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WHITE PAPER ON PYRETHROIDS

Pyrethroids and Health Effects

Pyrethroids have irritant and/or sensitizing properties. They are not easily absorbed through the skin, but are absorbed through the gut and pulmonary membrane. Tests of some pyrethroids on laboratory animals reveal striking neurotoxicity when administered by injection or orally. Systemic toxicity by inhalation and dermal absorption is low. The acute toxicity, calculated by LD50's, ranges from low to high, depending on the specific formulation. Low toxicity is attributed to two factors: limited absorption of some pyrethroids, and rapid biodegradation by mammalian liver enzymes (ester hydrolysis and oxidation). Insects, without this liver function, exhibit greater susceptibility to the chemicals (Reigart et al., 1999).

Pyrethroids interfere with the ionic conductance of nerve membranes by prolonging the sodium current. This stimulates nerves to discharge repeatedly causing hyper-excitability in poisoned animals. The World Health Organization explains that synthetic pyrethroids are neuropoisons acting on the axons in the peripheral and central nervous systems by interacting with sodium channels in mammals and/or insects. The main systems for metabolism include breakage of the ester bond by esterase action and oxidation at various parts of the molecule. Induction of liver microsomal enzymes has also been observed (WHO, 1999).

Signs and symptoms of poisoning by pyrethroids may take several forms. Because of the similarities to crude pyrethrum, pyrethroids may act as dermal and respiratory allergens. Exposure to pyrethroids has resulted in contact dermatitis and asthma-like reactions. Persons, especially children, with a history of allergies or asthma are particularly sensitive, and a strong cross-reactivity with ragweed pollen has been recognized. Severe anaphylactic (allergic) reactions with peripheral vascular collapse and respiratory difficulty are rare. Other symptoms of acute toxicity due to inhalation include sneezing, nasal stuffiness, headache, nausea, incoordination, tremors, convulsions, facial flushing and swelling, and burning and itching sensations. The most severe poisonings have been reported in infants, who are not able to efficiently break down pyrethroids (ETN, Pyrethroids, 1994). With orally ingested doses, nervous symptoms may occur, which include excitation and convulsions leading to paralysis, accompanied by muscular fibrillation and diarrhea (ETN, Pyrethroids, 1994). Death in these cases is due to respiratory failure. Symptoms of acute exposure last about 2 days.

Endocrine Disruption and Breast Cancer

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Many pyrethroids have also been linked to disruption of the endocrine system, which can adversely affect reproduction and sexual development, interfere with the immune system and increase chances of breast cancer. Pyrethroids contain human-made, or xenoestrogens, which can increase the amount of estrogen in the body (Garey et al., 1998). When tested, certain pyrethroids demonstrate significant estrogenicity and increase the levels of estrogen in breast cancer cells (Go et al., 1999). Because increased cell division enhances the chances for the formation of a malignant tumor in the breast, artificial hormones, like those found in pyrethroids, may increase breast cancer risk (PCBR, 1996). Some pyrethroids are classified by EPA as class C (possible human) carcinogens.

Pyrethroids and the Environment

While the development of the synthetic pyrethroids was heralded with claims of selective toxicity to insects, both pyrethroids and pyrethrins are extremely toxic to aquatic organisms, including fish such as the bluegill and lake trout, with LC50 values less than 1.0 parts per billion. These levels are similar to those for mosquito, blackfly and tsetse fly larvae, often the actual target of the pyrethroid application. Lobster, shrimp, mayfly nymphs and zooplankton are the most susceptible non-target aquatic organisms (Mueller-Beilschmidt, 1990). The nonlethal effects of pyrethroids on fish include damage to the gills and behavioral changes.

Pyrethroids are moderately toxic to birds, with most LD50 values greater than 1000 mg/kg. Birds can also be indirectly affected by pyrethroids, because of the threat to their food supply. Waterfowl and small insectivorous birds are the most susceptible (Mueller-Beilschmidt, 1990). Because pyrethroids are toxic to all insects, both beneficial insects and pests are affected by pyrethroid applications. In some cases, predator insects may be susceptible to a lower dose than the pest, disrupting the predator-prey relationship.

