Pyrethroids: A Natural Product for Crop Protection

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Abstract

Pyrethroids are the synthetic compounds derived from the *Chrysanthemum cinerariaefolium* plant. The first synthetic pyrethroids developed in the United States are allethrin and bioallethrin. According to the World Health Organization, the classification pyrethroids has a place in the fourth group of insecticides and includes 42 substances. More than 30% of pyrethroid insecticides are used worldwide. In the year 2015, the global market of pyrethroid insecticides has been estimated at USD 4.67 billion and is expected to touch USD 6.45 billion by the year 2021. Pyrethroid insecticides are potent against an extensive variety of pests belonging to the orders *Coleoptera*, *Diptera*, *Hemiptera*, *Hymenoptera*, *Lepidoptera*, *Orthoptera*, and *Thysanoptera*. Pyrethroid insecticides interrupt the functioning of the peripheral nervous system by reacting with the voltage-gated sodium channels and cause a series of bursts and paralyses. The low tendency to accumulate in organisms, short biodegradation period, and economic value have led to the overuse of pyrethroids with unavoidable consequences. The increase in the production of mites in cotton, in tea, and in vegetables was reported by the constant use of synthetic pyrethroids. Even at a very low

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concentration in water, pyrethroids are strongly absorbed by the gills of fish due to their lipophilic nature and lead to their toxicity and even altered homing ability in honeybees. Pyrethroid metabolites were detected in the breast milk of women in various parts of the world. Long-term exposure of pyrethroids leads to aggressive behavior in humans due to the leftover traces of pyrethroid metabolites in urine. Further research should be done to prove the toxicity of pesticides in the ecosystem, the effects of pesticide residues, and their interaction with nutrients.

Keywords
Pyrethroids · Insecticides · Sodium channel · Toxicity · Pyrethroid degradation, World Health Organization

8.1 Introduction

Pyrethroids are synthetic insecticides and are the structural modifications of pyrethrins which are extracted from *Chrysanthemum cinerariaefolium* flowers of the genus *Chrysanthemum.* Pyrethrins are the esters of cyclopentenolone alcohol and cyclopropane carboxylic acid, and in the existence of sunlight, moisture, and water, they increase the insecticidal potency and longevity (Elliott 1995). Pyrethroids keep the acid/alcohol configuration of pyrethrins and have similar chemical structures across the class. As a result, concern of health effects can be made on the full class of pyrethroids. Over dozens of pyrethroid molecules are registered in various regions of the world which find application in many products of agriculture, household, veterinary, and in the field of medicine. Pyrethroid class includes allethrin, bioallethrin, bifenthrin, cyfluthrin, cypermethrin, deltamethrin, d-phenothrin, esfenvalerate, fenvalerate, fenpropathrin, flumethrin, fluvalinate-tau, lambda-cyhalothrin, permethrin, prallethrin, resmethrin, tefluthrin, and tetramethrin.

From the last 20 years, pyrethroid use has risen with their extensive exposure to environment, humans, and aquatic animals. Pyrethroids have a half-life of less than 8 h (Kim et al. 2008; Godin et al. 2010). In population sampling programs, urinary metabolites of pyrethroid have been confirmed (Health Canada 2013; Dewailly et al. 2014; Lewis et al. 2014; CDC 2015). Only recognition does not determine that an antagonistic health consequence will arise. So, there is an unending interest in the possible relations of pyrethroid exposure and health effects, especially on environment levels.

8.2 History

The pyrethrum flowers were firstly used by Caucasian tribes in the early 1800s to control body lice and later on produced on a commercial level in Armenia in 1828. In Dalmatia (Yugoslavia) the production started in about 1840 and was

centered there until the First World War, in Japan before the Second World War, and after that in East Africa. Insect powder was first imported into the United States in about 1860, and several attempts were made for the next 90 years to produce the flowers commercially in this country but remained unsuccessful (Casida 1980). In the year 1940, Schechter and his colleagues developed the first synthetic pyrethroids, allethrin and bioallethrin, in the United States (Sanders and Taff 1954; BBSRC 2014). Pyrethroids are 20 times more successful in killing insects than dichloro-diphenyl-trichloroethane (DDT) without affecting environmental and human health (BBSRC 2014). Elliott's team at Rothamsted (United Kingdom) in the year 1962 developed a synthetic pyrethroid resmethrin by changing the molecular arrangement of naturally arising pyrethrin, and later on it was developed by the researchers at Sumitomo, a chemical company in Japan.

