{H}\right) \times CTT} \tag{20}$$

The exponent N is assigned an illustrative value of 1.5, $\frac{k_M}{H}$ is assigned a value of 0.002 h^{-1}, which is small in comparison to the reaction rate constant of 0.231 h^{-1}. $\frac{L}{U}$ is the transit time in h. The rate constant for CPYO reaction was increased to 0.139 h^{-1}, i.e., a half-life of 5 h and the yield of CPYO from CPY was increased to 70%. The CTD of CPY occurs when $\left(-\left(k_R + \frac{k_M}{H}\right) \times \frac{L}{U}\right)$ is 1.0, or equivalently when L is $\dfrac{U}{\left(k_R + \dfrac{k_M}{H}\right)}$.

These parameter assignments were selected by comparing available monitoring data to predicted values from the simulation model and adjusting parameters by hand until the selected input parameters resulted in simulated results that were comparable to measured concentrations. The objective was not to rigorously calibrate the model, but rather to test the feasibility of developing and applying the LRT model to estimate concentrations of CPY and CPYO at locations remote from site of application. The results of applying the model developed in this study are summarized for CPY (Table 10) and illustrated for CPY and CPYO (Fig. 4). Near the area of application, such as at a distance of 1 km and assuming a 0.1 h air transit time, air concentrations ($C_{1 km}$) were assigned a value of 100 ng CPY m^{-3} (~700 nPa). At these short transit times, relatively little of the CPY would have been transformed, although there might be transformation to CPYO on the surface and adjacent atmosphere if conditions are sunny and favor greater concentrations of •OH. Concentrations of CPY are primarily controlled by rates of evaporation and dispersion rather than reactions with •OH.

At a distance of 120 km and 8.4 h transit time, which is equivalent to two CTDs, 84% of the volatilized CPY would have been transformed and 16% would remain.

Table 10 Estimates of the transformation of CPY and concentrations in air at various distances downwind of an application

Distance km	Transit time h	F (reacted)	Conc. ng m^{-3}	Comment
1–3	0.1–0.2	<0.05	20–100	Application area
10	0.67	0.14	5	Local
30	2	0.38	0.7	Regional
60	4	0.62	0.15	One CTD
120	8	0.84	0.022	Two CTDs
180	12	0.94	0.005	Three CTDs
240	16	0.98	0.001	Four CTDs
300	20	0.99	0.0003	Five CTDs
1,000	67	>0.999	<0.0001	Fifteen CTDs

A wind speed of 14.4 km h^{-1} is assumed. The fraction reacted, F, is calculated assuming a half-life of 3 h as $e^{-0.231 \times t}$ where t is the transit time and the transformation rate constant is 0.231 h^{-1}
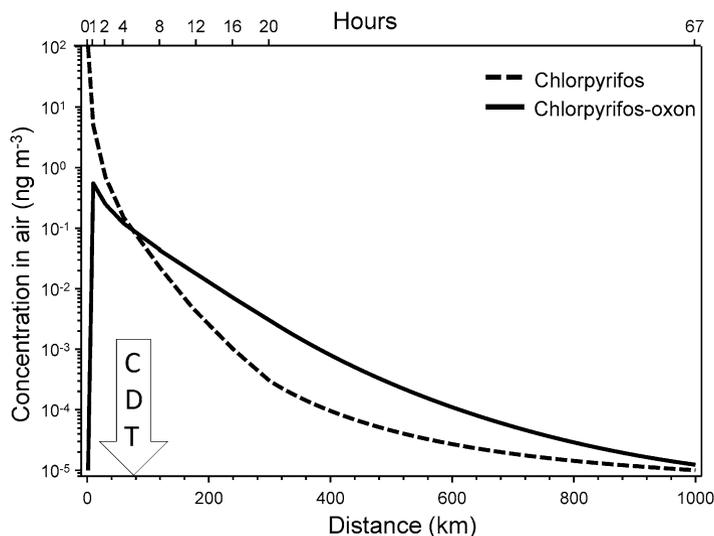
Fig. 4 Concentrations of CPY and CPYO modelled at various times and distances downwind from an application