Pyrethroids Residues / Persistence

As mentioned before, pyrethroids are designed to breakdown more slowly than the naturally occurring pyrethrins. While pyrethrins, extremely sensitive to light, heat and moisture, break down in a few hours, the synthetic pyrethroids are stable and persist in the environment much longer. With a few exceptions, pyrethroids break down most quickly in direct sunlight, usually just a few days after application, with a few exceptions. However, in areas with limited sunlight, such as grain silos and subway tunnels, pyrethroids can persist for months. For more specific breakdown times see the sections below on bifenthrin, cypermethrin, deltamethrin, fenvalerate, permethrin, resmethrin and sumithrin.

Synergists

Both pyrethroids and pyrethrins are often formulated with oils or petroleum distillates and packaged in combination with synergists, such as piperonyl butoxide (PBO) and n-octyl bicycloheptene dicarboximide (Gosselin et al., 1984). Synergists are added to increase the potency of the pesticide. A range of products from repellants to foggers to

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pediculicides (lice killers) to garden sprays contain synergists. Many formulations of synthetic pyrethroids, including ScourgeTM and AnvilTM, used along the East Coast for mosquito control to combat the West Nile Virus, contain the synergist PBO.

PBO inhibits important liver enzymes responsible for breakdown of some toxins, including the active ingredients of pesticides. Specifically, it has been shown to inhibit hepatic microsomal oxidase enzymes in laboratory rodents and interfere in humans. Because these enzymes act to detoxify many drugs and other chemicals, a heavy exposure to an insecticidal synergist may make a person temporarily vulnerable to a variety of toxic insults that would normally be easily tolerated. Symptoms of PBO poisoning include anorexia, vomiting, diarrhea, intestinal inflammation, pulmonary hemorrhage and perhaps mild central nervous system depression. Repeated contact may cause slight skin irritation. Chronic toxicity studies have shown increased liver weights, even at the lowest doses, 30 mg/kg/day. While not considered a carcinogen by EPA, animal studies have shown hepatocellular carcinomas, even treatments as low as 1.2% (Takahashi et al., 1994).

Bifenthrin (TalstarTM, BrigadeTM, CaptureTM)

Bifenthrin is an off-white to pale tan waxy solid, characterized by its slightly sweet smell. As a Restricted Use Pesticide, bifenthrin may only be purchased or applied by certified applicators or persons under the direct supervision of a certified applicator. EPA has registered bifenthrin for use on greenhouse ornamentals and cotton. Studies show bifenthrin to be relatively insoluble in water. Its half-life in soil can range anywhere from 7 days to 8 months depending on the soil type and the amount of air in the soil (ETN, Bifenthrin, 1995). Bifenthrin is one of a few synthetic pyrethroids that are relatively stable in direct sunlight. EPA has classified products containing bienthrin as toxicity class II (I = most toxic, IV = least toxic), and the word WARNING must appear on all product labels.

Bifenthrin is moderately toxic to mammals when ingested (oral rat LD50 = 54 to 70 mg/kg), and like all pyrethroids affects the central nervous system. Symptoms of poisoning include incoordination, tremor, salivation, vomiting, diarrhea, and irritability to sound and touch (ETN Bifenthrin, 1995). Although bifenthrin does not cause inflammation or irritation on human skin, it can cause a tingling sensation, lasting about 12 hours. A study on laboratory mice shows that bifenthrin causes gene mutation in white blood cells (ETN, Bifenthrin, 1995). EPA classifies bifenthrin as a Class C (possible human) carcinogen (EPA, 1997). Of concern in the environment, bifenthrin is very highly toxic to fish, crustaceans, other aquatic animals and bees, and is moderately toxic to birds. Scientists are particularly concerned about possible bioaccumulation in birds.

Bifenthrin

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Trade or other Names:
Bifenthrin, Bifenthrin 100EC, Biflex, Bifenthrine, Brigade,
Capture, FMC 54800, OMS3024, Torant (with Clofentezine), and
Zipak (with Amitraz)

Physical Properties:
CAS Number: 82657-04-3
Description: Light brown, aromatic odour
Molecular formula:
Molecular weight:
Melting point : 68-70.60C
Solubility: Water - 0.1 mg/L. Bifenthrin is soluble in methylene chloride, acetone, chloroform, ether and toluene. It is slightly soluble in heptane and methanol.
Specific gravity: 0.909

Regulatory Status:
AUSTRALIAN GUIDELINES
NOHSC: no standard
Schedule 6 poison (PESKEM, 1995). The pest control operator must be licensed under State legislation.
OVERSEAS GUIDELINES
US: Restricted Use Pesticide. Registered for use on greenhouse ornamentals and cotton.
ADI: 0.015 mg/kg
NOEL: 2.5 mg/kg/day (rat); 1.5 mg/kg/day (dog)
RfD: 0.015 mg/kg/day

Technical Info:
CATEGORY: Pyrethroid
USE

Domestic: Termiticide. Used as a pre-construction termite barrier.