Later on, in the year 1967, the Elliott team isolated an active compound from synthetic pyrethroid resmethrin and again produced a first-generation pyrethroid, bioresmethrin, which is a mixture of four diverse isomers. Permethrin, the first pyrethroid to be used for agricultural purposes which does not collapse quickly in sunlight, was developed in 1972 by Michael Elliott. With the growing concern of the bioaccumulation of pesticides, for incidence, the breakdown of DDT in sunlight and its persistence in the environment lead to its ban by the United States in the same year. Two new extremely potent insecticides cypermethrin and deltamethrin were developed by Michael Elliott along with his colleague Izuru Yamamoto in Japan in 1976. Sumitomo, a chemical company, developed fenvalerate pyrethroid in 1976. Pyrethroids generate 25.1% of the worldwide insecticide market in the year 1983, and around 33 million hectares of crops were treated with pyrethroids (Wirtz et al. 2009). Owing to the low toxicity of pyrethroids, deltamethrin, and permethrin to humans and other mammals, the World Health Organization (WHO) in the 1980s recommend their use in insecticide-treated nets (BBSRC 2014). The annual sales of synthetic pyrethroids reached US $1.2 billion in the early 1990s (Housset and Dickmann 2009). A study was conducted in the rural region of Gambia in 1991 in which children under the age of 5 are treated by using permethrin-treated mosquito nets, and a reduction in the number of deaths by around two-thirds was observed (Alonso et al. 1991). In the year 2002, deltamethrin turned out to be the world's major-selling pyrethroid with yearly sale of US $208 million (BBSRC 2014). A product is developed by the researchers at Rothamsted (UK) in 2004, which releases an enzyme inhibitor to disable the insect's resistance mechanism to overcome resistance to pyrethroid insecticides that is emerging in a number of insect crop pests (BBSRC 2014). In the year 2007, global sales of insecticides reached US $8 billion with 17% of global insecticides as pyrethroids (Davies et al. 2007; BBSRC 2014). To tackle the cases of malaria, WHO in the year 2011 recommended the utilization of long-lasting insecticidal mosquito nets (LLINs) which were developed at Rothamsted (UK) (Lengeler 2004).

8.3 Classes of Pyrethroids

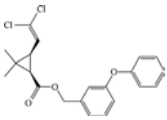
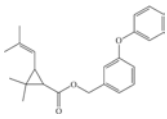
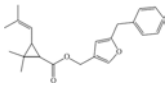
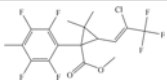
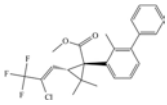
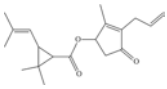
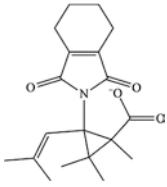
Pyrethroids are categorized into two classes, namely, class I and class II, on the basis of physical and toxicological properties (Gajendiran and Abraham 2018). Pyrethroids of class I contain cyclopropane carboxylic ester in their structure and include resmethrin, phenothrin, allethrin, tefluthrin, bifenthrin, permethrin, and tetramethrin. Class II pyrethroids contain a cyano group and include fenpropathrin, flumethrin, tralomethrin, deltamethrin, cyfluthrin, cyhalothrin, cypermethrin, fenvalerate, flucythrinate, and fluvalinate. These pyrethroids cause choreoathetosis and salivation. Pyrethroids are proficient in contrast to an extensive variety of pests which belong to the order Coleoptera, Hemiptera (Homoptera and Heteroptera), Diptera, Hymenoptera, Lepidoptera, Orthoptera, and Thysanoptera. Mostly, they are used for domestic purposes, for example, as a grain protectant, active in animal houses, fields, greenhouses, and in veterinary medicines (ATSDR 2003) (Table 8.1).