Concentrations of CPY in air would have decreased to 0.022 ng CPY m^{-3} (0.16 nPa). At this distance, transformation would have become a greater proportion of the total dissipation, and concentrations of CPYO would be expected to exceed those of CPY by a factor of 2, but may be affected by differing deposition rates. At steady state, rain water would be predicted to have a concentration of 0.1 ng CPY L^{-1} and snow a concentration of 1.5 ng CPY L^{-1}. If a very conservative CPY half-life of 12 h were assumed, the fraction of CPY transformed would be only 38% and much greater concentrations are expected. At a distance of 180 km and 12 h transit time, that is equivalent to three CTDs, 94% of CPY would be predicted to have been

transformed with only 4% remaining. Concentrations of CPY would be approximately 0.005 ng m^{-3} (0.035 nPa). Approximately 70% of the concentrations measured in air are in the range of 0.01–1.0 ng CPY m^{-3} and probably correspond to distances from sources of 30–200 km. Predicted concentrations in rain at steady state would be 0.02–2.0 ng CPY L^{1} and those in snow would be 0.3–30 ng CPY L^{-1}, with some 39% of the reported concentrations in snow being in this range. Most of these data are restricted to one region, the Sierra Nevada Mountains in the U.S. Predicted fugacities and concentrations in snow are speculative since the air/snow partition coefficient is uncertain and concentrations are undoubtedly influenced by timing of the snowfall relative to applications. Heavier snowfall, such as occurs in the Sierra Nevada might result in dilution in the precipitation and near-total scavenging of CPY from the atmosphere.

At a distance of 300 km and about 20 h transit time, which is equivalent to approximately five CTDs, 1.0% of the initial mass of CPY would remain because the CPY would have been subjected to nearly 7 half-lives. Concentrations at this distance from the source would likely be 0.0003 ng CPY m^{-3} (0.002 nPa) or less. Concentrations of 0.003 ng CPYO m^{-3} would be expected. Thus, at this distance from the source, CPYO would be the primary product present, at a concentration which is near the typical limit of quantitation. Rain, if at equilibrium with air, would be expected to contain a concentration of 0.001 ng CPY L^{-1} and snow 0.02 ng CPY L^{-1}. Given an assumed half-life of 3 h and the time to be transported this distance, it is unlikely that, under normal conditions, significant quantities could travel more than 300 km. Observations of detectable amounts of CPY at greater distances, such as 1,000 km, suggest that, at least under certain conditions, the half-life is longer than was assumed in this analysis. For example, significant concentrations of CPY have been measured in the Svalbard ice-cap (Hermanson et al. 2005). It is likely that these residues originated from Russia and were transported at times of lesser temperatures, greater wind speeds, and limited photolysis, which results in a longer CTD of the order of 300–1,000 km. Concentrations of CPY measured by Muir et al. (2004) in arctic lakes might also reflect slow transformation in the presence of smaller concentrations of •OH at these higher latitudes.

Monitoring data and the tentative modeling described here indicate that CPY and CPYO are detectable in air at concentrations exceeding 0.1 ng m^{-3} at distances of up to 60 km from the source and at 0.01 ng m^{-3} at distances up to 200 km, except in the Sierra Nevada where there are meteorological constraints on flows of air masses. There will be corresponding concentrations in rain, snow, and in terrestrial media such as pine needles and biota. There is an incentive to monitor these media because of the greater concentrations and increased analytical reliability. The "zone of potential influence" of LRT in this case is one to two CTDs or up to 60–120 km from the point of application. Reactivities of CPY and CPYO are such that concerns about LRT are much more localized than for organochlorines, which are more persistent and thus might have CTDs of thousands of km. The results of the analysis presented here suggest that it is feasible to extend assessments of LRT beyond the mere estimation of CTD and CTT to address the magnitude of the concentrations and fugacities along a typical LRT transect and to estimate absolute multi-media

concentrations and deposition rates. There is also a need to focus more on the transformation products such as CPYO, but major uncertainties exist about the formation rates and properties of transformation products which preclude full interpretation of monitoring data and modeling. It is likely that any risks associated with LRT are attributable more to CPYO than to CPY; however, the concentrations predicted in air and water are much smaller than toxicity values for either of these compounds (Giddings et al. 2014) and risks are *de minimis*. The proposed model can also be applied to gain an understanding of the likely effects of the various parameters such as wind speed and temperature.

