

Environmental Chemistry, Ecotoxicity, and Fate of Lambda-Cyhalothrin

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1 Introduction

Lambda-cyhalothrin is a pyrethroid insecticide. Pyrethroids are synthetic chemical analogues of pyrethrins, which are naturally occurring insecticidal compounds produced in the flowers of chrysanthemums (*Chrysanthemum cinerariaefolium*). Insecticidal products containing pyrethroids have been widely used to control insect pests in agriculture, public health, and homes and gardens (Amweg and Weston 2005; Oros and Werner 2005). In agriculture, target crops include cotton, cereals, hops, ornamentals, potatoes, and vegetables, with applications made to control aphid, coleopterous, and lepidopterous pests. Pyrethroids are important tools used in public health management where applications are made to control cockroaches, mosquitoes, ticks, and flies, which may act as disease vectors. Residential use of pyrethroid products has increased because of the suspension of organophosphate products containing chlorpyrifos or diazinon (Oros and Werner 2005; Weston et al. 2005).

Lambda-cyhalothrin is the active ingredient (a.i.) in several brand name products: Warrior, Scimitar, Karate, Demand, Icon, and Matador. Annual agricultural use of lambda-cyhalothrin in California has been consistent at approximately 30,000 lbs a.i. per annum from 2000 to 2003 and increased to ~40,000 lbs a.i. per annum between 2004 and 2006 (CDPR 2006). Residues of lambda-cyhalothrin have been detected in irrigation and storm runoff water and in their associated sediments. Residues have been detected in runoff resulting from agricultural, public health, and residential applications. For example, lambda-cyhalothrin was detected in water at 0.11–0.14 µg/L from agricultural watersheds in Stanislaus County, California. Lambda-cyhalothrin residues were detected in sediments obtained from sites sampled in Imperial, Monterey, Stanislaus, and Placer Counties. Residues in sediment ranged from 0.003 to 0.315 µg/g of dry wt (Starner 2007).

Toxicity tests conducted at levels of lambda-cyhalothrin residues measured in water or sediment indicate potential for effects on aquatic organisms including fish and amphipods (Amweg et al. 2005, 2006; Cavas and Ergene-Gozukara 2003; Gu et al. 2007; Heckmann and Friberg 2005; Lawler et al. 2007; Maund et al. 1998; Van Wijngaarden et al. 2005; Wang et al. 2007; Weston et al. 2004). Concerns have therefore been raised about the widespread use of lambda-cyhalothrin in California and its potential impact on aquatic ecosystems. This review is limited to literature available from peer-reviewed publications and approved documents and databases and is not deemed to be exhaustive. Research results from studies using multiple pyrethroids that included lambda-cyhalothrin were used in this review to augment data from studies conducted solely with lambda-cyhalothrin.

2 Chemistry of Lambda-Cyhalothrin

Lambda-cyhalothrin is a 1:1 mixture of two stereoisomers, (*S*)- α -cyano-3-phenoxybenzyl-(*Z*)-(1*R*,3*R*)-3-(2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethyl cyclopropanecarboxylate (Fig. 1a) and (*R*)- α -cyano-3-phenoxybenzyl-(*Z*)-(1*S*,3*S*)-

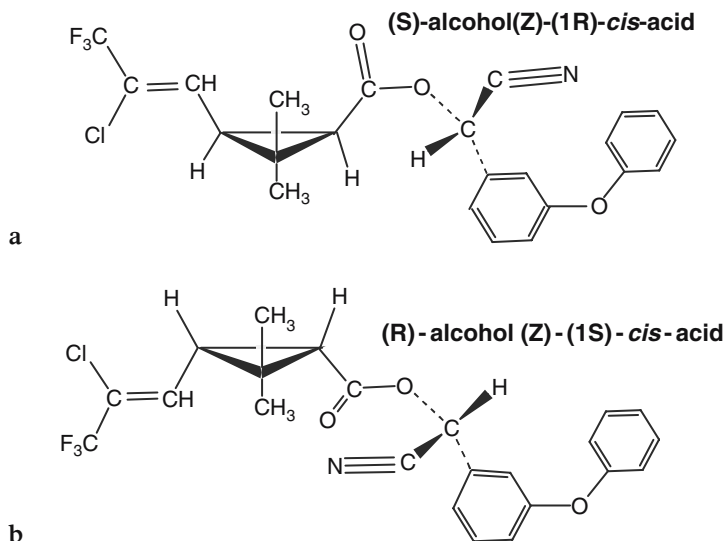


Fig. 1 The chemical structure of two isomers of lambda-cyhalothrin

3-(2-chloro-3, 3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate (Fig. 1b). Lambda-cyhalothrin was first reported by Robson and Crosby (1984) and was introduced in Central America and the Far East in 1985 by ICI Agrochemicals (now Syngenta).

2.1 Synthesis

Dried and ground pyrethrum chrysanthemum flowers were noted to be powerful insecticides in ancient China, but it took until the middle of the 20th century for the first improved chemical analogues of the natural pyrethrin a.i.s to be commercially synthesized. Naturally occurring pyrethrins are esters consisting of a so-called “acid” component, which has a cyclopropane core and an “alcohol” component. At first, synthetic pyrethroids were developed through alcohol substitutions. This early generation of synthetic pyrethroids had drawbacks, mostly the result of poor stability in sunlight. Photostability was greatly improved by substituting vinylic halogens in the acid component (Spurlock 2006). Additional α -cyano-substitution in the alcohol component by the National Research Development Corporation in the UK further improved light stability and insecticidal activity. The commercial product KARATE, whose a.i. is lambda-cyhalothrin, was registered for use by the U.S. Environmental Protection Agency (USEPA) in 1988 (Syngenta 2007).

