ENVIRONMENTAL FATE OF BIFENTHRIN

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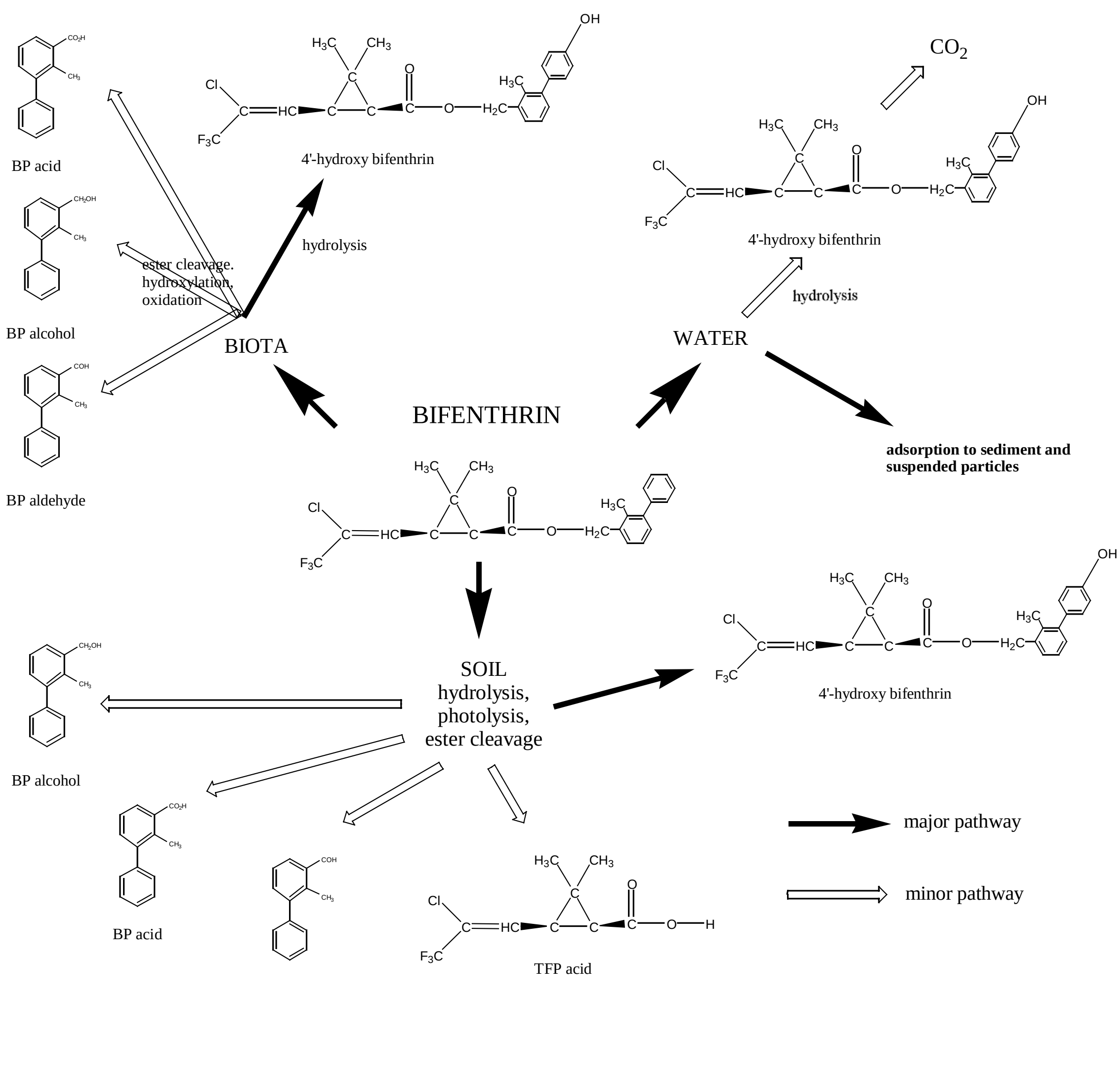
This document reviews all routes of environmental fate for bifenthrin ((2-methyl-1, 1-biphenyl-3-y1)-methyl-3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethyl cyclopropanecarboxylate) with an emphasis on its use in controlling red imported fire ants. Bifenthrin is a member of the pyrethroid family of chemicals.