3 Fate in Water

The fate of CPY in water was extensively reviewed by Racke (1993), and data are provided in (Solomon et al. 2013a); key points are summarized here with a focus on information that has become available since 1993. As discussed above, there are significant differences between dissipation and degradation of CPY in water, but earlier studies did not always distinguish between dissipation and degradation. In the laboratory, and in the absence of modifiers such as methanol, reported half-lives (DT_{50deg}) for hydrolysis in distilled and natural waters ranged from 1.5 to 142 d (SI Table 1) at pH values between 5 and 9 (Racke 1993), which are considered to represent realistic field values. The mean half-life of these values was 46 d and the geometric mean was 29 d. At pH <5, reported half-lives were generally longer (16–210 d) and at pH >9, shorter (0.1–10 d). The presence of copper (Cu^{++}) resulted in shorter half-lives (<1 d), even at pH <5 (Racke 1993). In studies published since 2000, similar half-lives have been reported (SI Table 1). A DT_{50deg} of 40 d for CPY was reported in distilled water but DT_{50deg} (120 to 40 d) varied in sterile natural waters from rivers flowing into Chesapeake Bay. Concentration of Cu^{++} was a major driver of rate of hydrolysis, although other factors such as salinity were also identified (Liu et al. 2001). Concentrations of total suspended solids (TSS) greater than 10 mg L^{-1} resulted in lesser rates of hydrolysis of CPY, but dissolved organic carbon did not affect the rate. In water, CPY has been shown to bind strongly with variable strength and reversibility to Ca-saturated reference smectites but strongly and with poor reversibility to Ca-saturated humic acid (from Aldrich) (Wu and Laird 2004). The binding to suspended clays might explain the effect of TSS on hydrolysis rate observed by Liu et al. Half-lives from the newer laboratory-studies ranged from 1.3 to 126 d with a mean and geometric mean of 23 and 13 d, respectively (SI Table 1). The overall mean and geometric mean were 37 and 21 d, respectively (SI Table 1).

Under field conditions, it is difficult to separate degradation from dissipation and the half-lives measured are normally based on the latter (DT_{50dis}). A number of reports have noted relatively rapid dissipation of CPY in microcosms. DT_{50dis} of 9.6–6.1 d in microcosms treated with 0.005–5 μg L^{-1} were reported in small laboratory-based studies conducted in mesocosms in the Netherlands (Daam and Van den Brink 2007). However, smaller DT_{50dis} values (<4 d) were reported for

outdoor mesocosms treated with 1 μg L^{-1} in Thailand (Daam et al. 2008). Using small (70-L) open-air estuarine microcosms to investigate dissipation of ^{14}C CPY, a DT_{50dis} of ~5 d was reported under tropical conditions with loss to air a major driver of dissipation (Nhan et al. 2002). In studies conducted in flowing, outdoor meso-cosms, a DT_{50dis} was reported to be <1 d, probably as a result of hydraulic dilution. However, in still-water-only laboratory mesocosms, DT_{50dis} ranged from 10 to 18 d (Pablo et al. 2008). Dissipation in small (2.4-L) laboratory microcosms with water and gravel was biphasic with a phase-1 DT_{50dis} of 2.25–3 d and a phase-2 DT_{50dis} of 14–18 d (Pablo et al. 2008). DT_{50dis} of CPY in microcosms was reported to be ~5 d from water (Bromilow et al. 2006). Overall, dissipation of CPY in natural waters under field conditions was rapid with the range of DT_{50dis} s from 4 to 10 with a geo-metric mean of 5 d (SI Table 1).