It is known that some isomers have a greater insecticidal effect than others, and this has led to the development of techniques to separate the more-active isomers and to convert the less-active isomers into the more-active ones. Conversion between

isomers is characterized by the base chemical, which promotes the desired epimerization through proton removal at the carbon atom bearing the cyano group (Cleugh and Milner 1994). Gamma-cyhalothrin is a single stereoisomer that has effective insecticidal activity, with a much lower total reported use in California (CDPR 2007).

2.2 Physicochemical Properties

Lambda-cyhalothrin is a colorless solid at room temperature but may appear yellowish in solution. Lambda-cyhalothrin has a low vapor pressure and Henry's law constant, which suggests that it is not easily volatilized into the atmosphere. This insecticide also has a high octanol–water partition coefficient (K_{ow}), so it tends to partition into lipids (Table 1). Normally, a pesticide with a high K_{ow} would signal a high potential to bioconcentrate.

The mean water–soil organic carbon partition coefficient (K_{oc}) is high, which indicates preferential affinity to organic matter and suggests that it is unlikely to contaminate groundwater because of a low potential to leach as dissolved residues in percolating water. The tendency to adsorb to suspended particulate materials in

Table 1 Physical, chemical, and environmental properties of lambda-cyhalothrin

CAS number	91465-08-6
US EPA PC Code	128897
CA DPR Chem Code	2297
Molecular formula	$C_{23}H_{19}ClF_3NO_3$
Molecular weight (g/mol)	449.9
Density (g/mL at 25°C)	1.33
Melting point (°C)	49.2
Boiling point (°C at 0.2 mmHg)	187–190
Vapor pressure (mPa at 20°C)	0.0002
Henry's law constant (Pa·m ³ /mole)	0.018
Water solubility (mg/L at 20°C)	0.005
Solubility in other solvents (e.g., acetone) (mg/L)	>500,000
Octanol–water partitioning (log K_{ow} at 20°C)	7.00
Hydrolysis half-life (d)	
pH 5	Stable
pH 7	Stable
pH 9	8.66
Photolysis half-life (d)	
Water at pH 5 and 25°C	24.5
Soil	53.7
Bioconcentration factor (BCF) (fish)	2,240
Soil adsorption K_{oc} (cm ³ /g)	247,000–330,000
Soil degradation half-life (d)	
Aerobic soil	42.6
Aquatic degradation half-life (d)	
aerobic aquatic	21.9

Source: CDPR 2007; Laskowski 2002; PAN 2007; Tomlin 2000; USDA 2007; USEPA 2007.

the water column, including clay particles and organic matter, provides the primary vector for transport through aquatic systems. Thus, the greatest risk to nontarget aquatic organisms would be through exposure to lambda-cyhalothrin-contaminated sediments. Adsorbed phases of chemical molecules generally show decreased degradation rates because residues are less accessible to breakdown by sunlight or microorganisms than when molecules are dissolved in the water column (Schwarzenbach et al. 1993). Sorption of lambda-cyhalothrin to suspended solids or bottom sediments may provide a mechanism to mitigate its acute toxicity to aquatic organisms by reducing its short-term bioavailability in the water column.

2.3 Mode of Action

Pyrethroids are axonic poisons that affect the nerve fiber by binding to a protein that regulates the voltage-gated sodium channel. Normally, this gate opens to cause stimulation of the nerve and closes to terminate the nerve signal. The channels are pathways through which ions are permitted to enter the axon and cause excitation. When the channels are left open, nerve cells produce repetitive discharges and eventually cause paralysis (Bradbury and Coats 1989; Shafer and Meyer 2004). Pyrethroids bind to this gate and prevent it from closing normally, which results in continuous nerve stimulation and tremors in poisoned insects. Poisoned organisms lose control of their nervous system and are unable to produce coordinated movement.

There are two groups of pyrethroids with distinctive poisoning symptoms, denoted as Type I and Type II. Chemically, Type II pyrethroids are distinguished from Type I pyrethroids by the presence of an α -cyano group in their structure. In comparison to Type I pyrethroids (e.g., permethrin), which exert their neurotoxicity primarily through interference with sodium channel function in the central nervous system, Type II pyrethroids (e.g., lambda-cyhalothrin) can also affect chloride and calcium channels that are important for proper nerve function (Burr and Ray 2004).

Because of the lipophilic nature of pyrethroids, biological membranes and tissues readily absorb them. Specifically, lambda-cyhalothrin penetrates the insect cuticle, disrupting nerve conduction within minutes; this leads to cessation of feeding, loss of muscular control, paralysis, and eventual death. Additional protection of the crop is provided by the insecticide's strong repellent effect toward insects.

3 Breakdown Mechanisms and Products

3.1 Photolysis

As indicated previously, the naturally occurring pyrethrins are unstable in light, while the photostability of recent synthetic pyrethroids has been improved. Photochemical studies with lambda-cyhalothrin were conducted under UV and

sunlight irradiation to understand photodegradation kinetics, pathways, and products (Fernandez-Alvarez et al. 2007; Ruzo et al. 1987). Exposure to UV light (18 W, 254 nm) for 20 min resulted in nearly complete degradation with losses greater than 95% of initial amounts applied (Fernandez-Alvarez et al. 2007). Photodegradation of lambda-cyhalothrin followed first-order kinetic behavior where the apparent first-order rate constant (k_{ap}) and half-life ($t_{1/2}$) were determined to be 0.163 min^{-1} and 4.26 min, respectively.

With the recent development of highly efficient extraction methods and high-resolution detection techniques, it is possible to identify multiple trace photoproducts and photodegradation pathways for lambda-cyhalothrin. Several pathways have been proposed for the photodegradation of lambda-cyhalothrin, including decarboxylation, reductive dehalogenation, and ester or other bond cleavage (Fernandez-Alvarez et al. 2007) (Fig. 2).

