Synthetic Pyrethroids: A Review

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Abstract- Pyrethroids are similar to the natural pesticide pyrethrum which is produced by Chrysanthemum flowers but it is a group of man-made pesticides. Active ingredients are found in pyrethroid insecticides are used by pest management professionals. Synthetic Pyrethroid group of compounds in the concentrations used for commercial household insects are relatively safe to human beings but are innocuous to insect pests because of low persistence in the environment. They are usually broken apart by sunlight in the atmosphere with in one to two days, and do not significantly affect groundwater quality. Pyrethroids insecticides are more stable analogs of natural insecticide and are based upon an ester found in extracts from Chyranthemum flowers. The insecticidal activity of these plant compounds is known for centuries but their use in the field is limited due to rapid breakdown in sunlight

Keywords- Chrysanthemum, Insecticides, Microorganisms, Pyrethroids

1 INTRODUCTION

India is an agrarian society. Adoption of modern farming techniques in India improved irrigation, high yielding varieties, agrochemicals and farm mechanization has made significant contributions towards raising food production. Simultaneously, large scale use of pesticides for control of insects, pests and agricultural importance has increased. The dilemma of using pesticides is that, they protect cops but their wide use is also associated with hazards ranging from acute toxicity to cumulative health effects [1, 2].

Pesticides are broadly classified as inorganic compounds and as organic compounds. Pesticides like synthetic pyrethroids and organophosphates are being widely used across the world. Frequent and enormous use of synthetic pyrethroids and organophosphates has posed the resistance problem, resurgence of the pest and health hazardous [3].

Commercial products contain pyrethroids used to control insects, including household insecticides, pet sprays and shampoos. Some pyrethroids are also used as lice treatments applied directly to the head and as mosquito repellents that can be applied to clothes. They are synthetic analogues and derivatives of the original pyrethrins and represent a diverse group over other powerful insecticides. Although they are based on the chemical modifications that make them more toxic and less degradable in environment [4].

2 CLASSIFICATION OF PYRETHROIDS

Pyrethroids can also be classified into two types on the basis of their mode of action (Table 1). Type I are based upon electrophysiological criteria. These compounds cause restlessness, in coordination and hypersensitivity followed by prostration and paralysis. Type II are classified on the basis of symptoms observed in pests, these compounds produce convulsive effects within minutes of dosing [5].

Table 1. Classification of synthetic pyrethroids

Pyrethrins	Type I pyrethroids	Type II pyrethroids
Constituents of natural pyrethrum extract	Derivatives of pyrethrins that do not include a cyano group and may elicit tumors	Derivatives of pyrethrins that include a cyano group and may elicit sinuous writhing and salivation.
Pyrethrin I	Allethrin	Cyfluthrin
Pyrethrin II	Bifenthrin	Cyhalothrin
Cinerin I	Permethrin	Cypermethrin
Cinerin II	Pheothrin	Fenvalerate
Jasmolin I	Resemethrin	Fenpropathrin
Jasmolin II	Tefluthrin	Flucythrinate
	Tetramethrin	Flumethrin
		Fluvlinate
		Tralomethrin

3 MODE OF ACTION

Pyrethrins have excellent insecticidal properties, including a higher potency for insects than for mammals, but because they are relatively unstable in environment, frequent application is necessary and can become expensive [6].

Through action on voltage gated sodium ion channels pyrethroids and pyrethrins affect nerve impulse transmission in insects mainly [7]. These were the first synthetic compounds with good knockdown activity, greater insecticidal activity and lower mammalian toxicity than the natural esters [6]. Toxicity of pyrethroids depends on its stereochemistry, the three dimensional configuration of the molecule. Each isomer has its own toxicity. Both cis- and trans- isomers show insecticidal activity but have differing mammalian toxicities, with the cis-isomers being more potent [5]. Acute toxicity of a mixture of two isomers depends on the ratio of the two isomers in the formulation. Most commercial formulations have a fixed isomeric ratio. Formulations made of a single isomer are likely to be much more toxic than those with 4 to 8 isomers [8].

The fate of pesticide applied to soil depends largely on its persistence and solubility properties. Once applied to cropland, pesticides may either be taken up by plants [9] or ingested by animals, insects or microorganisms in soil, or may move downward in the soil [10]. And either adheres to it or dissolve in water or may vaporize [11] and enter the atmosphere or may breakdown via microbial and chemical pathways in to other lesser toxic compound [12] or may leached out [13].