4 Fate in Soils and Sediments

Studies on the fate of CPY in soils and sediments were summarized in the review by Racke (1993) and discussed in the context of adsorption and desorption in a detailed review in 2012 (Gebremariam et al. 2012). Most of the half-lives in soil (DT_{50dis} and DT_{50deg}) summarized from laboratory studies in Racke (1993) were in the range of 1.9–120 d for rates of application associated with agricultural uses, with most in the range of 7–30 d (Table 6). Longer half-lives (DT_{50deg}) were reported for rates of application for the now-cancelled use for control of termites in soil. Half-lives in soil were dependent on temperature (a doubling in rate of degradation for a 10 °C increase in temperature) and soil pH, with faster rates at greater pH (0.0025 d^{-1} at pH 3.8 to 0.045 d^{-1} at pH 8) (Racke 1993). Mean and geometric mean values for all data (SI Table 2) were 82 and 32 d, respectively.

Generally, dissipation (DT_{50dis}) of CPY in soils under field conditions was reported to be more rapid than in the laboratory. The DT_{50dis} was reported to range from <2 to 120, with mean and geometric means of 32 and 22 d, respectively (SI Table 3); most values were in the range of 7–30 d (Table 6). Comparison of rates of dissipation of CPY from soils from Brazil under laboratory conditions suggested a tenfold greater rate of dissipation in the field than in the laboratory (Laabs et al. 2002).

Half-lives (DT_{50deg}) in sediments were reported to range from 6 to 223 d (SI Table 4), with longer times likely reflecting more anaerobic conditions. Some more recent studies have reported dissipation of CPY from sediments in microcosms, a more realistic scenario. The DT_{50dis} values for CPY were reported to range from 68 to 144 d in wetland sediments under flooded conditions (Budd et al. 2011). Measurements of dissipation of CPY from sediments collected in San Diego and Bonita Creeks (Orange County, CA, USA) gave DT_{50dis} values of 20 and 24 d under aerobic and 223 and 58 d under anaerobic conditions, respectively (Bondarenko and Gan 2004). DT_{50dis} of CPY in microcosms was reported to be 15–20 d from sedi-ment (Bromilow et al. 2006). The DT_{50dis} value measured in sediment in a laboratory-based marine microcosm study was approximately 6 d under tropical conditions

(Lalah et al. 2003), but was likely overestimated because metabolites were not separated from the ^{14}C CPY. The DT_{50dis} values measured in pore-water ranged from 7 to 14 d in water-gravel laboratory-based microcosms that were treated with 0.2–20 μg CPY L^{-1} (Pablo et al. 2008). The mean and geometric mean DT_{50dis}s for CPY in laboratory and microcosm tests were 68 and 39 d, respectively (SI Table 4).

5   Fate in Organisms

The fate of CPY in organisms is a function of absorption, distribution, metabolism and excretion (ADME) and has been well studied in mammals (Testai et al. 2010). Observations have also been recorded for other animals such as fish (Racke 1993; Barron and Woodburn 1995), aquatic organisms (Giesy et al. 1999) and birds (Solomon et al. 2001). The focus in this paper is on newer studies, and only key information from older studies will be addressed. Integration of the processes of ADME in organisms at quasi-equilibrium is described by several factors, which are ratios between abiotic and biotic compartments. These include bioconcentration factors (BCF), bioaccumulation factors (BAFs), biota/sediment accumulation factors (BSAFs) and, in the case of movement in the food web, biomagnification (BMFs) or trophic magnification factors (TMFs) (Gobas et al. 2009).

Several studies have been conducted in aquatic organisms to measure concentrations of CPY in fish and other organisms during uptake, at equilibrium, and during dissipation. These have been used to calculate various magnification factors. Bioconcentration factors (BCFs) reported from laboratory studies reviewed by Racke (1993) and Barron and Woodburn (1995) in 17 species of freshwater (FW) and salt-water fish exposed to CPY at concentrations <10 μg/L for ≥26 d ranged from 396 to 5,100 with a mean of 1,129 and a geometric mean of 848 (SI Table 5). Similar values were observed in several studies conducted in microcosms or ponds under field conditions, which also have been reviewed in Racke (1993). Here the mean BCF was 1,734 and geometric mean 935 (SI Table 5). Assuming a K_{OW} of 100,000 and a lipid content of 5% suggests an equilibrium BCF of 5,000, but lower than equilibrium values can be expected as a result of metabolic conversion and slow uptake.