The photoproduct decarboxycyhalothrin (P4) of lambda-cyhalothrin is generated by the decarboxylation pathway. The ester bond cleavage of lambda-

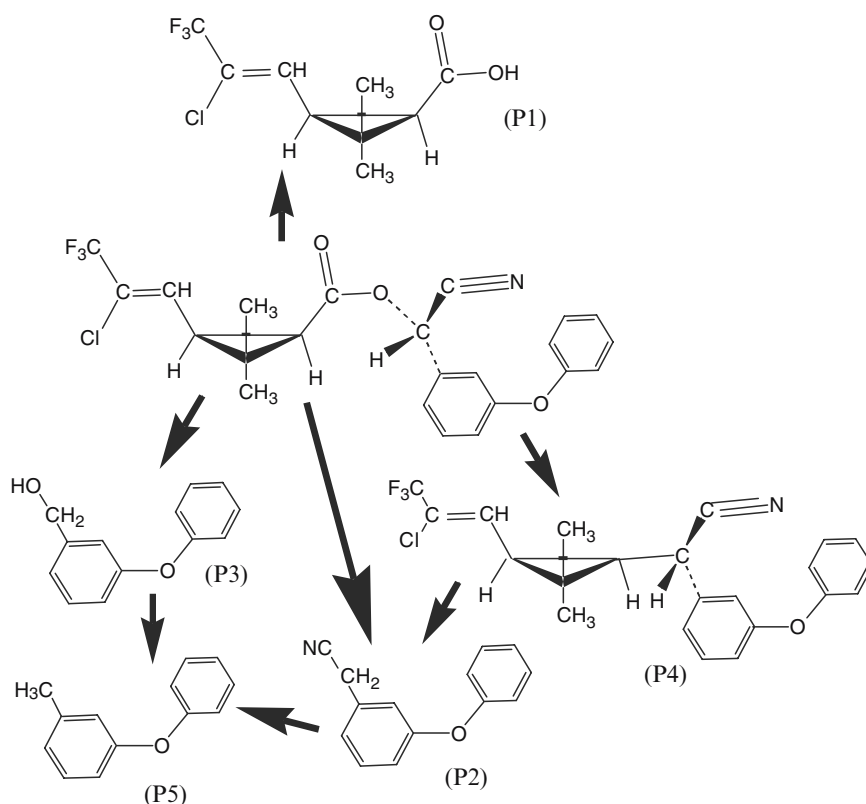


Fig. 2 Photodegradation pathways and products for lambda-cyhalothrin

cyhalothrin generates 3-(2-chloro-3,3,3-trifluoroprop-1-en-1-yl)-2,2-dimethyl cyclopropanecarboxylic acid (P1) and (3-phenoxyphenyl)acetonitrile (P2). The photoproduct P2 can also be generated by C–C bond cleavage of photoproduct P4. Photoproduct P3 ((3-phenoxyphenyl)methanol) can be generated by the ester cleavage and subsequent loss of the cyano group of lambda-cyhalothrin. The photoproduct 1-methyl-3-phenoxybenzene (P5) may be formed by hydroxyl or cyano group losses from P3 or P2 (Fernandez-Alvarez et al. 2007).

3.2 Hydrolysis

Lambda-cyhalothrin is stable at pH below 8, whereas under alkaline conditions it hydrolyzes through nucleophilic attack of the hydroxyl ion. A cyanohydrin derivative is formed, which degrades to yield HCN and the corresponding aldehyde (Fig. 3) (Gupta et al. 1998).

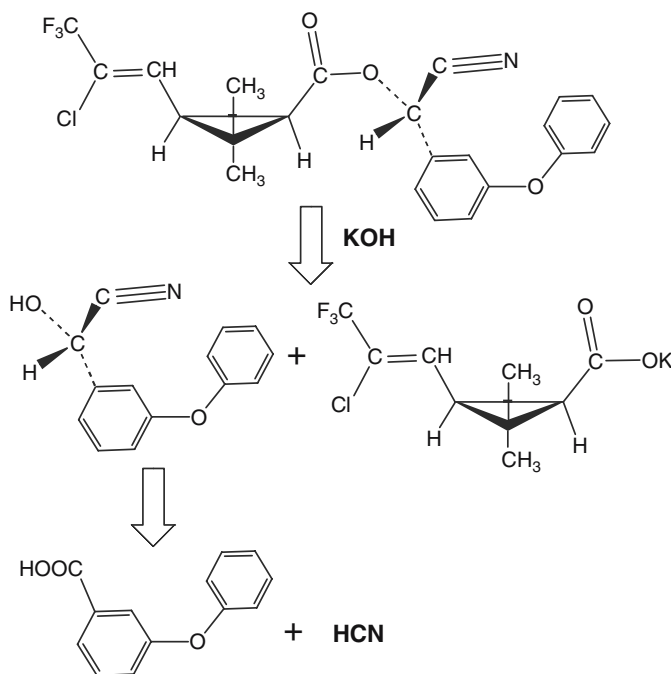


Fig. 3 Hydrolysis products of lambda-cyhalothrin

3.3 *Microbial Degradation*

In laboratory studies, the dissipation of lambda-cyhalothrin in soil was mainly through biodegradation, as indicated by the rapid loss of lambda-cyhalothrin in non-sterile soil compared to sterile soil (Wang et al. 1997). Only one degradate, which was (*RS*)- α -cyano-3-(4-hydroxyphenoxy)benzyl-(*Z*)-(1*RS*)-*cis*-3-(2-chloro-3, 3, 3-trifluoropropenyl)-2,2-dimethylcyclopropanecarboxylate, was determined as a major breakdown product comprising 10% of the initial lambda-cyhalothrin concentration (European-Commission 2001).