8.4 Mode of Action of Pyrethroids

The molecular targets of pyrethroid class of insecticides are the same in case of mammals and insects. Mode of action includes voltage-gated sodium, nicotinic receptors, chloride and calcium channels, intercellular gap junctions, gamma-aminobutyric acid (GABA)-gated chlorine channels, and membrane depolarization (Forshaw and Ray 1990; Song and Narahashi, 1996a, b). Mammals are vulnerable to pyrethroid toxicosis in small amount as compared to insects, the primary reason being higher body temperatures, rapid metabolic clearance, and a lower sympathy for pyrethroids (Song and Narahashi 1996b; Gammon et al. 2012). This particular insecticidal class slows the opening and closing of the sodium channels, causing the subsequent excitation of the cell (Marban et al. 1989). The action potential for type II pyrethroids is more durable than for type I. The direct exposure of pyrethroids causes paresthesia of the sensory nerve endings. This leads to the repetitive firing of the fibers. Sodium channels must be reformed by the insecticide to produce definite neurological signs and symptoms. In higher concentrations, pyrethroids of class II may act on GABA-gated chloride channels (Bloomquist et al. 1986) and control the cell excitability when it comes in contact with the voltage-dependent chloride channels existing in the brain, nerve, muscle, and salivary gland. Different forms of functional chloride channels are present when related to the sodium channels. Most of the insecticide-sensitive channels have been found to be linked with the Maxi chloride channel class, which gets triggered by various modes of excitation such as depolarization and protein kinase C phosphorylation. This particular channel has high conductivity and is calcium-independent.

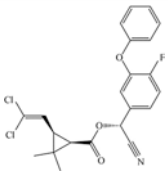
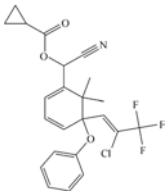
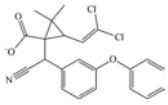
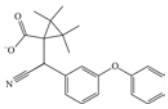
There are a number of ways by which pyrethroids can penetrate into the body of an organism. One way is non-stereospecific in which pyrethroids permeate quickly from the epidermis, followed by uptake by the blood or hemolymph carrier proteins and continuously delivered all over the body. The main route of pyrethroid delivery to the central nervous system is along the epidermis cells. They directly enter into

Table 8.1 Classes of the pyrethroids used for crop protection, household, animal house, and veterinary

Pyrethroid	Class	Trade name	Molecular structure	Types of crop	Insecticidal role	Insecticidal role other than crop
Permethrin	I	Ambush		Cotton, wheat, maize, alfalfa, potato, spinach, green pepper, mushroom	Beetle, bollworm, budworm, termites, and weevils, moths	Ants, fleas, flies, lice, mosquitoes
Phenothrin	I	Sumithrin		NA	NA	Flies, gnats, mosquitoes, cockroaches, and lice
Resmethrin	I	Chrysron		NA	NA	Flies, gnats, mosquitoes, fleas, ticks, and black flies
Tefluthrin	I	Force		Sugar beet, cabbage, maize, carrot	White grub, southern corn leaf beetle, flea beetle, and chinch bug	NA
Bifenthrin	I	Brigade		Corn, hops, raspberries	Beetles, weevil, aphids, moths, locust	Mosquitoes, lice, bedbugs, cockroaches
Allethrin	I	Pynamin		NA	NA	Flies, mosquitoes, and ants
Tetramethrin	I	Neo-Pynamin		NA	NA	Wasps, hornets, roaches, ants, fleas, and mosquitoes

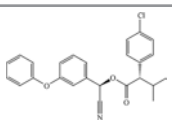
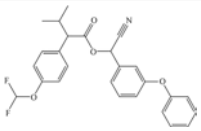
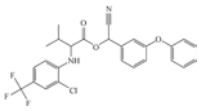
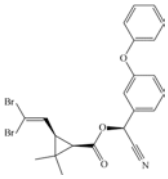
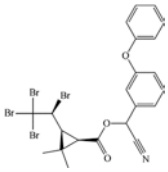
(continued)

Table 8.1 (continued)

Pyrethroid	Class	Trade name	Molecular structure	Types of crop	Insecticidal role	Insecticidal role other than crop
Cyfluthrin	II	Baythroid		Artichokes, brassica crops, caneberries, canola, *Crambe*, rapeseed, cilantro, coriander, citrus, com, cotton, cucurbits, beans, peas, grapes, hops, lettuce (head), mayhaw, okra, peanut, pears, roots crops, soybean, spinach, tobacco, tomato	Aphids, cabbage stem flea beetle, rape winter stem weevil	Houseflies, cockroaches, mosquitoes
Cyhalothrin	II	Commodore		Tomato, Bengal gram, chili, grapes, onion, soya bean	Bedbugs, beetles, moths, weevils	Houseflies, ked, lice, mosquitoes
Cypermethrin	II	Ammo, Cymbush		Wheat, okra, sunflower, cabbage	Moths	Cockroaches, mosquitoes, flies
Fenpropathrin	II	Danitol, Meothrin		Tea, chili	Aphids, beet armyworm, mealybug, potato leafhopper, moths, leafrollers, and lace bugs	Mites

(continued)

Table 8.1 (continued)