Several studies on uptake of CPY from water and sediments have been reported since 2000 (Table 11). Results of several other recently-published studies were not usable. Two studies of marine clams were conducted using ^{14}C-CPY but results were only reported as percentages (Kale et al. 2002; Nhan et al. 2002) and BCFs could not be calculated. Uptake of CPY from water by the fish, hybrid red tilapia, was measured by gas-chromatography (Thomas and Mansingh 2002) but a BCF could not be calculated. A study of uptake and depuration of ^{14}C-CPY reported BCFs for 15 species of FW aquatic invertebrates (Rubach et al. 2010). Unfortunately, the BCFs were based on total ^{14}C in the organisms and, because the ^{14}C-label was in the di-ethyl-phosphorothiol moiety of the CPY molecule, radioactivity measured in the organisms did not represent only CPY, but included other phosphorylated proteins such as AChE, BuChE, and paraoxonase. Therefore, as has been pointed

Table 11 Bioaccumulation factors for CPY in various biota from studies conducted after 2000

Species	Taxon	BCF/BAF/BSAF	Time of exposure (d)	Exposure-concentration	Reference	Comment
Crassostrea virginica	Mollusk	BCF±SD 565±172	28-exposure, 14-depuration	0.61 µg/L	Woodburn et al. (2003)	Determined using [2,6-pyridine ^{14}C]-CPY
Lumbriculus variagatus	Oligochaete	BAF 1.8 13.9 17.2 57.3 BSAF 67.1 99.2 34.9 6.2	12	385 54 25.4 29.9 µg/kg dwt in sediment	Jantunen et al. (2008)	Determined using ^{14}C-pyridine-labelled CPY. TOC in sediments=21.5, 3.5, 1.7, 0.13, resp. BSAF normalized for lipid and OC
Aphanius iberus	Fish	BCF 3.1	3	3.2 µg/L	Varo et al. (2000)	Approaching equilibrium at 72 h. Analysis by GLC
Danio rerio eleutheroembryos	Fish	BCF 3,548 6,918 Geometric mean=4,954	2-exposure 3-depuration	1 µg/L 10 µg/L	El-Amrani et al. (2012)	Determined using GLC analysis. Results might overestimate BCFs—metabolism not fully developed
Aphanius iberus	Fish	BMF±SD 0.30±0.2	32	94±41 ng/g lipid wt	Varo et al. (2002)	Lipid corrected based on conc. in food, analysis by GLC

out previously (Ashauer et al. 2012), these data were unusable. Uptake of CPY was rapid in *Gammarus pulex* (Ashauer et al. 2012), with equilibrium reached in less than 1 d. Formation of an unidentified metabolite and CPYO were rapid with rate constants of 3.5 and 0.132 d^{-1}, respectively. The elimination rate constant CPYO in *G. pulex* was 0.298 d^{-1}. Because the ^{14}C-label was in the Et-O moieties in the molecule, a BCF for CPY could not be calculated. In a study in laboratory-based marine microcosms, BCFs of 89–278 and 95–460 were reported in oysters and fish, respectively (Lalah et al. 2003), but were likely overestimated as the metabolites were not separated from the ^{14}C-CPY. Studies with usable results demonstrate that in most cases, BCFs, BAFs, and BSAFs are small (<2,000) and not indicative of bioaccumulation or toxicologically significant exposures to predators via the food chain (Table 11). The two new reports of BCFs from fish (Table 11) were based on very short exposures (≤3 d), and thus, cannot be compared or combined with the studies reviewed by Racke (1993), which were conducted for ≥28 d. The one report of a BMF (0.32 in the fish *Aphaniusiberus*) was based on an exposure of 32 d and is not indicative of biomagnification (Varo et al. 2002). One study in eleutheroembryos of *Danio rerio* reported a BCF value greater than 2,000 (El-Amrani et al. 2012), most likely because metabolic capacity in this early a stage of development is not fully developed.