4 Environmental Fate of Lambda-Cyhalothrin

4.1 *Dissipation in Water*

Lambda-cyhalothrin rapidly dissipates from water (Farmer et al. 1995). The fate of lambda-cyhalothrin was compared in mesotrophic and eutrophic ditch microcosms where it was applied three times at 1-wk intervals at concentrations of 10, 25, 50, 100, and 250 ng/L. The rate of dissipation of lambda-cyhalothrin in the water column of the two systems was similar where, after 1 d, only 30% of the amount applied remained in the water phase (Roessink et al. 2005). Similarly, in an investigation of the fate of both gamma- and lambda-cyhalothrin in laboratory-simulated rice paddy water, their concentrations decreased rapidly, with no gamma-cyhalothrin or lambda-cyhalothrin detected after 3 and 4 d, respectively (Wang et al. 2007). Last, after simulating a seasonal exposure equivalent to 12 “drift” and 6 “runoff” events, each delivering a dose equivalent to that expected from a typical event under field conditions, the lambda-cyhalothrin concentration measured after the final application was less than 2 ng/L (Hadfield et al. 1993).

4.2 *Interaction with Soil and Sediment*

4.2.1 *Adsorption*

Adsorption is one of the key processes controlling the fate of pyrethroids, which, as indicated by their high K_{oc} values, results in rapid and strong adsorption to soils and sediments. Ali and Baugh (2003) investigated the adsorption of lambda-cyhalothrin to silica, which is the major mineral component in soil. They discovered much-reduced sorption to the mineral component, implying that discharge of pyrethroids to water bodies is mainly in the sorbed soil organic phase. In another study of sorption to mineral components of soil, four pyrethroids were used to investigate selective interactions with corundum, quartz, montmorillonite, and kaolinite. Initial pyrethroid

concentrations ranged from 1 to 100 $\mu\text{g/L}$. Sorption to glass centrifuge tubes used in the batch experiments was significant and accounted for 25%–60% of total sorption (Oudou and Hansen 2002; Zhou et al. 1995). All corrected adsorption isotherms fit the Freundlich equation with exponential n values ranging between 0.9 and 1.1. These n values indicated little curvature in the adsorption isotherm. Bonding affinities per unit surface area decreased in the order corundum > quartz > montmorillonite > kaolinite. All minerals showed the same selectivity order with respect to sorption affinity of the four pyrethroids: lambda-cyhalothrin > deltamethrin > cypermethrin > fenvalerate (Oudou and Hansen 2002).

Adsorption is a surface phenomenon that for pyrethroids has been shown to depend on the surface area and the organic carbon content of the adsorption. Sorption–desorption equilibria of six pyrethroids (permethrin, cyfluthrin, cypermethrin, lambda-cyhalothrin, deltamethrin, and fenvalerate) were determined after 24-hr equilibrium in soils with an organic carbon content that ranged from 1.15% to 2.46%. Again, the Freundlich equation fit the adsorption isotherms well, with the values of the exponent n around unity. The desorbed amount of lambda-cyhalothrin after five steps of desorption using deionized water was only 4.68% of the original amount, indicating that lambda-cyhalothrin adsorption to soil was virtually irreversible in water (Ali and Baugh 2003).

The phase distribution of lambda-cyhalothrin was investigated as a function of contact time in sediment (Bondarenko et al. 2006). For freshwater sediments at 9 d, the dissolved fraction measured by solid-phase microextraction ranged from 1.7% to 16.3% of the total pore-water concentration as determined by liquid–liquid extraction. The dissolved fraction decreased substantially with contact time to less than 5% at 30 d after sediment dosing. The dissolved fraction was lower in the marine sediment, ranging from 1.1% to 4.2%. Consequently, the apparent K_{OC} and dissolved organic carbon partition coefficient (K_{DOC}) values increased significantly over the contact time, especially in the freshwater sediment, suggesting that phase distribution was not at equilibrium after 9 d.

In general, the adsorption capacity of all soils with different organic content was much higher than that of pure mineral particles, suggesting that lambda-cyhalothrin had partitioned into the organic carbon phase as well as adsorbed onto the particle surfaces. However, in investigations of the adsorptive capacity of organic coatings on minerals, Zhou et al. (1995) discovered that adsorption was not constant and that it decreased with increasing polarity and decreasing aromaticity of organic sorbents. This result implied that the quantity, as well as the quality, of the organic matter on particle surfaces should be characterized to better predict contaminant transport in aquatic and soil environments.

4.2.2 Effect of pH on Lambda-Cyhalothrin Adsorption

The effect of pH on sorption was examined by conducting experiments over a range of four different pH values: 2, 4, 6, or 9 (Ali and Baugh 2003). The results showed that, over this range, pH did not have a significant impact, although soil-sorbed

lambda-cyhalothrin at pH <4 was slightly higher than at pH 9. The results support the assumption that the adsorption of lambda-cyhalothrin is not significantly affected by changing the surface charge density of soil or organic matter.

4.2.3 Terrestrial Dissipation Studies

The dissipation of lambda-cyhalothrin in laboratory-controlled soils was mainly through biodegradation, as indicated by the rapid loss of lambda-cyhalothrin in nonsterile soil when compared to a sterile soil (Wang et al. 1997). However, the shape of the dissipation curve potentially indicated that processes primarily responsible for degradation differed over time. In the cotton soil, dissipation of lambda-cyhalothrin was fast in the first few days, which could indicate that degradation was initially through photolysis and hydrolysis chemical processes. The subsequent dissipation rate showed a steady slow decline, which could be evidence of microbial degradation. Dissipation curves for a Brazilian Oxisol-Typic Haplustox can be described by biexponential functions for lambda-cyhalothrin (Laabs et al. 2000). Soil in pans was treated with lambda-cyhalothrin at 15 g/ha using an indoor track sprayer, and the pans were dug into adjacent fallow and cropped areas of a field. Overall, the initial lambda-cyhalothrin residues (32 ppb or 11.8 g/ha) dissipated with a DT_{50} of 1.3 wk and a DT_{90} of 14.5 wk (disappearance time for first 50% and 90% of residue, respectively). Among treatments, residues in the soil pans shaded by the crop canopy declined faster (DT_{90} of 12.8 wk) than residues in the fallow area (DT_{90} of 16.2 wk). Compared with bare fallow, soil surface temperatures on warm, summer days were 8°–16°C cooler within the crop canopy. Also, the surface 0–2.5 cm of soil within the canopy took longer to dry out after a rainfall. It was hypothesized that the more ideal soil temperature and moisture conditions within the crop canopy increased the microbial degradation of lambda-cyhalothrin. One year after application, only 3.2% of the initial residues were recovered in the fallow area (Hill and Inaba 1991).