Pyrethroid	Class	Trade name	Molecular structure	Types of crop	Insecticidal role	Insecticidal role other than crop
Fenvalerate	II	Pydrin, Ectrin		Cauliflower	Beetles, locusts, moths	Cockroaches, flies, mosquitoes
Flucythrinate	II	Cybolt		Lettuce, apples, cabbage, maize, cotton seed	Bollworms, leafworms, sucking insects, whiteflies, and beetles	NA
Fluvalinate	II	Klartan, Mavrik		Cotton	Aphids, leafhoppers, moths, spider mites, thrips, and whiteflies	NA
Deltamethrin	II	Butoflin, Butoss		Wheat, rice	Aphids, beetles, bollworm, budworm, caterpillars, cicadas, moths, tortrix moths, weevils, whitefly, and winter moths	NA
Tralomethrin	II	Scout X-TRA		NA	NA	Ants and cockroaches

NA Not Applicable
Adapted from Gajendiran and Abraham (2018)

the central nervous system (CNS) via acting together with sensory organs of the peripheral nervous system. Also, they enter the body through the air in the vapor phase. Invertebrates and vertebrate insects are delicate to pyrethroids (Soderlund and Bloomquist 1989).

The peripheral and central nervous system of insects both are affected with the pyrethroids. Initially, they stimulate the nerve cells for the production of repetitive

discharges which eventually cause paralysis. For the production of repetitive discharges, only a minor section of the sodium channel inhabitants is reformed by pyrethroids as with DDT. After alteration by pyrethroids, the sodium channels retain their capability to conduct Na^+, and the channels will remain open as the insecticide interferes with it and get closed either by inactivation or deactivation. The membrane potential is moved for the functioning of nerve cells in a comparatively stable form of abnormal hyperexcitability. In insects a sublethal effect known as "knockdown" is produced. Due to greater lipophilicity, the pyrethroids enters to the target more quickly and delivers better knockdown levels. Type I pyrethroids (e.g., permethrin) are capable of influencing repetitive firing in axons, restlessness, un-coordination, and hyperactivity followed by prostration and paralysis and are usually good knockdown agents as shown in Fig. 8.1. Pyrethroids of the class II (e.g., deltamethrin) with cyano group at the α-benzylic position (the α-carbon of the 3-phenoxybenzyl alcohol) caused a noticeable uncontrollable stage bringing about better kill because depolarization of the nerve axons and terminals is unalterable as shown in Fig. 8.1 (Bloomquist 1996).

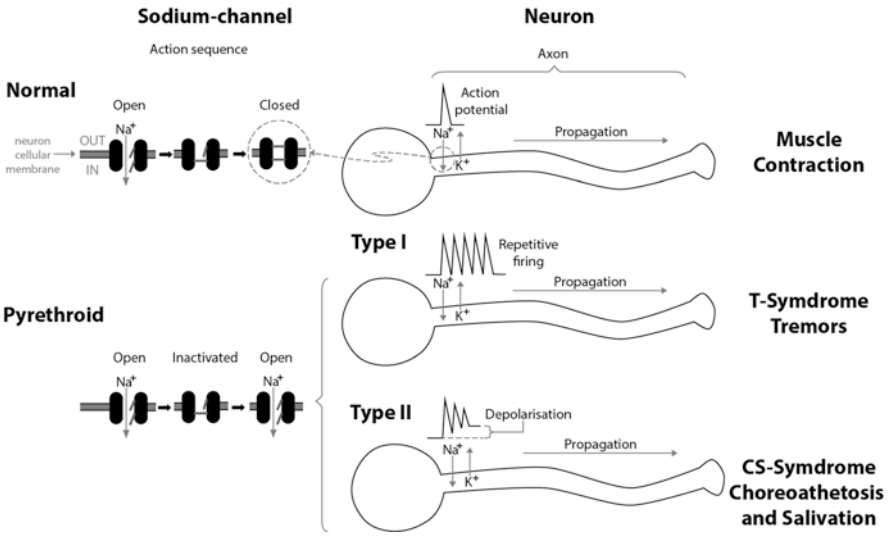


Fig. 8.1 Mode of action of pyrethroids on neurons. The top diagram shows the normal functioning of sodium channels which open, allowing sodium to pass, but then close after the action potential. This single action potential propagates through the nerve tail (axon) and triggers muscle contraction. Upon exposure to pyrethroids, the sodium channels malfunction and may remain open instead of returning to a closed state after initiation of the action potential. This will lead to repetitive firing (in type I pyrethroids) or depolarization (in type II pyrethroids) leading to tremors or involuntary movements (choreoathetosis) depending on the type of pyrethroid. Note that the T (fine tremors) and CS (choreoathetosis and salivation) syndromes are not as clearly differentiated as initially characterized in the pyrethroid literature and mixed symptoms may occur. (Adopted from Hénault-Ethier et al. 2016)