6　Assessment of Chlorpyrifos as a POP or PBT

The Stockholm convention (United Nations Environmental Programme 2001) and the UN-ECE POP Protocol (United Nations Economic Commission for Europe 1998) was established to identify and manage organic chemicals that are persistent, bioaccumulative, and toxic (PBT), in that they have the potential to exceed the threshold for toxicity, and to be transported to remote regions (persistent organic pollutants, POPs). Classification criteria for POPs were developed from the physical, chemical, biological, and environmental properties of the so-called "dirty dozen" (Ritter et al. 1995a, b) and are based on trigger values for persistence (P) bioaccumulation (B), toxicity (T), and propensity for long range transport (LRT) (Table 12). Several other initiatives to assess chemicals for properties that might confer P, B, and T have been put in place. These are the Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR 1992), the Toxic Substances Management Policy (Environment Canada 1995), the Toxics Release Inventory Reporting (USEPA 1999a), the New Chemicals Program (USEPA 1999b), REACH (European Community 2011). These initiatives exclude pesticides but EC regulation No. 1107/2009 (European Community 2009) is specifically directed towards pesticides and is the focus of further discussion here. EC regulation No. 1107 uses classification criteria similar to those of the POPs (Table 12), but these are somewhat more conservative for P and B. The criteria used to classify the PBT character of pesticides under EC regulation No. 1107/2009 are simple (Table 12); the process is basically a hazard assessment that does not make full use of the rich

Table 12 Criteria for the categorization of compounds as POPs or PBT

Persistent (P)	Bioaccumulative (B)	Toxicity (T)	Potential for long-range transport (LRT)
POP (Stockholm Convention)			
Water: $DT_{50}>$ 2 months	BCF >5,000 or Log $K_{OW}>5$	No specific criteria other than "significant adverse effects"	Air: $DT_{50}>2$ d or monitoring modeling or data that shows long-range transport
Sediment: $DT_{50}>$ 6 months	Other, e.g., very toxic or bioaccumulation in nontarget species.		
Soil: $DT_{50}>$ 6 months			
Other evidence of persistence	*Trigger values for BMF, BAF, and BSAF not available*		
PBT (EC No. 1107/2009)			
Marine water: t½ >60 d	BCF >2,000 in aquatic species. *Trigger values for BMF, BAF, and BSAF not available*	Chronic NOEC <0.01 mg/L or is a carcinogen, mutagen, or toxic for reproduction, or other evidence of toxicity. *Trigger values for non-aquatic species not available*	None
Fresh water t½ >40 d			
Marine sediment: t½ >180 d			
Freshwater sediment: t½ >120 d			
Soil: t½ >120 d			

From European Community (2009); United Nations Economic Commission for Europe (1998); United Nations Environmental Programme (2001). Author comments in *italics*

set of data available for risk assessment of pesticides (Solomon et al. 2013). In addition, as has been pointed out previously, classification criteria are inconsistent for PBT among regulations in various jurisdictions (Moermond et al. 2011) and, in some cases, appropriate criteria and/or guidance are not provided (Solomon et al. 2013). Under EC regulation No. 1107/2009, exceeding trigger values for P, B, and T results in a ban and, exceeding two of three, results in being listed for substitution with pesticides that are less P, B, and/or T. In the sections below, we assess CPY as a POP and PBT based on criteria for POPs (Stockholm) and PBT (EC regulation No. 1107/2009). To our knowledge, neither CPY nor CPYO are officially being considered for classification as POPs or PBTs, although, some have suggested that they be considered (Watts 2012).

In assessing P and B for chemicals, the concern is for the general environment, not for a particular local scenario. Because extreme values that are observed in specific situations are not representative of all locations, it is best to use mean values. Moreover, because many P or B processes are driven by first-order kinetics, the geometric mean value is most appropriate for comparing triggers for classification. Accordingly, these were used in the following sections.

Classification as a POP. CPY does not meet the criteria for P, B, and LRT for classification as a POP. Persistence in water, sediment, and soil (Table 6) is less than the trigger values (Sects. 3 and 4, above), and there is no evidence to suggest ecologically

significant persistence in the environments of use. The geometric mean of half-life values in water tested in the laboratory was 21 d. Half-lives in water in the presence of sediments in the field were even smaller (geometric mean of 5 d). These are less than the trigger values of 60 d for POPs. Geometric mean half-lives in soil tested under laboratory and field conditions had geometric means of 32 and 22 d, respectively, both of which are less than the 180 d trigger. The geometric mean DT_{50dis}s for CPY in sediments tested in the laboratory and microcosms was 39 d, which is less than the trigger value of 180 d.