After application, a large portion of insecticides accumulates in the top soil layer where maximum microbiological activities occur [14]. Pyrethrins have little residual effect. Most studies indicated that pesticides have a limited effect on microbial activities related to soil fertility [15]. As a result, they are often combined with small amounts of antioxidants to prolong their effectiveness. Pyrethrum compounds are broken down in water to nontoxic products, also are inactivated and decomposed by exposure to light and air. Pyrethrins are also rapidly decomposed by mild acids and alkalis. The insecticide treatments have been observed to have significant effects on the microbial population and activities but the microorganisms recovered rapidly. These effects were not drastic but when compared with those reference chemicals or treatments, such as autoclaving. There is little evidence to suggest that these pesticides treatments have any prolonged deleterious effects on the soil microbial activities [16].

4 USES

Pyrethroids are broad spectrum insecticides, effective against a wide range of insect pests of the orders *Coleoptera, Diptera, Hemiptera (Homoptera* and *Heteroptera*), *Hymenoptera, Lepidoptera, Orthoptera* and *Thysanoptera*. Prior to harvest, they are sprayed over edible products to control pests and are also used as household insecticides and grain protectants. They are employed in animal houses, fields, green houses and extensively used in veterinary medicine [17]. (Table 2).

Several studies indicated that insecticides have little effect on microbial activities and biochemical changes related to soil fertility. Synthetic Pyrethroids are neither fully metabolized nor quickly detoxicated and therefore create serious problems of residue accumulation [18]. Soil is a dynamic, living matrix that is an essential part of the ecosystem. It is critical resource not only for agricultural production and food security but also towards maintenance of most life processes. The functions of soil biota are central to decomposition processes and nutrient cycling. Soil is considered a storehouse of microbial activity, though the space occupied by living microorganisms is estimated to be less than 5% of total space. Therefore, major microbial activity is confined to the hotspot. i.e. aggregates with accumulated organic matter, rhizosphere [19,20].

Because an active microbial population continually contributes to the exoenzyme fraction, any pesticide induced changes in microflora during the course of experiment are reflected in time related assays [21] Soil high in organic matter provides a ready substrate on which a wide range of chemicals that reach soils may be adsorbed [22]. It appears that enzyme activities in field soils

decrease temporarily after the addition of some pesticides.

Table 2. Applications of pyrethroids

Pyrethroids	Insects	Crops	Other locations and Apllications
Allethrin	Flies, Mosquitoes, Ants	N/A	Residential, public health, animal houses, topical application in pet sprays and shampoos
Bifenthrin	Beetles, houseflies, Weevils, Mosquitoes, Lice, bedbugs, aphids, moths, Cockroaches, locust	Alfaalfa, beans, cantaloupes, cereals, corn, cotton, field and grass seed, hops, melons, oilseed rape, potatoes, peas, raspberries, watermelons, squash	N/A
Bioresmethrin	Houseflies, Mosquitoes, Cockroaches	N/A	Household, public health, animal houses
Cyfluthrin	Aphids, Cabbage stem flea beetle, cockroaches, houseflies, Mosquitoes, rape winter stem weevil	rape, pears, potatoes, rice,sugar beet, sugarcane, tobacco, vegetables	
Cyhalothrin	Bedbugs, beetles, houseflies, ked, lice, mosquitoes, moths, weevils	N/A	Public health, animal houses, inert surfaces
Cypermethrin	Cockroaches, flies, mosquitoes, moths	Cotton, lettuce, onions, pears, peaches, pecans, sugar beets	Residential and commercial buildings, animal houses
Deltamethrin	Aphids, beetles, bollworm, budworm, caterpillers, cicadas, coding moths, totrix moths, weevils, whitefly, winter moths	Alfalfa, beet, cereals, coffee, cotton, figs, fruits, hops, miaze,oilseed rape, olives, oilpalms, potatoes, rice, soybeans, sunflowers, tea, tobacco, vegetables	Forests, households, animal houses, stored products
Esfenvalerate	Beetles, moths	Cabbage, corn, cotton, fruit trees, grains,groundnuts, maize, pecan, potatoes,sorghum, soybeans, sugarcane, sunflowers,	Ornamentals, non cropland