The influence of temperature and moisture on the degradation and persistence of lambda-cyhalothrin was investigated using laboratory incubation and lysimeters on a sandy loam soil (Typic Ustocurepts) in Pakistan (Tariq et al. 2006). Drainage from the lysimeters was sampled on days 49, 52, 59, 73, 100, 113, and 119 against the pesticide application on days 37, 63, 82, 108, and 137 after the sowing of cotton. The dissipation of lambda-cyhalothrin followed second-order kinetics. The results of incubation studies showed that increasing temperature and moisture content significantly reduced the $t_{1/2}$ values of pesticides in laboratory-controlled soils (Tariq et al. 2006; Wang et al. 1997).

Hydrosol (sediment) appeared to act as a sink for lambda-cyhalothrin (Hadfield et al. 1993). Under the stringent test conditions of the mesocosm study, lambda-cyhalothrin residues in the hydrosol (1.1% organic matter) reached 3.2 µg/kg following the seasonal exposure. Residues in the hydrosol reached a maximum level of approximately 25 µg/kg in one sampling zone at one interval and thereafter declined to a level of 9 µg/kg within 4 mon.

4.2.4 Transport in Soil

In a study to evaluate the leaching potential of eight pesticides in a Brazilian Oxisol, lambda-cyhalothrin was applied onto a Typic Haplustox that contained ~50% clay and 26.3 g/kg organic carbon in the top 10-cm soil layer (Laabs et al. 2000). Mobility within the soil profile and subsequent leaching were studied for a period of 28 d after application. The bulk of lambda-cyhalothrin residues were recovered within the top 15 cm of the soil. In lysimeter percolates collected at 35 cm soil depth, less than 0.03% of the applied amount of lambda-cyhalothrin was recovered. The relative contamination potential of pesticides, according to the lysimeter study results, was ranked as follows: metolachlor > atrazine = simazine >> monocrotophos > endosulfan > chlorpyrifos > trifluralin > lambda-cyhalothrin. This same order of contamination potential was achieved by ranking the pesticides according to their effective sorption coefficient (K_e), which is the ratio of K_{oc} to field-dissipation half-life.

The potential for pesticide transport in preferential flow in an Oxisol was investigated in a study where lambda-cyhalothrin was applied on to a Typic Haplustox (Reichenberger et al. 2002). After application, a tracer solution containing 5 g/L of the dye Brilliant Blue FCF and 0.015 M KBr was applied at a rate of 40 mm/d in duplicate experiments over a period of 3 d. The solution was applied using either a tension infiltrometer (3.3 cm tension) or manual irrigation with a watering can. The soil monoliths were then opened and the soil layers at 0–5, 5–10, 10–20, 20–30, and 30–40 cm were quantitatively removed. Although the highest concentrations of lambda-cyhalothrin were found in the top 0–10 cm layer, detection of lambda-cyhalothrin in the deeper 10–30 cm soil layer was determined to result from preferential flow (Reichenberger et al. 2002; Tariq et al. 2006).

5 Ecotoxicity of Lambda-Cyhalothrin

Lambda-cyhalothrin is slightly to highly toxic to terrestrial and aquatic organisms. This review focuses on aquatic toxicity because aquatic organisms are most likely to be exposed to lambda-cyhalothrin residue levels found in water and associated sediment. It is worth noting that the reported oral LD_{50} (48 hr) for mallard duck was >3950 mg/kg, and that the oral LD_{50} (48 hr) was 0.038 µg/bee and the contact LD_{50} (48 h) was 0.909 µg/bee, indicating relatively low toxicity to ducks but high toxicity to bees (European-Commission 2001).

5.1 Fish and Shellfish

Lambda-cyhalothrin is highly toxic to a number of fish and shellfish. The reported LC_{50} (96 hr) is 210 ng/L for bluegill sunfish, 240 ng/L for rainbow trout, 360 ng/L for *Daphnia magna*, 4.9 ng/L for mysid shrimp, and 0.8 ng/L for sheepshead min-

now. An EC_{50} , the concentration at which the effect occurs in 50% of the test population, for eastern oyster is 0.59 ng/L. A bioconcentration factor (BCF) of 2240 has been reported in fish (species unspecified), but concentration was confined to nonedible tissues and rapid depuration was observed (USDA 2007; USEPA 2007).

Because lambda-cyhalothrin is commonly applied to rice fields to control insects, potential water and sediment contamination may lead to toxicity in aquatic organisms such as mosquitofish, shrimps, crabs, and clams. Replicated enclosures in a rice field were sprayed with the lambda-cyhalothrin product Warrior at 5.8 g a.i./ha. Mosquitofish were added either before the spray or 7 d later. Of those added before the spray, none survived. Most fish added 7 d later survived (Lawler et al. 2003). Lambda-cyhalothrin showed high toxicity to shrimp (*Macrobrachium nipponensis* de Haan) and zebrafish (*Brachydanio rerio* H.B). The 96-hr LC_{50} was 20–70 ng/L for shrimp and 0.98–7.55 $\mu\text{g/L}$ for zebrafish. In drainage water ponds with lambda-cyhalothrin concentrations ranging from 0.45 to 0.90 $\mu\text{g/L}$, the 96-hr mortality was 100% for shrimp, but the drainage water showed no toxicity to shrimp on the fourth day after application of lambda-cyhalothrin (Gu et al. 2007). The 96-hr LC_{50} values for lambda-cyhalothrin and gamma-cyhalothrin were similar for zebrafish (1.93 $\mu\text{g/L}$ for gamma and 1.94 $\mu\text{g/L}$ for lambda). However, lambda-cyhalothrin was more toxic (LC_{50} , 0.04 $\mu\text{g/L}$) than gamma-cyhalothrin (LC_{50} , 0.28 $\mu\text{g/L}$) to shrimp, possibly implying that the toxicity to shrimp is likely stereochemistry dependent (Wang et al. 2007).

