Environmental Fate of Permethrin

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This document reviews the environmental fate of permethrin. The chemical name (IUPAC) given for permethrin is (3-phenoxyphenyl)-methyl (+)cis-trans-3-(2,2-dicloroethenyl)-2, 2-dimethylcyclopropanecarboxylate. The Chemical Abstracts Services (CAS) number for permethrin is 52645-53-1. Products containing permethrin include Ambush, Dragnet, Easygone, Hot Shot, Permectrin, Pounce, Raid, and Unicorn. There are over 600 different permethrin products registered for use in California (DPR Product/Label Database, 2002).

General Information and Mode of Action

Permethrin is a broad spectrum non-systemic synthetic pyrethroid insecticide. Current uses of permethrin include insecticide, termiticide, and wood preservative. Permethrin is primarily a contact poison that depends on disturbance of axonic nerve impulse conduction, causing rapid paralysis followed by death. Specific crop uses include alfalfa, almonds, avocados, celery, conifers, corn, cotton, filberts, lettuce, pears, soybeans, squash, walnuts, plus many others. A few of the target pests include alfalfa weevil, armyworms, leafhoppers, green fruitworm, European corn borer, flea beetles, stink bugs, termites, mosquitoes, ticks, and lice. (Buchel, 1983; Farm Chemicals Handbook, 2001; Thomson, 1994)

Permethrin is a nonpolar chemical with low water solubility, low volatility, high octanol-water partition coefficient, and a high affinity for soil and sediment making it generally immobile in soil. At acidic and neutral pH's permethrin is relatively stable, but will hydrolyze slowly under alkaline conditions. Permethrin is moderately susceptible to degradation via photolysis in water and soil (Laskowski, 2002).

Physical-Chemical Properties

Molecular weight	391.28
Water solubility	5.5×10^{-3} ppm (25°C) [b]
Vapor pressure	1.5×10^{-8} mmHg [b]
Hydrolysis half-life	
	stable (pH 5, 20 °C) [b]
	stable (pH 7, 20 °C) [b]
	242 d (pH 9, 20 °C) [b]
Aqueous photolysis half-life	51-71 days (pH=5, 25°C) [a]

	110 days (pH=5) [b]
Anaerobic soil degradation half-life	<3.5-17.5days (25°C, 7.4%om) [a] 3.5-7days (25°C, 12.1% om) [a] 197 d (25°C) [b]
Aerobic soil degradation half-life	3.5-17.5 day (25°C, 7.4% om)[a] 3.5-10.5 days (25°C, 12.1% om)[a] 31.5-42 days (25°C, 1.3% om)[a] 10.5-14 days (25°C, 51.3% om)[a] Range: 11.6-113 days, average: 39.5 days n=8[b]
Soil photolysis half-life	254-324 days (25°C, 4.53% OC) [a] 104 d[b]
Henry's law constant:	
Cis isomer	1.0×10^{-7} (25°C) [a]
Trans isomer	5.10×10^{-8} (25°C)[a] 1.4×10^{-6} atm m^3 mol^{-1} (calculated from solubility, vapor pressure and molecular weight)[b]
Octanol-water coefficient (K_{OW})	1.26×10^{6} [b]
Soil adsorption coefficient (K_{OC})	Range: 16,400 - 550,000 Average: 81,600 n=76 [b]

Physical-Chemical Property data in this table are compiled from registration studies conducted by pesticide manufacturers in compliance with the requirements of state or federal pesticide registration process.