Geometric means of values for BCF, BAF, and BSAF measured in the laboratory (assumed to be equivalent, Sect. 5, and Table 11) and the field were 848 and 935, respectively, all of which were less than the trigger value of 5,000. Studies of trophic magnification of CPY in the field were not found in the literature but, based on food-chain magnification measured in model ecosystems with ^{14}C-labelled material (Metcalf and Sanborn 1975), CPY does not magnify to the same extent as any of the currently identified POPs that were also tested.

The criterion for toxicity, "significant adverse effects", used to classify chemicals a POP, is somewhat vague (Solomon et al. 2009) in that specific numerical criteria are not provided. All pesticides are toxic to some organisms; otherwise they would not be used. However, in the context of POPs and LRT, adverse effects are more properly interpreted as ecologically significant outcomes on survival, growth, development, and reproduction in organisms well outside the boundaries of the site of application. Based on the conclusions of several of the companion papers, CPY does not exceed the trigger for "significant adverse effects" in or outside the regions of use (Cutler et al. 2014; Giddings et al. 2014; Moore et al. 2014).

The half-life of CPY in the atmosphere of 1.4 d does not exceed the trigger value of 2 d for LRT. CPY is found at distances from areas of application, and even in remote locations (Sect. 2.1); but the concentrations in air (Table 1), rain and snow (Table 2), aquatic and terrestrial media (Table 3), and biota (Table 4) are small and less than the threshold of toxicity for aquatic organisms and birds (Giddings et al. 2014; Moore et al. 2014). Even assuming a longer half life of 3 d as was done earlier, the concentrations at remote locations are low and do not approach toxicity thresholds.

Assessment of CPYO as a POP is complicated by the fact that it is a degradation product of CPY and is usually present with the parent material in the environment as well as during tests of effects of CPY. By itself, CPYO also does not exceed the triggers for POPs (Table 12) with respect to persistence in water, soil, and sediment (Table 7). No data were available for BCF of CPYO, but studies with ring-labelled CPY provide equivalency for CPYO and it does not trigger the criterion for B. Toxicity for CPYO is subsumed in that of CPY and it does not trigger "significant adverse effects". The half-life in air of approximately 11 h (Table 7) is less than 25% of the LRT trigger of 2 d. In addition, replacement of the =S with =O in CPYO increases polarity; CPYO is about 25-fold more water soluble, and has a K_{OW} that is 100-fold smaller than that of CPY (Table 7). Thus, CPYO will partition more into water in the atmosphere (precipitation) and will be more likely to rain-out into surface water or snow. Because of the greater electronegativity of the P-atom, CPYO is more reactive than CPY and will undergo hydrolysis more rapidly than CPY; the half-life in water (Table 7) is approximately half that of CPY (Table 6). Thus, CPYO

will partition out of air into water, where it is less persistent. The overall persistence in these two media is not suggestive of the characteristics of a POP. Concentrations in surface waters in remote locations (Sect. 2.4 and Fig. 4) are less than amounts that would cause toxicity (Giddings et al. 2014). In addition, adverse effects in aquatic organisms have not been linked to exposures to CPY (Datta et al. 1998; Davidson et al. 2012), and, by extension to the oxon that might be formed. Thus, neither CPY nor CPYO trigger the criteria for POPs and LRT.

Classification as a PBT. In terms of assessment of PBT under EC regulation No. 1107/2009, there is no guidance for using multiple values for P and B. However, because of the multiple uses of CPY over a large number of agricultural sites, the geometric mean is the most appropriate value to compare to the trigger value. In addition, values derived under field conditions can be used for validation. For surface waters, the geometric mean of laboratory-based half-lives was 21 d but, under more realistic conditions in microcosms, half-lives were less than 10 d (Sect. 3). These are less than the trigger of 40 d. Based on these values, the trigger value for P is not exceeded. Geometric mean half-lives in soil tested under laboratory and field conditions were 32 and 22 d, respectively. These are less than the trigger of 120 d. The geometric mean DT_{50dis} for CPY in sediments tested in the laboratory and microcosms was 39 d, less than the trigger value of 120 d.