5.2 *Macrophytes*

The structure of an ecosystem determines the final effect of pesticide exposure to macrophytes (Wendt-Rasch et al. 2004). Using a pesticide mixture containing lambda-cyhalothrin applied to 10 mesotrophic aquatic ecosystems dominated by submerged macrophytes (*Elodea*) and 10 simulated eutrophic ecosystems with a high *Lemna* surface coverage, significant increases in the biomass and alterations of species composition of the periphytic algae were observed in the *Elodea*-dominated microcosms, but no effect on *Myriophyllum spicatum* growth was observed. The opposite was found in the *Lemna*-dominated microcosms, in which decreased growth of *M. spicatum* was observed but no alterations were observed in the periphytic community. Furthermore, application of 0.17 and 1.7 g a.i. ha^{-1} lambda-cyhalothrin to pond mesocosms failed to produce adverse effects on macrophytes (Farmer et al. 1995).

5.3 *Invertebrates*

Lambda-cyhalothrin effects on mesotrophic (macrophyte-dominated) and eutrophic (phytoplankton-dominated) ditch microcosms were studied; applications were made three times at 1-wk intervals and at concentrations of 10, 25, 50, 100, and

250 ng/L (Roessink et al. 2005). Initial, direct effects were primarily on arthropod taxa. The most sensitive species was the phantom midge (*Chaoborus obscuripes*). At treatment levels of 25 ng/L and higher, apparent population and community responses occurred. At treatments of 100 and 250 ng/L, the rate of recovery of the macroinvertebrate community was lower in the macrophyte-dominated systems, primarily because of a prolonged decline of the amphipod *Gammarus pulex*. This species occurred at high densities only in the macrophyte-dominated enclosures. Indirect effects (e.g., increase of rotifers and microcrustaceans) were more pronounced in the plankton-dominated test systems, particularly at treatment levels of 25 ng/L and higher.

Simulated aquatic ditch mesocosms were used to understand the toxic effects of potential spray drift from a typical crop application of pesticides including lambda-cyhalothrin. Spray application to the water surface was at 0.2%, 1%, and 5% of the recommended label rates. To interpret the observed effects, treatment concentrations were expressed in toxic units ($TU = \text{actual concentration}/EC_{50}$) (Arts et al. 2006), which describe the relative toxicity of the compounds with common toxicity test organisms (*Daphnia* and algae). After treatment, lambda-cyhalothrin disappeared from the water phase within 2 d. At the 5% treatment level, exposure concentrations exceeded $0.1 TU_{Daphnia}$, and this resulted in long-term effects on zooplankton and macroinvertebrates, some of which did not fully recover by the end of the study (Arts et al. 2006). Previous studies with pesticides in experimental ecosystems have demonstrated that effects on primary producers are likely to occur at $TU_{Algae} > 0.1$ and effects on invertebrates are likely to occur at $TU > 0.01-0.1$ (Van Wijngaarden et al. 2004, 2005).

5.4 Sediment Toxicity

Recent studies have shown that pyrethroids including lambda-cyhalothrin are commonly found in aquatic sediments in the heavily agricultural Central Valley of California, and therefore the toxicity of sediment-associated pyrethroid residues to aquatic organisms has been actively investigated (Amweg et al. 2005; Weston et al. 2004). Seventy sediment samples were collected from 42 sites over a 10-county area in the agriculture-dominated Central Valley of California, with most sites located in irrigation canals and small creeks dominated by agricultural effluent. Significant mortality was observed with the amphipod *Hyaella azteca* at 42% of the locations and for the midge *Chironomus tentans* at 40% of the sites. Using a toxicity unit analysis, measured pyrethroid concentrations were sufficiently high to have contributed to the toxicity in 40% of samples toxic to *C. tentans* and nearly 70% of samples toxic to *H. azteca* (Weston et al. 2004).

In a follow-up aquatic toxicity study with six pyrethroids (Amweg et al. 2005), the average 10-d median lethal concentration LC_{50} of sediment-associated residues of lambda-cyhalothrin was $0.45 \mu\text{g/g OC}$ (organic carbon adjusted), corresponding to an estimated pore-water concentration of 1.4 ng/L. Lambda-cyhalothrin would

be acutely toxic to *H. azteca* at the concentration of 5.6 ng/g dry wt of sediment. Growth was typically inhibited at concentrations below the LC_{50} ; animal biomass on average was 38% below controls when exposed to lambda-cyhalothrin concentrations roughly one-third to one-half the LC_{50} ; i.e., the growth lowest-observable-effect concentration (LOEC) was 0.19 $\mu\text{g/g}$ OC. Survival data indicate that exposure occurs primarily via the interstitial water rather than the particulate phase.

If only the dissolved concentration is bioavailable (Gan et al. 2006; Maund et al. 1998), these observations suggest that contact time after sediment dosing may greatly affect the bioavailability and, hence, the toxicity of pyrethroids. Therefore, a long contact time (30 d) is recommended for sediment toxicity testing of this class of compounds. The dependence of bioavailability on contact time also implies that test conditions must be standardized to allow comparison between laboratory-dosed samples and field samples (Bondarenko et al. 2006).