[a] DPR Pesticide Chemistry database
[b] Laskowksi, D.A., 2002

Toxicity[c]

Daphnia Magna LC_{50}, 48hr	0.075 ppb
Fathead Minnow LC_{50}, 96hr	2.0 ppb
Rainbow Trout LC_{50}, 96hr	9.8 ppb
Bluegill Sunfish LC_{50}, 96hr	6.1 ppb (bioconcentration factor: 107X)
Bobwhite Quail LC_{50}, 8 days	>10,000 ppm
Mallard Duck LC_{50}, 8 days	>10,000 ppm
Mallard Duck LD_{50}	>4640 mg/kg
Honeybee LD_{50}, 48hr	0.05 µg/bee
Rat oral LD_{50}, Male	4000 mg/kg

[c] DPR Pesticide Ecotoxicity Database, 2002

Environmental Fate

Water/Sediment

Sharom and Solomon (1981) studied degradation of radiolabeled cis- and trans-permethrin in lake water (pH=7.8) and flooded lake sediment (43% organic matter) at 21°C under sterilized and unsterilized conditions. After 12 weeks, the percent of initially applied trans-permethrin remaining was as follows: unsterilized lake water, 0%; unsterilized flooded sediment, 32%; sterilized lake water, 30%; and sterilized flooded sediment, 55%. In the case of cis-permethrin, less than 50% of the initially applied material remained in unsterilized lake water after the 12 weeks. Approximately 85% of cis-permethrin initially applied remained after 12 weeks in unsterilized flooded sediment, sterilized lake water, and sterilized flooded sediment. These data indicate that the degradation of permethrin is more rapid in lake water than in flooded sediment, suggesting that permethrin in the aqueous phase is less stable than adsorbed permethrin. In addition, the cis isomer was more stable toward degradation than the trans isomer.

Permethrin has a very high affinity for soils and sediment in aqueous systems. Sharom and Solomon (1981) studied soprtion and desorption of permethrin in lake sediment. They found that more than 95% of permethrin applied was adsorbed on the lake sediment after 1 hour, while approximately 7-9% of the adsorbed permethrin was desorbed by four 10-mL rinses with distilled water.

Schimmel et al. (1983) measured the persistence of permethrin in seawater and in sediment/seawater mixtures. Persistence in seawater was measured using samples containing 1 ppm of permethrin. In samples that were exposed to sunlight, permethrin was found to have a half-life of 14 days. Samples not exposed to sunlight showed no significant change in the concentration of permethrin after 14 days. For sediment/seawater mixtures, 10 g (wet wt.) sediment (48% organic matter) was mixed with a pesticide-seawater solution containing 1 ppm of permethrin. The half-life of permethrin in the sediment/seawater mixture was determined to be < 2.5 days. In similar tests using sterile sediment, there was no significant change in pesticide concentration over the course of the study (28 days). The authors concluded that photolysis might be an important pathway for permethrin degradation in seawater, while microbial activity may be a major factor in the degradation of permethrin in sediment/seawater samples.

Kreutzweiser and Wood (1991) studied the effect of permethrin drift on forest streams via experimental applications. Permethrin was applied aerially at a nominal rate of 17.5 g active ingredient/ha to streams with temperatures ranging from 13-15°C and a pH range of 7.0-7.5. The mean calculated half-life of permethrin in stream water from 17 oversprayed sites was determined to be 10.3 hours with a range of 1.8-20.4 hours. Sites located downstream of application had a mean calculated half-life of 3.9 hours. Of sediment samples collected, less than 8% contained the detectable concentration of permethrin (>5ng/g). When compared to pond sediments, the lower organic fraction of sediments in running water and declining ambient concentrations may provide some explanation for the low level of permethrin accumulation in the sediment.

Rawn et al. studied the fate of radiolabeled permethrin in artificial outdoor ponds. In two separate pond experiments, permethrin was applied a rate of 15 ug/L and residues were measured in water and hydrosoil (nutrient-rich pore water within the bottom sediment of a water body). In one experiment, permethrin levels in water decreased from 15.5 ug/L at 2 hours post-application to 3.3 ug/L at 12 hours post-application, and were below the limit of detection (0.01 ug/L) after 7 days. Residues in hydrosoil reached a maximum of 120 ug/L at 48 hours post-application, and permethrin was still present at 1.0 ug/L after 1 year. In a second experiment, permethrin levels in water decreased from 29.0 ug/L at 2 hours-post application to 5.9 ug/L at 12 hours post-application. Levels in hydrosoils were 38 ug/L at 24 hours post-application and were still present at 5.0 ug/L after 323 days. The authors found permethrin residues to be persistent in hydrosoil – the major sink for permethrin in the ponds. Additionally, the photolytic half-life of permethrin in pond water (10.1 ug/L *trans* and 11.4 ug/L *cis*) was determined to be 19.6 $\pm$ 2.3 hours for the *trans* isomer and 27.1 $\pm$ 4.4 for the *cis* isomer.