Bifenthrin Degradation



Physical Properties

Molecular weight	422.9
Water solubility (at 25°C)	0.1mg/L
Vapor pressure (at 25°C)	1.81×10^{-7} mm/Hg
Henry's constant (pH 7, 25°C)	7.20×10^{-3} atm m^3/mol
Hydrolysis half-life (in natural water, at pH 6.7 and 25°C)	Stable
Octanol-water coefficient (Kow)	1.0×10^6
Anaerobic half-life	97-156 days
Aerobic half-life	65-125 days
Field dissipation half-life	122 to 345 days
Specific gravity (at 25°C)	1.212 g/ml
Bio-concentration factor (whole body, bluegill sunfish)	6000x
Soil adsorption coefficient (Koc)	$1.31 - 3.02 \times 10^5$
Photolysis	276-416 days

Toxicity

Rat	LD_{50} 54 - 70 mg/kg
Mallard	LD_{50} 2,150 mg/kg
Bobwhite Quail	LD_{50} 1,800 mg/kg
Mallard	LC_{50} 1,280 ppm
Bobwhite Quail	LC_{50} 4,450 ppm
Rainbow trout (96 hour)	LC_{50} 0.00015 ppm
Bluegill sunfish (96 hour)	LC_{50} 0.00035 ppm
Daphnia magna (96 hour)	LC_{50} 0.0016 ppm

(Farm Chemicals Handbook, 1998)

General Characteristics and Mode of Action

Bifenthrin is a member of the synthetic pyrethroid family of pesticides. Like most pyrethroid pesticides, bifenthrin affects the central and peripheral nervous system of insects causing paralysis (Miller and Salgado, 1985). Because of their high toxicity to aquatic organisms, bifenthrin products are registered as "restricted use pesticides", to be sold only to and used by Certified Pesticide Applicators. In addition to Red Imported Fire

Ant (RIFA) control, bifenthrin is used as a miticide and acaricide in orchards, nurseries, and homes.

Bifenthrin is a third-generation synthetic pyrethroid chemical. This group is characterized by greater photostability and greater insecticidal activity than previous pyrethroids (Mokry and Hoagland, 1989.) Little research has been done specifically on bifenthrin's mode of action on invertebrates or vertebrates, however, most investigations have found that the pyrethroid family of pesticides demonstrate very similar effects on invertebrate nervous systems (Miller and Salgado, 1985).

Pyrethroids utilize a number of different pathways to cause nervous system damage in invertebrates (Miller and Salgado, 1985). Significant among these is interference with sodium channel gating in the nerve cell endings (Lund and Narahashi, 1981). By acting on the sodium channels to depolarize the pre-synaptic terminals, pyrethroid insecticides effectively paralyze organisms by severely limiting neuro-transmission (Salgado et al, 1983). This paralysis is often preceded by spastic activity of the organism due to the hyper-activity of nerve endings. The spastic activity is caused by sodium channels repeatedly polarizing and depolarizing, mimicking neuro-transmission where none is actually taking place.

Pyrethroids have also been shown to inhibit ATPase enzyme production (Clark and Matsumura, 1982). This is of primary importance in understanding why aquatic organisms are much more susceptible to pyrethroid insecticides than terrestrial organisms. Freshwater aquatic organisms must maintain ionic balances and osmoregulation in an extremely dilute environment. Active transport at cellular walls is needed to maintain critical cellular ion levels against a concentration gradient. ATPase enzymes provide the energy needed by cells to maintain this gradient. By inhibiting ATPase enzymes, pyrethroids breakdown the critical concentration gradient, eventually leading to death of the organism. Pyrethroids have the most serious effects on fish and gill breathing aquatic insects because of the large surface area available to de-ionize after ATPase inhibition (Siegfried, 1993).