5.5 Effects on Soil Fauna

Species sensitivity distributions (SSD) and 5% hazardous concentrations (HC5) are distribution-based approaches for assessing environmental risks of pollutants, e.g., lambda-cyhalothrin risks to soil invertebrate communities. From a systematic review of literature, a total of 1950 laboratory toxicity test results were obtained, representing 250 pesticides including lambda-cyhalothrin and 67 invertebrate taxa. The majority (96%) of pesticides have toxicity data on fewer than 5 species. Based on a minimum of 5 species, the best available endpoint data (acute mortality median lethal concentration) enabled SSD and HC5 to be calculated for 11 pesticides including lambda-cyhalothrin. Arthropods and oligochaetes exhibit pronounced differences in their sensitivity to most of these pesticides. The standard test earthworm species, *Eisenia fetida sensu lato*, is least sensitive to insecticides based on acute mortality, whereas the standard *Collembola* test species, *Folsomia candida*, is among the most sensitive species for a broad range of toxic modes of action (biocide, fungicide, herbicide, and insecticide) (Frampton et al. 2006). To assess the effects of lambda-cyhalothrin on soil invertebrates under tropical conditions, ecotoxicological semifield studies were conducted using intact soil-core terrestrial model ecosystems (TMEs) (Forster et al. 2006). Earthworms, isopods, and diplopods were added to intact soil cores and the mortality of soil invertebrates was determined. The results indicated that lambda-cyhalothrin was toxic to isopods and millipedes, whereas no effect on arthropods was detected in the field.

To evaluate possible microbial community changes in a sandy loam soil in response to the addition of lambda-cyhalothrin, the following properties were determined: active soil microbial biomass, concentrations of ammonium and nitrate ions, numbers of total cultivable bacteria, fungi, nitrogen-fixing bacteria, and nitrifying and denitrifying bacteria (Cycon et al. 2006). Substrate-induced respiration (SIR) increased with time in controls ranging from 13.7 to 23.7 mg $\text{O}_2/$

kg dry soil/hr and in pesticide-treated soil ranging from 12–13 to 23–25 O₂/kg dry soil/hr on days 1 and 28, respectively. The concentrations of nitrate and ammonium ions, numbers of total cultivable bacteria, denitrifying bacteria, nitrogen-fixing bacteria, and fungi were either unaffected or even stimulated by the pesticide treatments.

5.5 Bioaccumulation

The interaction of lambda-cyhalothrin with larvae of the aquatic insect *Chironomus riparius* was studied in laboratory sediment–water systems (Hamer et al. 1999). *C. riparius*, a nonbiting midge, is widely used for investigating toxicity and bioaccumulation of contaminants in sediment. Ten different sediments were used. ¹⁴C-Labeled lambda-cyhalothrin was applied to sediment slurries and *C. riparius* was exposed in the test system for 48 hr. In all the sediment–water test systems, >99% of the ¹⁴C-labeled lambda-cyhalothrin was adsorbed onto the sediment. BCFs based on the aqueous-phase concentrations showed little difference among systems, ranging from 1,300 to 3,400 with a mean of 2,300 and with a coefficient of variation of 25%. These values were very similar to a BCF of 2,000 that was determined in water alone after 48 hr. These BCF values are similar to chlorpyrifos, which is 1,374, but higher than diazinon, which is 500 (PAN 2007). BCFs based on measured concentrations of extractable ¹⁴C-lambda-cyhalothrin in the sediment phase were always <1, ranging from 0.11 to 0.84 with a mean of 0.39 and coefficient of variation of 61%. Sediment BCFs were inversely proportional to the measured sediment K_d s, which ranged from 3,290 to 22,100; that is, the higher the proportion of the chemical that was adsorbed, the lower the sediment BCF. The results of the study supported equilibrium partitioning theory. In sediment–water systems, the lambda-cyhalothrin that was bioavailable is equivalent to the amount that is measured in the water phase.

6 Mitigating Runoff of Residues Through Plant Interaction

Because lambda-cyhalothrin residues in water and sediment may exert adverse impacts on aquatic life, management practices have been investigated and developed to mitigate such impact. Plants have long been recognized to have the ability to sequester a variety of contaminants (e.g., organic or inorganic chemicals) in water, sediment, and soil (Bouldin et al. 2006; Burken and Schnoor 1997; Henderson et al. 2007; Mertens et al. 2006; Montes-Bayon et al. 2002; Siciliano et al. 1998; Wild et al. 2005). In recent years, the efficacy of vegetated ditches to reduce pesticide residues in agricultural runoff has been

extensively studied. The results indicate that vegetated ditches are useful for the reduction of lambda-cyhalothrin in stormwater or agricultural runoff (Bennett et al. 2005; Bouldin et al. 2005; Leistra et al. 2004; Moore et al. 2001; Roessink et al. 2005). Pesticide uptake, adsorption, and accelerated degradation by plants in a vegetated ditch are the principal mechanisms of mitigation by plants, as described next.

6.1 Assimilation by Plants

Macrophytes (e.g., *Juncus effusus* and *Ludwigia peploides*) can take up a significant portion of lambda-cyhalothrin residues in water. Eight days after application, 98.2% of lambda-cyhalothrin was found in the roots of *L. peploides*. Translocation of lambda-cyhalothrin in *J. effusus* resulted in 25.4% of pesticide uptake partitioning into upper plant biomass. These macrophytes showed species- and pesticide-specific uptake rates, and therefore the selection of high-uptake plants enhances mitigation capabilities in edge-of-field conveyance structures (Bouldin et al. 2006).