8.5 Current Uses of Pyrethroids

From the past 20 years, synthetic pyrethroids have been used in various crops to control pests (Maund et al. 2001), but they are becoming more and more popular even after the ban on the usage of cholinesterase-retarding insecticides (Feo et al. 2010; Luo and Zhang 2011). The ban on the use of two commonly used organophosphate (OP) pesticides, chlorpyrifos and diazinon, by the Environmental Protection Agency (EPA) in the year 2000–2001 resulted in the substantial rise in the marketplace diffusion of the pyrethroid products (EPA 2000, 2001). Due to the wide spectrum, high efficiency, low toxicity to mammals and avian, and biodegradability, the pyrethroids have a large share in the insecticidal market (Pap et al. 1996).

Nowadays, more than 30% of insecticides are used worldwide mostly in the field of horticulture, agriculture, forestry, public health and household purposes (Barr et al. 2010; Feo et al. 2010). The usage of synthetic pyrethroids and pyrethrins to control vector has been accepted by WHO and recommended the use of pyrethroids (lambda-cyhalothrin, bifenthrin, deltamethrin, cyfluthrin) for spraying indoor against malarial vectors (Walker 2000; Raghavendra et al. 2011). Pyrethroids are also applied on bed nets to control malarial vector (WHOPES 2005; Raghavendra et al. 2011).

According to the Environmental Protection Agency (EPA) data, about 1 million kg permethrin are used every year in agricultural, in household, and in public health fields (Feo et al. 2010). In 2015, the global market of pyrethroid insecticides has been evaluated at USD 4.67 billion and is expected to touch USD 6.45 billion by the year 2021 (Business Wire 2016).

8.6 Toxicity

Skin exposure is the most common route of entry for the insecticide pyrethroids (Gammon et al. 2012; Anadon et al. 2013). Its bioavailability usually accounts to 1% when exposed dermally. Absorption usually occurs via the stomach after an oral exposure in humans and mostly accounts to 36%. Soon after absorption, the insecticide gets quickly dispersed due to their lipophilicity and produce uncontrollable effects such as increased salivation and hyperexcitability. Majority of the pyrethroid formulations which are marketed contain solvents which are also the main cause of toxicity (Malik et al. 2010; Ensley 2018).

The half-life of this particular class of insecticide is usually hours (in blood plasma), while oral exposure is relatively shorter than the dermal exposure. Cyfluthrin has a half-life of 19–86 min. Acute toxicity is the major neurotoxicity caused due to pyrethroid exposure. Fishes are highly sensitive to pyrethroid (Ansari and Kumar 1988; Ensley 2018). Household exposure of fish to the insecticide can arise when the premises are sprayed with it. Birds are considered to be tolerant toward pyrethroid but they tend to be carriers. It has been reported that the LD_{50} value is greater than 1000 mg/Kg (Mueller-Beilschmidt 1990). Half-life values of the different pyrethroid compounds have been enlisted in Table 8.2. Clinical signs

Table 8.2 Half-life of pyrethroid compounds in environment

	Photolysis		Soil degradation	
Pyrethroid	Half-life in water	Half-life in soil	Aerobic soil	Anaerobic soil
Bifenthrin	408	96.9	96.3	425
Cyfluthrin	0.673	5.02	11.5	33.6
Cypermethrin	30.1	165	27.6	55
Deltamethrin	55.5	34.7	24.2	28.9
Esfenvalerate	17.2	10	38.6	90.4
Fenpropathrin	603	4.47	22.3	276
γ-Cyhalothrin	24.5	53.7	42.6	–
Pennethrin	110	104	39.5	197
Tralomethrin	2.47	3.87	3.25	5

Adopted from Laskowski (2002)

and symptoms after exposure have been observed to be almost similar when it comes to mammals such as cats and dogs. Some of which are as follows: salivation, vomiting, seizures, dyspnea, prostration, weakness, and eventually death (Ensley 2018). Apart from neurotoxicity, pyrethroids can also cause dermal, hepatic, renal, cardiac, endocrine disruption, reproduction, and developmental effects in mammals (Drago et al. 2014; Atmaca and Aksoy 2015; Hossain et al. 2015; Botnariu et al. 2016; Ben Slima et al. 2016; Malik et al. 2017; Ensley 2018).