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Air: Bifenthrin has a vapor pressure of 1.81×10^{-7} mm/Hg and a Henry's law constant of 7.20×10^{-3} atm m^3/mol (FMC 50429-007, 1983). These values indicate that bifenthrin has a low potential to volatilize into air when applied to dry soil, and a somewhat higher potential when applied to wet soil (Linde, 1994). However, because of its very low water solubility and high affinity for soils, bifenthrin has a very low tendency to volatilize from wet soil (EFED, 1999). Bifenthrin may be found in air attached to soil particles or as spray drift.

Water: Bifenthrin is a non-polar molecule that has a high octanol-water coefficient (Kow = 1.0×10^{6}). Since water is polar, bifenthrin has a low solubility and a correspondingly strong tendency to bind to soil (Linde, 1994). Drenner et al. (1992) found that bifenthrin concentrations in tank mesocosms dropped to 21% of the applied levels after 7 days. He concluded that this was probably due to adsorption of bifenthrin to tank walls and suspended soil and organic sediment (Drenner et al. 1992). Bifenthrin can move through surface water when bound to suspended sediment.

Bifenthrin was found to be stable to abiotic hydrolysis at pH 5, 7, and 9, at 25°C over a 30-day period (FMC 50429-024, 1983). This is surprising because of the presence of a carboxylate ester linkage in bifenthrin which is usually a point of hydrolysis in similar chemicals. The presence of acetonitrile co-solvents may have affected hydrolysis in the FMC study (EFED, 1999). The aqueous photolysis half life of 276 days for 14-C-cyclopropyl and 416 days for C-14-phenyl labeled bifenthrin indicates photo-stability (EFED, 1999).

Soil: Because of its high Koc value ($1.31x10^5$ - $3.02x10^5$), bifenthrin binds tighlty to soil particles, and tends not to move through soils. Bifenthrin has a strong affinity for organic carbon, and displays a relatively high Koc. The photodegradation half-life on soil exposed to natural sunlight was 106 days for C-14 phenyl labeled bifenthrin and 147 days for C-14 cyclopropyl labeled bifenthrin (FMC 50429-025, 1983). Aerobic soil metabolism half-lives for C-14 phenyl labeled bifenthrin ranged from 97 to 156 days depending on the type of soil utilized in the tests. C-14 Cyclopropyl-labeled bifenthrin showed aerobic half-lives of 129 to 250 days, again depending on soil type (FMC 50429-024, appendix 2, 1983). Both labeled compounds produced only small quantities of minor degradation products (i.e. less than 10% of applied total), the most significant of which was 4'-hydroxy bifenthrin at 3.0% – 5.6% (EFED, 1999). Flooded soil tests have shown both formulations of bifenthrin to be virtually stable to anaerobic soil metabolism. No major degradates were found, but 4'-hydroxy bifenthrin accounted for 4.5% of the total applied after 30 days of anaerobic conditions (FMC 50429-025, 1983). Field dissipation half-life tests have been conducted for bifenthrin in a wide range of soils and conditions. Half-lives ranged from 122 to 345 days (FMC 50429-025, 1983).

Biota: The mode of action and chemical characteristics of bifenthrin make it very effective against insects yet relatively benign to mammals and birds when applied properly (Mokry and Hoagland, 1989). Very high bioconcentration factor (≈6000x, whole body, bluegill sunfish) combined with the persistence of bifenthrin in natural settings could lead to exposure risks for predatory birds and mammals that feed on aquatic organisms. In aquatic systems that have high sediment and/or organic carbon loads, the risks to non-benthic feeding aquatic species are somewhat mitigated by the affinity of pyrethroids, including bifenthrin, for suspended soil particulate and organic carbon (Muir et al., 1985).