The geometric mean values for BCF or BAF tested in the laboratory and the field were 848 and 935, respectively (Sect. 5). These are less that the trigger value of 2,000. Moreover, CPY does not trigger the criterion for Pv or Bv. In addition, CPYO also does not trigger the criteria for P and B or Pv or Bv.

The trigger of 10 µg L^{-1} for T is exceeded for CPY; the most sensitive NOEC reported for aquatic organisms is 0.005 µg L^{-1} for *Simocephalus vetulus* in a microcosm experiment (Daam and Van den Brink 2007). Since CPY is an insecticide, toxicity to arthropods is expected, however; the key question is the relevance of this to the exposures in the general environment and, as discussed in the companion papers (Giddings et al. 2014; Williams et al. 2014), this is not indicative of significant ecotoxicological risks in the North-American environment, even in areas close to where it is applied. In aquatic organisms, CPYO has similar toxicity to CPY (Giddings et al. 2014), but it is only infrequently found in surface waters and then only at very small concentrations (Williams et al. 2013). This is consistent with the greater reactivity of CPYO and its rapid hydrolysis in the environment. Thus, although formed from CPY in the atmosphere, CPYO is not persistent enough to present a risk to aquatic organisms, although it does trigger the T criterion under EC 1107/2009.

7 Summary

The fate and movement of the organophosphorus insecticide chlorpyrifos (CPY; CAS No.2921-88-2) and its metabolite chlorpyrifos-oxon (CPYO; CAS No.5598-15-2) determine exposures in terrestrial and aquatic environments.

Detectable concentrations of the organophosphorus insecticide CPY in air, rain, snow and other environmental media have been measured in North America and other locations at considerable distances from likely agricultural sources, which indicates the potential for long range transport (LRT) in the atmosphere. This issue was addressed by first compiling monitoring results for CPY in all relevant environmental media. As a contribution to the risk assessment of CPY in remote regions, a simple mass balance model was developed to quantify likely concentrations at locations ranging from local sites of application to more remote locations up to hundreds of km distant. Physical-chemical properties of CPY were reviewed and a set of consistent values for those properties that determine partitioning and reactivity were compiled and evaluated for use in the model. The model quantifies transformation and deposition processes and includes a tentative treatment of dispersion to lesser atmospheric concentrations. The model also addressed formation and fate of CPYO, which is the major transformation product of CPY. The Characteristic Travel Distance (CTD) at which 63% of the original mass of volatilized CPY is degraded or deposited-based on a conservative concentration of •OH radicals of 0.7×10^6 molecules cm^{-3} and a half-life of 3 h, was estimated to be 62 km. At lesser concentrations of •OH radical, such as occurs at night and at lesser temperatures, the CTD is proportionally greater. By including monitoring data from a variety of media, including air, rain, snow and biota, all monitored concentrations can be converted to the equilibrium criterion of fugacity, thus providing a synoptic assessment of concentrations of CPY and CPYO in multiple media. The calculated fugacities of CPY in air and other media decrease proportionally with increasing distance from sources, which can provide an approximate prediction of downwind concentrations and fugacities in media and can contribute to improved risk assessments for CPY and especially CPYO at locations remote from points of application, but still subject to LRT. The model yielded estimated concentrations that are generally consistent with concentrations measured, which suggests that the canonical fate and transport processes were included in the simulation model. The equations included in the model enable both masses and concentrations of CPY and CPYO to be estimated as a function of distance downwind following application. While the analysis provided here is useful and an improvement over previous estimates of LRT of CPY and CPYO, there is still need for improved estimates of the chemical-physical properties of CPYO.

Based on the persistence in water, soils, and sediments, its bioconcentration and biomagnification in organisms, and its potential for long-range transport, CPY and CPYO do not trigger the criteria for classification as a POP under the Stockholm convention or a PB chemical under EC 1107/2009. Nonetheless, CPY is toxic at concentrations less than the trigger for classification as T under EC1107/2009; however, this simple trigger needs to be placed in the context of low risks to non-target organisms close to the areas of use. Overall, CPY and CPYO are judged to not trigger the PBT criteria of EC 1107/2009.

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