8.7 Effect on Human Health

Usage of permethrin in household causes allergies and asthma, chiefly in children. A research conducted on 300 children residing in the Baltimore region presented a decline in the anti-inflammatory level IL-10 (Interleukin) in plasma as when related to people who are not in touch with pyrethroids (Skolarczyk et al. 2017). Similarly, when 5% permethrin was applied on the skin of 20-month-old child travailing from scabies showed symptoms of nausea, metabolic acidosis, respiratory distress, vomiting, and tachycardia (Goksugur et al. 2015). Metabolites of permethrin in concentrations 1.45–24.2 ng/g were recognized in the breast milk of women in Spain, Brazil, and Columbia (Corcellas et al. 2014). Long-term exposures of permethrin in children were described to cause an increase in the level of urine, behavioral changes, and an increase in aggressive behaviors shown in Fig. 8.2 (Outhlote and Bouchard 2013).

Similarly, exposure of deltamethrin at a dose level of 0.25–1% to humans for a long time through insecticidal mosquito nets caused lacrimation, limb spasms, abdominal pain, weakness, nausea, headaches, diarrhea, vomiting, apathy, ataxia, convulsions, and allergic reactions (Kumar et al. 2011). Permethrin metabolites were examined in the urine of 6-year-old children residing in Brittany (France) (Glorennec et al. 2017). The recommended dosage level of pyrethroids on a daily basis is 0.01 mg/kg, and poisoning symptoms occur after dosage of 2–250 mg/kg body weight. Aggregation of deltamethrin takes place in brain neurons when

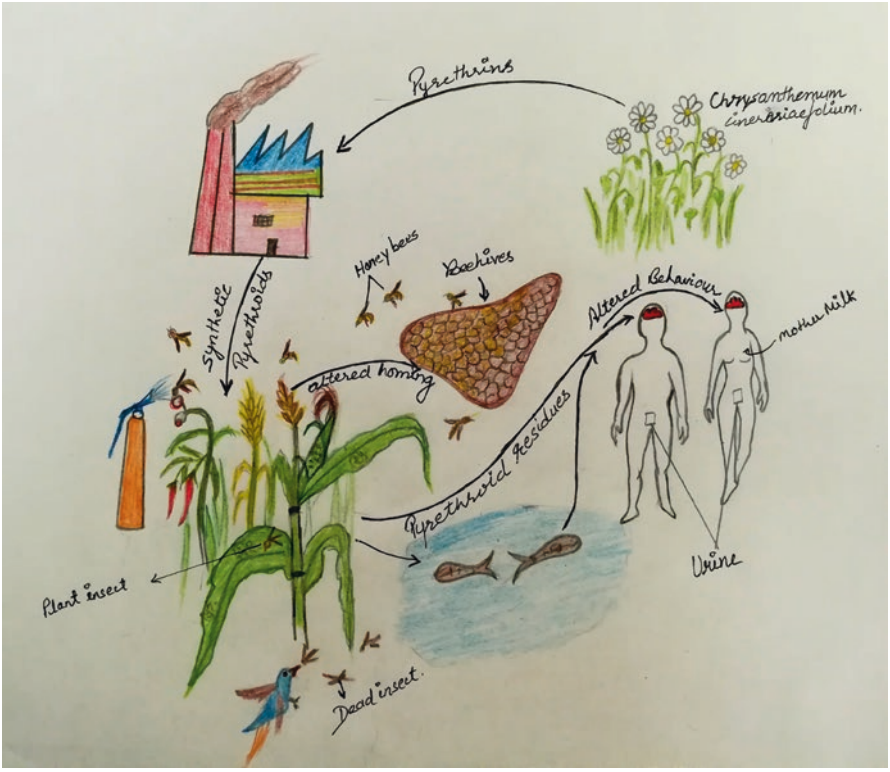


Fig. 8.2 Biomagnification of the pyrethroids in the ecosystem

administered orally or through the skin (Husain et al. 1996; Kim et al. 2008; Viel et al. 2015). Even exposure of deltamethrin in the course of pregnancy results in detrimental health effects such as fetal central nervous system (Husain et al. 1996; Viel et al. 2015). Children undergo sleep disorders, memory impairment, poor verbal abilities, and decrease in intelligence (Elwan et al. 2006; Viel et al. 2015). Deltamethrin contributes to Parkinson's disease by acting on the neuronal dopamine carrier (Elwan et al. 2006).