		sweetcorn, tomatoes, vegetables, wheat	
Fenvalerate	Beetles, cockroaches, flies, locusts, mosquitoes, moths	Alfalfa hay, apples, beet, cereals, cotton, corn, cucurbita, fruit greenbeans, groundnuts, hops, maize, nuts, oilseed rape, olives, potatoes, sorghum, soybeans, squash, sugarcane, sunflower, vegetables,vines, tobacco	Ornamentals, forestry, non crop land
Fluvalinate	Aphids, leaf hoppers, moths, spider mites, thrips, white flies	Apples, cereals, cotton, pears, peaches, tobacco, vegetables, vines	Outdoor and indoor ornamentals, turf
Permethrin	Ants, beetle, bollworm, budworm, fleas, flies, lice, moths, mosquitoes, termites, weevils	Alfalfa hay, corn, cotton, grains, lettuce, onion, peaches, potatoes, sweetcorn, tomatoes, wheat	Home gardens, green houses, pet sprays and shampoos

The major role in the metabolism of constituents of soil is played by microorganisms as they are scavengers in soil and degrade a great variety of insecticides to derive energy and other nutrients for their metabolism [23]. While some insecticides exert adverse effect on the proliferation of microorganisms and their associated transformations in soil [24].

The present pyrethroid insecticides are not very toxic to a wide range of nontarget organisms because of their low application rates. When tested towards fungal and bacterial population in soil and sediment, pyrethroids (deltamethrin, fenvalerate, and cypermethrin) all yield no response to short term inhibition or stimulation [21]**.** Ahmed and Casida [25] studied the accumulation of insecticides in the microbes. The rate of accumulation was very rapid in the beginning and maximum amount was accumulated within 2-6 hr and decreased with increase in biomass.

When exposed to different types and concentrations of insecticides, bacterial resistance and growth stimulation were found to be different. In the area of contamination of pesticides one of the major problems is their long persistence in nature that amplifies the toxicity and health risk problems asides from toxicity and carcinogenicity of pesticides [26].On the application of cypermethrin to *Pseudomonas*, the count increases with low concentration but at high concentration the number of organism significantly decrease during 24 hr of incubation when compared to control. Incorporation of insecticides in general, stimulated the proliferation of (total) bacteria, actinomycetes and fungi. These reports sustains the reports of Das *et al*., [27]. BHC, Phorate and Fenvelerate significantly augmented the proliferation of all microorganisms. This indicates greater utilization of insecticides as well as their degraded products by microorganism to derive energy and other nutrients for their metabolism [23].

High doses of Cypermethrin may exert transient effects on microflora activity in soil but they are short lived and minor in nature [16]. Grant and Betts [28] found that after 96 h of incubation *Pseudomonas* degraded the cypermethrin greatly than *Serratia.* The mechanism for the degradation was co-metabolism rather than diauxic growth

[29]. There is an evidence to support that if concentration of xenobiotic present is not high enough then its only degradation route may be via co-metabolism [30].

Persson [31] reported that the insecticide deltamethrin had no significant effect on bacterial activity and its degradation is very slow because of high log K_{aw} of 4.7 thus adsorbs strongly to particles in water. Also it is readily degraded by microorganisms and their products are less toxic.

Recent studies showed that synthetic pyrethroids could move via surface run off into aquatic system. Lee *et al*. [32] isolated 56 synthetic pyrethroids from contaminated sediments, of which six were evaluated for transformation of bifenthrin and permethrin in sediment phase.

5. MECHANISM OF TOXICITY

Synthetic pyrethroids are classified into two types, according to their chemical structure: type I pyrethroids, which do not contain an alpha-cyano group in their molecule and which cause mainly tremors (T-syndrome); and type II pyrethroids, which do contain an alpha-cyano group and which cause choreoathetosis and salivation (CS-syndrome) [33]. Many pyrethroids exhibit both T and CS characteristics, and sometimes these two syndromes combine [34,35]. In mammals the toxicity of pyrethroids is caused by insecticidal activity. The difference in the toxicity is mainly in the voltage-sensitive sodium channels in insects (target organisms) and mammals [36,34]. Invertebrates and some cold-blooded species are more susceptible to the toxic effects of pyrethroids than vertebrates [36]. In case of humans occupational exposure to pyrethroids may occur through dermal contact and inhalation of dust and sprays. Inhalation by industrial workers is the main route of exposure while skin is the main route of exposure in workers applying the compounds in agriculture or public health [37].