Photolysis of permethrin in water under artificial light (? = 290 nm) results in cyclopropane ring isomerization and ester cleavage. The major degradates resulting from photolysis in water are 3-phenoxybenzyl alcohol and dichlorovinyl acid (Holmstead et al, 1978).

Soil

As indicated by its high K_{oc} (Table 1), permethrin has a strong tendency to bind to soil and sediment. As such, permethrin is not likely to leach through soil or move in the aqueous phase in runoff water. However, sediment bound permethrin residues can be transported into surface waters along with sediment during heavy runoff events.

The degradation of cis- and trans-permethrin in Dubbs fine sandy loam soil (pH=5.9; organic matter content 1.0%) incubated at 10, 25, and 40°C was measured by Jordan et al. (1982) in the laboratory. Permethrin was applied at 1 ppm and incubation periods ranged from 0-64 days. The estimated half-lives, at 10, 25, 40°C, for cis-permethrin were 55, 12, and 27 days and for trans-permethrin were 14, 5,and 4 days, respectively. Degradation of permethrin was most rapid at 25°C.

The importance of microbial activity on the degradation of permethrin was studied by Chapman et al. (1981) using sterilized and natural soils. Permethrin was applied at 1 ppm to dried natural mineral soil (pH = 8.0-8.1), natural organic soil (pH = 7.1-7.2), sterilized organic soil (pH = 6.5-6.9), and sterilized mineral soil (pH = 7.7-8.1). After 8 weeks the percentages of permethrin remaining in soil were 6%, 16%, 100%, and 101%, respectively. Chapman et al. (1981) concluded that microorganisms are more important than purely physical and chemical processes in the degradation of permethrin.

Jordan and Kaufman (1986) measured the degradation of cis and trans permethrin under anaerobic conditions in Memphis silt loam soil (pH=5.8; organic matter content, 0.7%). Permethrin was applied at 0.1 and 1.0 ppm to 50g (dry weight) soil, flooded with 75 mL of sterile distilled water, and then incubated at 25° C in the dark. The soil was analyzed six times in a 64-day period. The degradates were identical to those obtained from aqueous photolysis: dichlorovinyl acid and 3-phenoxybenzyl alcohol. The half-life of trans-permethrin applied at 0.1 and 1.0 ppm was estimated to be 32 and 34 days, respectively. The half-life of cis-permethrin

was found to be greater than 64 days. After 64 days the percentage of trans-permethrin remaining in the soil was 34.2 % (0.1 ppm applied) and 30.3 % (1.0 ppm applied). For cis-permethrin the percent remaining after 64 days was 65.0-73.4% (0.1 ppm applied) and 61.5-69.8% (1ppm applied). Similar to the findings of Sharom and Solomon (1981) in lake sediment, these results indicate that the cis isomer is more persistent in soil than the trans isomer.

The photolytic degradation products of permethrin in soil are also the same as those in water: 3-phenoxybenzyl alcohol and dichlorovinyl acid. As in water these products are obtained through ester cleavage (Holmstead et al., 1978).

Air

Although there is a possibility of drift when applied aerially, permethrin is not likely to volatilize based on its low vapor pressure and low Henry's law constant (Table 1).

Biota

Toxicity and Bioconcentration Factor

Permethrin, like many of the synthetic pyrethroids, presents a relatively low toxicological hazard to birds and mammals, but is extremely toxic to some fish and aquatic arthropods (Coats and Bradbury, 1989). Permethrin is also classified as "highly toxic" to honey bees. Permethrin's high octanol-water partition coefficient suggests that it may have a tendency to bioaccumulate into living organisms (Ney, 1990). Permethrin has a strong tendency to adsorb to sediments in aquatic systems, thereby mitigating permethrin aquatic toxicity by reducing bioavailability. Consequently there is uncertainty about the applicability of some laboratory-obtained LC_{50}s to actual environmental situations – especially for organisms that reside in the water column such as fish and aquatic arthropods.