Alpha-cypermethrin metabolites were observed in the urine of people working in the cotton fields which further caused skin abrasions on the face and neck (Singleton et al. 2014). In contrast to permethrin, prolonged exposure of alpha-cypermethrin affects the central nervous system and induces complications with motor coordination and learning, but aggressive behaviors have not been observed (Manna et al. 2005). Through free radical formation, cypermethrin induces neurotoxicity, reduces the antioxidant defense mechanism, and inhibits the acetylcholinesterase (AChE) activity by acting together with the anionic substrate binding site (Sharma et al. 2014). Resveratrol improved the brain damage caused by cypermethrin by reducing oxidative stress and enhancing AChE activity in Wistar rats (Sharma et al. 2014).

Mcdaniel and Moser (1993) have concluded that Cypermethrin causes detrimental effects such as neurobehavioral changes in pawing, burrowing, salivation, choreoathetosis, hypothermia, and reduction in the motor activity (Mcdaniel and Moser 1993). Noticeable neuromuscular weakness, lateral head movements, variations in stimuli, equilibrium changes, retropulsion, and increased urination were also observed in cypermethrin toxicity (Mcdaniel and Moser 1993). Both the acute and toxic reactions of cypermethrin on the seminal gland, a rise in the height, multiplying of the cells, and a progressive appearance of mast cells have been observed (Mun et al. 2005; Rodriguez et al. 2009). Cypermethrin stands a highly used pesticide in agricultural practices as well as in household practices to fight against insects, but their consistent use may cause chronic toxicity among humans that may disturb the male fertility in upcoming years and also affect the food (Manna et al. 2005).

8.8 Effect on Animal Health

Pyrethroids are highly lethal to fish as they affect them indirectly through insecticide-affected food materials (WHO 2014; Hossain et al. 2017). Deltamethrin is the most toxic insecticide and allethrin as the least toxic followed by intermediately toxic pyrethroids, fenvalerate, permethrin, and cypermethrin (WHO 2014). LC_{50} values for fish are less than 1.0 parts per billion (ppb) in 40% cases. Fenvalerate mainly affects the nervous system of the teleost fish. There is an alteration in the calcium uptake, abnormal excretion rates of sodium and potassium, and increase in level of urine osmolality due to the production of osmoregulatory imbalance from fenvalerate (Shafer et al. 2008; Omotoso et al. 2014; Dohlman et al. 2016). This insecticide histologically damages the gill surface of fish by accumulating in the gills and causes mucus secretion, increases the aeration capacity, and decreases oxygen uptake efficiency in gills. Fenvalerate poisoning in fish causes reduction in the schooling behavior, inability to swim close to the surface of water, hyperactivity, buoyancy loss, raised cough level, increase in the secretion of gill mucus, head shaking, and lethargy prior to death (Kotila and Yön 2015).

Alteration in the behavior of honeybees to maintenance, feeding, and communication were observed when they are exposed to permethrin. Bees which receive surface exposure in the concentration of 0.001 μg permethrin were involved in trembling dances, self-cleaning, rotation, leg rubbing, and abdomen tucking than the nonexposed bees (Cox and Wilson 1984). About 90% of bees arrive to their hive within 30 s of journey, while among the deltamethrin-treated bees, only 9% were capable to return within this time. A change in the flight patterns and homing abilities was observed when forager honeybees were exposed to 2.5 ng deltamethrin per bee in relation to nonexposed bees (Vandame et al. 1995). Permethrin-exposed bees spend less time in walking, giving food, and antennae touching. Dietary exposures of pyrethroid concentrations (i.e., as in nectar or syrup) cause irregularities in behavior and fall in the fertility. The bees which feed on syrup comprising 940 μg/L deltamethrin were reported to exhibit learned alignment toward an odor stimulus by

nearly 11–24% (Decourtye et al. 2005). Bifenthrin or deltamethrin fed diet at concentration level of 4.0, 7.9, 15.5, 30.6, and 60.2 mg/L or 20.0, 36.0, 64.8, 116.6, and 210.0 mg/L caused adverse impact in honeybees. Similarly, ingestion of bifenthrin and deltamethrin reduced the production of egg and the period in the egg stage. Exposure of deltamethrin lowered the capping frequency and prolongs the extent of the undeveloped stage (Dai et al. 2010).

The pyrethroids also influence birds because of the threat to their food supply. Small insectivorous and waterfowl are more prone to pyrethroids (Peter et al. 1996). They are mostly unaffected by pyrethroids as compared to mammals (Addy-Orduna et al. 2011). Quail ejected fenvalerate more quickly and showed poorer absorption and fast metabolism. The LD_{50} value of 4000 mg/kg body weight and 450 mg/kg body weight in quail and rat was observed when fenvalerate was administered orally which is nearly an order of 10 magnitudes higher (Dayal et al. 2003).