6. CONCLUSION

To conclude, pyrethroids are characterized by a moderate acute toxicity and do not show any evidence of long-term toxicity in humans. They do not pose any significant health risk when they are used in compliance with their directions for use and are intended to limit human exposure within the levels recommended for their specific applications. Despite the absence of demonstrated or predicted health effects, unnecessary exposure to pyrethroids – as for all chemicals – should be avoided: they should be only used when there is a need, and levels of exposure and amounts used should be kept to a minimum that still guarantees the desired public health effect.

REFERENCES

1. D.R. Morgan, *The BMA guide to pesticides, chemicals and health.* British Medical Association: U.K. vii: 215, 1992.
2. M. Hussain, *Environmental degradation, realities and remedies*. Ferozsons (Pvt) Ltd. Lahore, Pakistan; 1998.
3. K.N. Mehrotra, Pyrethroids resistant insect pest management. Indian experience. *Pesticide Research Journal*, vol 2, no. 1, pp. 44-52, 1990.
4. C.D.S. Tomlin, (ed.). *The Pesticide Manual-World Compendium*. 11th ed. British Crop Protection Council Surrey, England, 577, 1997.
5. D.E. Ray, *Pesticides derived from plants and other organisms.* In: W.J. Hays Jr. and E.R. Laws (Eds.). Handbook of Pesticide Technology. Toronto: Academic Press, vol. 2, pp. 585-593, 1991.
6. M.Elliott, "Synthetic pyrethroids. In: Elliott M, ed. Synthetic pyrethroids." *American Chemical Society Symosium Series 42. Washington DC: American Chemical Society*, pp. 1-28,1997.
7. D.M. Soderlund and J.R. Bloomquist, Review: Neurotoxic actions of pyrethroid insecticides. *Annu Rev Entomol,* vol. 34, pp. 77-96, 1989.
8. S.P. Bradbury and J.R. Coats, Review: Comparative toxicology of the pyrethroid insecticides. *Rev Environ Contam Toxicol.* 1989; 108:133-77.
9. D.R. Nair, J.G. Burken, L.A. Licht and J.L. Schnoor, Mineralization and uptake of triazine pesticide in soil-plant systems. *J Environ Eng*, vol. 119, no. 5, pp. 842-854, 1993.