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Agricultural: In the US registered for use on greenhouse ornamentals and cotton (Extoxnet). In Australia, registered for use on apples, bananas, carnations, cotton, ornamentals, pears and roses (PESKEM, 1995).

Industrial:

ACUTE TOXICITY
Bifenthrin is moderately toxic to mammals when ingested (Extoxnet). Large doses may cause incoordination, tremor, salivation, vomiting, diarrhea, and irritability to sound and touch
Moderately irritating to the eyes. Contact with skin may be irritating. Dermal sensitisation may occur.

CHRONIC TOXICITY
Repeated exposure of laboratory animals to bifenthrin caused tremors.

Carcinogenic: The EPA has classified bifenthrin as a
Class C carcinogen, a possible human carcinogen (Extoxnet).
Mutagenic: Evidence of mutagenic effects from exposure to bifenthrin is inconclusive (Extoxnet).
Teratogenic: Bifenthrin does not demonstrate any teratogenic effects at the highest levels tested (100 ppm, approximately 5.5 mg/kg/day) in a two-generation study in rats (Extoxnet).
Reproductive effects: The dose at which no toxic effect of bifenthrin is observed on the mother (maternal toxicity NOEL) is 1 mg/kg/day for rats and 2.67 mg/kg/day for rabbits (Extoxnet).

FATE IN THE ENVIRONMENT
Low mobility in most types of soil. Its half-life in soil is 7 days to 8 months depending on the soil type and the amount of air in the soil. It is also relatively insoluble in water, so it has a low potential for contaminating groundwater (Extoxnet).

ACTION ON ANIMALS
Bifenthrin is moderately toxic to many species of birds, very highly toxic to fish, crustaceans and aquatic animals, and is toxic to bees (Extoxnet).
Toxic to fish.
LD50 oral: rat - 531 mg/kg
LD50 rabbits (dermal): 2000 mg/kg

ACTION ON PLANTS
Bifenthrin is not absorbed by plant foliage, nor does it translocate in the plant (Extoxnet).

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REGULATORY STATUS

Bifenthrin is a Restricted Use Pesticide (RUP). It is for retail sale to and use only by certified applicators or persons under their direct supervision. It is only for the uses covered by the applicators certification (2). In the U.S., bifenthrin is registered for use on greenhouse ornamentals and cotton (4).

INTRODUCTION

Bifenthrin is a member of the pyrethroid chemical class. It is an insecticide and acaricide which affects the nervous system and causes paralysis in insects (1, 2). It is very highly toxic to fish and aquatic organisms (2, 3). The U.S. EPA has classified bifenthrin as Toxicity Class II-moderately toxic. Products containing bifenthrin must bear the SIGNAL WORD: WARNING. It is available as an emulsifiable concentrate or a wettable powder (4).

TOXICOLOGICAL EFFECTS

ACUTE TOXICITY

Bifenthrin is moderately toxic to mammals when ingested. Large doses may cause incoordination, tremor, salivation, vomiting, diarrhea, and irritability to sound and touch (10). The dose at which half of the test animal die, the LD50, for bifenthrin is about 54 mg/kg in female rats and 70 mg/kg in male rats (5). The LD50 for rabbits whose skin is exposed to bifenthrin is greater than 2,000 mg/kg (2). Bifenthrin does not sensitize the skin of guinea pigs (3). Although it does not cause inflammation or irritation on human skin, it can cause a tingling sensation which lasts about 12 hours. It is virtually non-irritating to rabbit eyes (10).

CHRONIC TOXICITY

Reproductive Effects

The dose at which no toxic effect of bifenthrin is observed on the mother (maternal toxicity NOEL) is 1 mg/kg/day for rats and 2.67 mg/kg/day for rabbits. At higher doses, test animals had tremors (9). The dose at which no toxic effect is observed on development (developmental toxicity NOEL) is 1 mg/kg/day for rats and is greater than 8 mg/kg/day for rabbits (2).