8.9 Degradation of Pyrethroid Residues

On the basis of clinical information and laboratory work, the pyrethroids hold estrogenic and antiprogestagenic actions and are categorized as endocrine disruptors (Garey and Wolff 1998). As a result, it is vital to create quick and proficient degradation methods to eradicate or decrease their amount in the environment. Biotic and abiotic methods comprising of photooxidation, chemical oxidation, and biodegradation degrade pyrethroids in the natural environment (Abraham and Silambarasan 2014; Abraham and Silambarasan 2016). Mainly, they are degraded by chemicals and native microorganisms present in the soil. Microorganisms play a substantial role in degradation of pyrethroids in the soil and sediments. Degradation frequency lies mainly on the type of pyrethroids, soil, climate, and the kind of microorganism and the size of their population. *Pseudomonas aeruginosa* CMG 154 make use of cypermethrin as the source of carbon (Thatheyus and Selvam 2013). The effectiveness of *Enterobacter asburiae* and *Pseudomonas stutzeri* for degradation of cypermethrin at concentration of 500 ppm was predicted (Thatheyus and Selvam 2013).

Lee et al. (2003) studied the capability of six bacterial strains and transformed bifenthrin and permethrin by isolating these bacteria from contaminated sediments. A degradation of permethrin and bifenthrin in the aqueous phase and reduction in their half-life from 700 h to 30–131 h were observed by using *Stenotrophomonas acidaminiphila*. Permethrin isomers can be degraded by using *Aeromonas sobria*, *Erwinia carotovora*, and *Yersinia*, and reduction by tenfold in the half-life of *cis*- and *trans*-permethrin was observed. Permethrin, deltamethrin, Fastac, fenvalerate, and fluvalinate were also degraded by using *Bacillus cereus*, *Achromobacter* spp., and *Pseudomonas fluorescens*. Of all the pyrethroids and deltamethrins, permethrin has a half-life of 21–28 days and can be degraded quickly (Maloney et al. 1988). The isolation of *Serratia plymuthica* and *Pseudomonas fluorescens* from synthetic pyrethroids-contaminated (SPs) farmland was noticed to degrade SPs by at least 50%. Biodegradation is a practical and suitable way for purifying SPs before disposing them either into soil, dip trough, or into the river (Grant et al. 2002).

8.10 Conclusion and Future Prospects

The resistance to change under the influence of radiant energy property of pyrethroids leads to discovery of the first pyrethroid, permethrin, and consequently this increases their use for management of pests. Pyrethroids are the broad-spectrum insecticides, that is, represent various compounds that are very toxic to nontarget land-dwelling insects and many aquatic organisms. The environmental providence and physical properties of pyrethrins and pyrethroids are clearly understood. Pyrethroids are sustained in the soil and sediments with a half-life greater than 30 days, but in contrast to legacy pesticide DDT, their half-lives are considerably lower. The sediment-residing invertebrates are mostly influenced by the pyrethroids because of their extensive half-lives mainly in urban areas where these insecticides are mostly used. Pyrethroids can be immediately biodegraded and are not biomagnified through different levels of the food chain. The research and expansion in the discovery of pyrethroids on commercial basis have mostly come to an end since the late 1990s, but in spite of this, efforts are going on to bring together isomer combinations of compounds like cypermethrin and cyhalothrin. With the ban on the use of fenvalerate and esfenvalerate, there is progress in the development of pyrethroids by many manufacturers in Japan which developed metofluthrin for commercial use; pyrethroid development appears to be well past its maximum (Matsuo et al. 2005). The pseudo-pyrethroids like etofenprox are the key for the continued commercialization of pyrethroids in Europe and the United States that are widely used and present lower acute toxicity to aquatic organisms. After 1984, pyrethrins, pyrethroids, and their synergists that were registered are presently experiencing process reviews in the United States to evaluate the efficacy of recent regulatory decisions and to consider new data. The registration review is concentrated on the progressive neurotoxicity. Pyrethroids are commonly being used for the past 40 years even though they are not pest-specific. However, they are target specific to an extensive range of pests and have low application amount, low mammalian toxicity, and a favorable environmental providence outline. The pyrethrins and pyrethroids will keep on being utilized in the future provided their utilization in a suitable way, and rules for them should be based on scientific indications.

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