10. C.H. Sujatha, and J. Chacko, Organophosphorous pesticide adsorption variability in diverse estuarine sediments. *Toxicol Environ Chem*, vol. 36, no. 1, pp. 65-73, 1992.
11. R.J. Maguire, Aquatic environmental fate of Deltamethrin. *Water Science and Technology*, vol. 25, no. 11, pp. 99-102, 1992.
12. M.K. Pillai, Pesticide pollution of soil, water and air in Delhi area, India. *Sci Total Envrionment*, vol. 55, no. 1, pp. 321-327, 1986.
13. S. Li and J. Migita, Pesticide runoff from paddy field and its impact on receiving water. *Water Sci Technol*, vol. 25, pp. 69-76, 1992.
14. M. Alexander, "Introduction to soil microbiology". Wiley Eastern Limited, New Delhi, India. ISBN 0-85226-013-X; 1978.
15. C.M. Tu and J.R.W. Miles, Interaction between insecticides and soil microbes. *Res Rev*, vol. 64, pp. 17-65, 1976.
16. C.M. Tu, Influence of pesticides and some of the oxidized analogues on microbial populations, nitrification and respiration activities in soil. *Bulletin Environment Contamination Toxicology*, vol. 24, no. 1, pp. 13-19, 1980.
17. D.J. Ecobichon, *Toxic effects of pesticides*. Chapter 22. In: Klaassen CD, Amdur MO, Doull J. (eds). Casarett & Doull's Toxicology: The Bask Science of Poisons, 5th edn. McGraw-Hill, Health Professions Division. New York, NY, pp. 643-690, 1996.
18. A. Dhawan and K. Kaur, Toxic effects of synthetic pyrethroids on *Cyprinus Carpio* linn eggs. *Bulletin Environment Contamination Toxicology*, vol. 57, pp. 999-1002, 1996.
19. J.M. Lynch, *Introduction: some consequences of microbial rhizosphere competence for plant and soil*. In: Lynch JM ed., The Rhizosphere, John Wiley and Sons, Chichester, UK, pp. 1-10, 1990.
20. R. Pinton, Z. Varanini, Z and P. Nannipieri, *The Rhizosphere: Biodiversity and organic substances at the Soil-Plant interface*, Marcel Dekker, New York; 2001.
21. C.M. Tu, Effects of some pesticides on enzyme activities in an organic soil. *Bulletin Environment Contamination Toxicology*, vol. 24, pp. 109-114, 1981.
22. C.A. Edwards, Insecticide residues in soils. *Residue Reviews*, vol. 13, pp. 83-132, 1966.
23. S. Bhuyan, B. Sreedharan, T.K. Adhya and N. Sethunathan, Enhanced biodegradation of γ-hexachlorocyclohexane (γ- HCH) in HCH (commercial) acclimatized flooded soil: Factors affecting its development and persistence. *Pesticide Science*, vol. 38, pp. 49-55, 1993.
24. M.V. Martinez-Toledo, V. Salmeron and J. Gonzalez-Lopez, Effect of organophosphorous insecticide, phenofos on agricultural soil microflora. *Chemosphere*, vol. 24, pp. 71-80, 1992.
25. M.K. Ahmed and J.E. Casida, Metabolism of some organophosphorous insecticides by microorganisms. *Journal of Economic Entomology*, vol. 51, pp. 59-63, 1958.
26. H. Mugni, P. Demetrio, G. Bulus, A. Ronco and C. Bonetto, Effect of aquatic vegetation on the persistence of cypermethrin toxicity in water. *Bulletin Environment Contamination Toxicology*, vol. 86, no. 1, pp. 23-27, 2011.
27. A.C. Das, A. Chakravarty, P. Sukul and D. Mukherjee, Insecticides: Their effects on microorganisms and persistence in rice soil. *Microbiological Research*, vol. 50, pp. 187-194, 1995.
28. R.J. Grant and W.B. Betts, Mineral and carbon usage of two synthetic pyrethroid degrading bacterial isolates. *Journal of Applied Microbiology*, vol. 97, no.3, pp. 656-662, 2004.
29. M.A. Sogorb and E. Vilanova, Enzymes involved in the detoxification of organophosphorous, carbamate and pyrethroid insecticides through hydrolysis. *Toxicology Letters*, vol. 128, pp. 215-228, 2002.
30. E.S.B. Limbert and W.B. Netts, Biodegradation of trace levels of a complex organic pollutant mixture. *Microbios*, vol. 78, no. 317, pp. 237-243, 1994.
31. M. Persson, "Effects of modern pesticides on bacterial activity and denitrification in lake sediment". Master thesis. Department of Environmental Assessment, Swedish University of Agricultural Sciences, vol. 20, 2000.
32. S. Lee, J.Y. Gan, J.S. Kim, J.N. Kabashima, and D.E. Crowley, Microbial transformation

of pyrethroid insecticides in aqueous and sediment phases. *Environ Toxicol Chem*, vol. 23, no. 1, pp. 1-6, 2004.

33. W.F. Tordoir, M. Maroni and F. He, *Health surveillance of pesticide workers*. A manual for occupational health professionals (ICOH–ICPS–WHO, vol. 91, 1994.
34. D.M. Soderlund, J.M. Clark, L.P. Sheets, L.S. Mullin, V.J. Piccirillo, D. Sargent, J.T. Stevens and M.L. Weiner, Mechanisms of pyrethroid neurotoxicity: Implications for cumulative risk assessment. *Toxicology*, vol. 171, pp. 3-59, 2002.
35. W.N. Aldridge, An assessment of the toxicological properties of pyrethroids and their neurotoxicity. *Toxicology*, vol. 21, no. 2, pp. 89-104, 1990.
36. T. Narahashi, K.S. Ginsburg, K. Nagata, J.H. Song and H. Tatebayashi, Ion channels as targets for insecticides. *Neurotoxicology*, vol. 19, no. 4-5, pp. 581-590, 1998.
37. IPCS – International Programme on Chemical Safety. Cyhalothrin. Environmental Health Criteria 99. Geneva, World Health Organization; 1990.