Drenner et al. (1992) examined the effects of sediment bound bifenthrin on gizzard shad (*Dorosoma cepedianum*) and plankton in a mesocosm. Complete mortality of gizzard shad occurred when mean peak concentrations of bifenthrin reached 7.75 ppb, partial mortality was observed at concentrations of 0.185, 0.250 and 1.55 ppb. Behavioral responses at concentrations greater than 0.185 ppb included slow swimming, gulping for air near the waters surface, opercle flaring, and increased cough rate (Bradbury and Coats, 1989). Copepods were highly sensitive to sediment bound bifenthrin, experiencing mortality at the 0.090 ppb level, the lowest concentration that was applied. Hoagland et al. (1993) found similar mortality of copepods and cladocerans at concentrations of 39 ppb of sediment bound bifenthrin. Both results can be attributed to the feeding habits of the organisms studied. Gizzard shad are detritus feeders and copepods and cladocerans rely on suspended organic matter for nutrition, both food sources are typically strong adsorption sites for bifenthrin (Drenner et al. 1992).

Mokry and Hoagland investigated the toxicity of third generation synthetic pyrethroids (bifenthrin, cyfluthrin, lambda cyhalothrin, and tralomethrin) compared to a first generation synthetic pyrethroid (permethrin). The third generation pyrethroids, including bifenthrin, were found to be more toxic to both *Ceriodaphnia dubia* and *Daphnia magna*. Reported bifenthrin LC_{50} for *C. dubia* was calculated to be 0.07 ppb, LC_{50} for *D. Magna* was 0.32 ppb. Permethrin toxicity values were 1.25 ppb for *D. Magna* and 0.55 ppb for *C. dubia*. The authors suggested that increased toxicity of third generation pyrethroids was due to their greater environmental persistence, and to a lesser degree, their increased insecticidal activity (Mokry and Hoagland, 1989).

A popular practice among nursery operators is to mix granular formulations of pesticides into potting soils to deter insect infestations (Drees et al. 1998). The LC50s and LC90s [of bifenthrin to female alates of imported fire ants (*Solenopsis invicta*)] were 1,100 ppb and 5,200 ppb, respectively (Oi and Williams, 1992). The concentration needed to achieve 100% mortality was estimated to be 7,100 ppb (5,100-9,800 ppb, 95% CL). The authors also investigated the repellency of potting soil to fire ant infestation at different rates of bifenthrin application (0, 1,100, 5,200, and 25,000 ppb). As application rates increased, infestation rates decreased. At the rate of 25,000 ppb, only one pot out of 100 temporarily showed any infestation after 2 weeks (Oi and Williams, 1996).

Conclusion

Bifenthrin is a third-generation synthetic pyrethroid insecticide, characterized by strong environmental persistence and high insecticidal activity. It is effective as a stomach or contact insecticide that affects the nervous system of vertebrates and invertebrates. Bifenthrin acts on sodium channels at the nerve cell endings to depolarize the pre-synaptic terminals. It has also been shown to affect cellular ATP-ase production. Bifenthrin is highly toxic to fish and aquatic organisms and it should not be applied near water sources. This insecticide is relatively benign to mammals and birds, but its high bio-concentration factor can affect higher-level predators.

Bifenthrin is virtually stable to aqueous hydrolysis and photolysis with only one minor by-product, **4'-**hydroxy bifenthrin. Because of its high octanol water coefficient and ability to adsorb to soils, bifenthrin has a low potential to contaminate ground water. Sediment bound bifenthrin could contaminate surface water sources during runoff events.

Bifenthrin adsorbs to soil and sediment, and has an especially strong affinity for soils with high organic carbon content. The photodegradation half-life for bifenthrin on soil was >100 days, which is considered stable. Aerobic half lives in a wide range of soils for both C-14 phenyl and C-14 cyclopropyl labeled bifenthrin are generally over 100 days, again considered stable. Bifenthrin has been shown to be stable to anaerobic soil metabolism, and the only minor degradate of either aerobic or anaerobic metabolism is **4'**-OH-bifenthrin. Field dissipation half lives for bifenthrin are also stable at >120 days.

Toxicity to aquatic organisms is somewhat mitigated by bifenthrin’s strong soil adsorption characteristics. Binding to water carried sediment and river and lake beds apparently limits the availability of the compound to some species, however, detritus feeding species and cladocerans have been shown to be affected by soil bound sediment. Mammals seem to be unaffected by exposure to bifenthrin, except at very high dosage levels.

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