6.2 Adsorption and Degradation by Plants

Plants growing in an agricultural drainage ditch not only slow water flow and absorb chemicals dissolved in water, but they will also act as surfaces for pesticide adsorption and catalysts for their degradation. Many studies have been conducted to investigate the effectiveness of vegetated drainage ditches for reducing pesticide residue export from agricultural lands to creeks and rivers (Bennett et al. 2005; Bouldin et al. 2005; Moore et al. 2001). By incorporating vegetated drainage ditches into a watershed management program, agriculture can continue to decrease potential non-point source threats to downstream aquatic receiving systems. Overall results of previous studies illustrate that aquatic macrophytes play an important role in the retention and distribution of pyrethroids, including lambda-cyhalothrin, in vegetated agricultural drainage ditches.

The reduction effectiveness of pesticides through a drainage ditch is usually described by the percentage of reduction of the pesticide:

$$\text{Reduction\%} = (\text{conc. at inlet} - \text{conc. at outlet}) \times 100 / \text{conc. at inlet}$$

The reduction% is affected by several factors including the length and slope of ditch, the type and density of vegetation, and the type of soil (Arts et al. 2006; Bennett et al. 2005; Bouldin et al. 2005; Leistra et al. 2004; Milam et al. 2004; Moore et al. 2001; Roessink et al. 2005).

Laboratory studies indicated that adsorption to macrophytes was extensive and essentially irreversible, and that degradation of lambda-cyhalothrin occurred rapidly by cleavage of the ester bond. In the indoor microcosm, which contained water,

sediment, and macrophytes, degradation was also rapid, with DT_{50} and DT_{90} values of less than 3 and 19 hr, respectively, for dissipation from the water column and less than 3 and 56 hr, respectively, for dissipation from the whole system (Hand et al. 2001). The adsorption of lambda-cyhalothrin by *Ludwigia peploides* (water primrose) and *Juncus effusus* (soft rush) was significant and reached as high as 86.50 $\mu\text{g}/\text{kg}$ (Bouldin et al. 2005).

In a vegetated drainage ditch study, following initiation of simulated runoff, mean percentages of lambda-cyhalothrin concentrations in water and sediment in the ditch were 12% and 1%, respectively. Lambda-cyhalothrin mean percentage concentrations in plants [*Polygonum* (water smartweed), *Leersia* (cutgrass), and *Sporobolus* (smutgrass)] were 87%. The concentrations in water decreased to levels safe for nontarget species 50 m downstream from the point of input (Moore et al. 2001).

A controlled-release runoff simulation was conducted on a 650-m vegetated drainage ditch in the Mississippi Delta. Lambda-cyhalothrin was released into the ditch in a water–sediment slurry (Bennett et al. 2005). Samples of water, sediment, and plants were collected and analyzed for lambda-cyhalothrin concentrations. Three hours following runoff initiation, inlet lambda-cyhalothrin water concentration was 374 $\mu\text{g}/\text{L}$ in the inlet and 7.24 $\mu\text{g}/\text{L}$ at 200 m downstream. No lambda-cyhalothrin residues were detected at the 400-m sampling site. A similar trend was observed throughout the first 7 d of the study where water concentrations were elevated at the front end of the ditch (~25 m) and greatly reduced downstream at the 400-m sampling site. Regression formulas predicted that lambda-cyhalothrin concentrations in ditch water were reduced to 10% of the initial value within 280 m downstream from point of input. Mass balance calculations determined that ditch plants constituted the major sink and/or sorption site responsible for the rapid aqueous pyrethroid dissipation.

In a ditch study conducted in the Netherlands, concentrations of lambda-cyhalothrin decreased rapidly in the water column: 24%–40% of the dose remained in the water 1 d after application, and it had decreased to 1.8%–6.5% after 3 d (Leistra et al. 2004). At the highest plant density, lambda-cyhalothrin residues in the plant compartment reached a maximum of 50% of the dose after 1 d; at intermediate and low plant densities, this maximum was only 3%–11% of the dose (after 1–2 d). The percentage of the insecticide in the ditch sediment was 12% or less of the dose and tended to be lower at higher plant densities. Alkaline hydrolysis in the water near the surface of macrophytes and phytoplankton is considered to be the main dissipation process for lambda-cyhalothrin.

7 Summary

Lambda-cyhalothrin is a pyrethroid insecticide used for controlling pest insects in agriculture, public health, and in construction and households. Lambda-cyhalothrin is characterized by low vapor pressure and a low Henry's law constant but by a high

octanol–water partition coefficient (K_{ow}) and high water–solid-organic carbon partition coefficient (K_{oc}) values. Lambda-cyhalothrin is quite stable in water at pH < 8, whereas it hydrolyzes to form HCN and aldehyde under alkaline conditions. Although lambda-cyhalothrin is relatively photostable under natural irradiation, with a half-life > 3 wk, its photolysis process is fast under UV irradiation, with a half-life < 10 min. The fate of lambda-cyhalothrin in aquatic ecosystems depends on the nature of system components such as suspended solids (mineral and organic particulates) and aquatic organisms (algae, macrophytes, or aquatic animals). Lambda-cyhalothrin residues dissolved in water decrease rapidly if suspended solids and/or aquatic organisms are present because lambda-cyhalothrin molecules are strongly adsorbed by particulates and plants. Adsorbed lambda-cyhalothrin molecules show decreased degradation rates because they are less accessible to breakdown than free molecules in the water column. On the other hand, lambda-cyhalothrin adsorbed to suspended solids or bottom sediments may provide a mechanism to mitigate its acute toxicity to aquatic organisms by reducing their short-term bioavailability in the water column. The widespread use of lambda-cyhalothrin has resulted in residues in sediment, which have been found to be toxic to aquatic organisms including fish and amphipods. Mitigation measures have been used to reduce the adverse impact of lambda-cyhalothrin contributed from agricultural or urban runoff. Mitigation may be achieved by reducing the quantity of runoff and suspended solid content in runoff through wetlands, detention ponds, or vegetated ditches.

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