Teratogenic Effects

Bifenthrin does not demonstrate any teratogenic effects at the highest levels tested (100 ppm, approximately 5.5 mg/kg/day) in a two- generational study in rats (5).

Mutagenic Effects

Evidence of mutagenic effects from exposure to bifenthrin are inconclusive. Studies of mouse white blood cells were positive for gene mutation. However, other tests of bifenthrin's mutagenic effects, including the Ames test and studies in live rat bone marrow cells, were negative (2).

Carcinogenic Effects

There was no evidence of cancer in a 2-year study of rats who ate as much as 10 mg/kg/day of bifenthrin. However, an 87 week feeding study of mice with doses of 7, 29, 71, and 86 mg/kg showed a significantly higher, dose related trend of increased tumor incidence in the male urinary bladder (5, 9). The incidence was significantly increased at 86 mg/kg/day. Also, females had higher incidences of lung cancer than the controls at doses of 7 mg/kg and higher (9). The EPA has classified bifenthrin as a class C carcinogen, a possible human carcinogen (2, 5).

Organ Toxicity

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Pyrethroids are poisons that affect the electrical impulses in nerves, over-stimulating nerve cells causing tremors and eventually causing paralysis (2).

Fate in Humans and Animals

Bifenthrin is absorbed through intact skin when applied topically (10). It undergoes similar modes of breakdown within animal systems as other pyrethroid insecticides. In mammals, bifenthrin is rapidly broken down and promptly excreted. Rats treated with 4 to 5 mg/kg, excreted 70 % in the urine and 20% in the feces within 7 days. After 7 days, the remaining bifenthrin was found accumulated in tissues with high fat content such as the skin and fat in males and females and the ovaries of females (9). Bifenthrin is less toxic to warm-blooded animals, such as mammals, than to cold-blooded animals (10).

ECOLOGICAL EFFECTS

Effects on Birds

Bifenthrin is moderately toxic to many species of birds (1). The dietary concentration (8 day) at which half of the test animals die, the LC50, is 1,280 ppm for mallard ducks and 4,450 ppm for bobwhite quail (7). The acute oral LD50 is 1,800 mg/kg for bobwhite quail and 2,150 mg/kg for mallard ducks. There is concern about possible bioaccumulation in birds (5).

Effects on Aquatic Organisms

Bifenthrin is very highly toxic to fish, crustaceans and aquatic animals (1, 2). The LC50 after a 96-hour exposure is 0.00015 mg/l for rainbow trout, 0.00035 mg/l for bluegill, and 0.0016 mg/l for Daphnia (4, 5). Because of its low water soilubility and high affinity for soil, bifenthrin is not likely to be found in aquatic systems.

Effects on Other Animals (Nontarget species)

Bifenthrin is toxic to bees (3).

ENVIRONMENTAL FATE

Breakdown of Chemical in Soil & Groundwater

Bifenthrin does not move in soils with large amounts of organic matter, clay and silt. It also has a low mobility in sandy soils that are low in organic matter. Bifenthrin is relatively insoluble in water, so there are no concerns about groundwater contamination through leaching. It's half-life in soil, the amount of time it takes to degrade to half of its original concentration, is 7 days to 8 months depending on the soil type and the amount of air in the soil (2, 3).

Breakdown of Chemical in Vegetation

Bifenthrin is not absorbed by plant foliage, nor does it translocate in the plant (5).

PHYSICAL PROPERTIES AND GUIDELINES

Bifenthrin is an off-white to pale tan waxy solid with a faint, slightly sweet smell (5). It is photostable, stable to hydrolysis, has minimal volatility, and is stable in storage. It has a negative temperature coefficient, so it works better at lower temperatures (8).

Physical Properties:

CAS #: 82657-04-3

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Chemical Name: (2-methyl-1, 1-biphenyl-3-y1)-methyl-3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethyl cyclopropanecarboxylate
Melting point: 68-70.6 degrees C (5)
Solubility in water: 0.1 mg/l (4)
Solubility in solvents: Bifenthrin is soluble in methylene chloride, acetone, chloroform, ether and toluene. It is slightly soluble in heptane and methanol (4).
Partition Coefficient (octonal/water) Kow = 1,000,000 (4)

Exposure Guidelines:
ADI: 0.015 mg/kg (4)
NOEL: 2.5 mg/kg/day (rat); 1.5 mg/kg/day (dog) (2, 6)
RfD: 0.015 mg/kg/day (6)

Soil:

Residual soil activity: Bifenthrin is generally active in the soil. Some bifenthrin is absorbed from the soil by plants.
Adsorption: Bifenthrin is immobile in soil containing large amounts of organic matter, clay and silt. Mobility is low in soils with low exchange capacity such as sandy soil not containing much organic matter. Bifenthrin tightly binds to soil soon after application.
Persistence and agents of degradation: Bifenthrin remains unchanged in the soil for varying lengths of time, depending on soil texture and organic matter content. The half-life of bifenthrin can range from 7 days to 8 months. Degradation is dependent upon oxidative microbial activity on soil-bound bifenthrin.
Metabolites/degradation products and potential environmental effects: The main break-down products of bifenthrin in the soil are 2-methyl-3-phenyl-benzyl alcohol, 2-methyl-3-phenylbenzoic acid, 2-methyl-3-phenylbenzaldehyde, 4'-hydroxy bifenthrin, and cis,trans-4-(2-chloro-3,3,3-trifluoro-1-propenyl)-3,3-dimethylcyclopropanecarboxylic acid. Aerobic soil degradation and metabolism studies conducted by the manufacturer and accepted by the EPA indicate that the metabolites are futher degraded by conversion to carbon dioxide. The level of metabolites detected in these studies was not significant.
Non-target toxicity:

Soil microorganisms: Insufficient information available.
Plants: Bifenthrin is not toxic to most plants.
Aquatic animals: Bifenthrin is highly toxic to fish and aquatic invertebrate animals. It builds up (bioaccumulates) in fish. Acute toxic level:
species LC50 Source Table
fish 0.10-0.18 ppb (Table II, Aquatic)
water flea 1.6 ppb (Table II, Aquatic)

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Terrestrial animals: Bifenthrin is slightly toxic to birds and moderately toxic to mammals. It is highly toxic to bees. Bifenthrin is toxic to many insects, mites and spiders. Acute toxic level:
species LD50 Source Table
mallards 2,150 mg/kg (Table II, Avian)
quail 1,800 mg/kg (Table II, Avian)
honey bee 0.0146 micrograms/bee ---

Threatened and endangered species: The use of bifenthrin is prohibited in areas where its use may result in exposure of endangered species to bifenthrin. Prior to use in a particular county contact the local extension service for procedures and precautions to use to protect endangered species.

V. Toxicology Data

Acute toxicity:

Acute oral toxicity: In tests in rats, the acute oral LD50 for bifenthrin was 53.8 mg/kg for females and 70.1 mg/kg for males. (Toxicity Category II, Table I, Oral)
Acute dermal toxicity: The acute dermal LD50 for bifenthrin was >2,000 mg/kg in rabbits. (Toxicity Category III, Table I, Dermal)
Primary irritation score: Bifenthrin has not been shown to be a skin irritant.
Primary eye irritation: In tests in rabbits, bifenthrinwas virtually nonirritating to the eyes.
Acute inhalation: The LC50 in rats was 1.86 mg/L for the Capture 2EC formulation.

Chronic toxicity:

Carcinogenicity: In a 2 year study in rats fed up to 200 ppm, bifenthrin showed no evidence of carcinogenicity. In an 87 to 92 week study in mice, there was an increase in the number of bladder tumors at the highest dose tested (600 ppm in the feed).

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Developmental: In rats, the no observed effect level for developmental toxicity was 1 mg/kg per day. In a study in rabbits the no observed effect level for developmental toxicity was >8 mg/kg per day.
Reproduction: In a two generation feeding study in rats, the no observed effect level for reproductive toxicity was >100 ppm.
Mutagenicity: One laboratory test for gene mutation was positive, but four other tests for mutagenicity were negative.
Hazard: Based on the results of animal studies, bifenthrin is not classified as a teratogen or a reproductive inhibitor. Bifenthrin has been classified by the EPA as Class C (possible human) carcinogen. Bifenthrin is neurotoxic.