Conrad et al. (1999) studied the acute toxicity of *Chironomus riparius* using a laboratory water-only test, a laboratory sediment test, and a field (outdoor pond) toxicity test. *C. riparius* was exposed to permethrin at nominal concentrations ranging from 0-62.5 µg/L for 96 hours at 20°C in the water-only test. The measured 96-hr LC_{50} was 2.89 µg/L. In the laboratory sediment toxicity test, permethrin was applied to sediment to give nominal concentrations of 0-4300 ng/g. *C. riparius* was exposed to the permethrin-spiked sediment for 10 days, and the estimated 10-day LC_{50} was 2.11 µg/g. For the field toxicity test, outdoor ponds were dosed with permethrin to give nominal concentrations ranging from 0-100 µg/L. Samples of pond sediment were taken to determine permethrin concentration as well as larval density and adult emergence of *C. riparius* up to the 52nd day after dosing. After the duration of the experiment, it was determined that ponds dosed at 10 µg/L and above caused a significant decline in larval density and adult emergence of *C. riparius*. The bioavailability of permethrin to *C. riparius* was found to decrease rapidly after spiking the outdoor ponds, which is probably due to the binding of permethrin to the sediment and other surfaces**.** By comparing the 10-day sediment LC_{50} value (2.11 µg/g) to the highest measured concentration of permethrin in pond sediment (0.22 ug/g), the authors concluded that acute lethal effects would not be expected due to sediment-bound permethrin in the outdoor ponds. The 48-hr LC_{50} value of 9.72 µg/L was comparable to the smallest nominal pond dose of 10 µg/L, suggesting the significant effects on C. riparius were due to exposure to

aqueous residues. Conrad et al. (1999) stated that it is therefore probable that the observed effects in the field were due to concentrations of the test substance in the water column immediately after dosing.

Increases in clay content and organic carbon content decrease the acute and chronic toxicity of permethrin to *C. riparius* by reducing bioavailability (Fleming et al., 1998). Similarly, *C. tentans* larvae exposed to permethrin-spiked sand (0.1% organic carbon) were found to contain higher levels of permethrin than the larvae exposed to permethrin spiked river sediment (7% sand, 45% silt, 48% clay, 2.3% organic carbon) or pond sediment (25% silt, 75% clay, 3.7% organic carbon)(Muir et al., 1983).

In a study by Jolly et al. (1978), acute toxicity (96-hour lethality tests) was measured for several freshwater organisms in water. Water used in the test was maintained at 24°C with pH=8.4. The measured LC_{50} (in µg/L) values were as follows: crayfish (newly hatched), 0.39; crayfish (juvenile) 0.62; channel catfish, 1.10; largemouth bass, 8.50; mosquitofish, 15.00; and bullfrog, 7,033.00.

The lethality of permethrin to Atlantic salmon (*Salmo salar*) was measured in static conditions at 10°C by McLeese et al. (1980). The measured 96-hr LC_{50} was 6.02 µg/L. Atlantic salmon was also found to concentrate permethrin by a factor of 73 with an exposure time of 89 hours and a concentration of 6.9 µg permethrin /L in the exposure water (McLeese et al., 1980).

Glickman et al. (1981) studied the acute toxicity and the uptake and elimination of permethrin by rainbow trout. The determined 24-hr LC_{50} for rainbow trout was 18 ug/L for exposure in static water. Fish were exposed to permethrin at the initial concentration of 5 µg/L. Samples were taken at various times for a 24-hour period. The concentration of permethrin measured in rainbow trout liver tissues was ~ 0.4 µg/g after 1 hour, whereas the concentration of permethrin in fat tissues was ~ 0.4 µg/g after 4 hours. The half-life of permethrin in fat tissues of rainbow trout exposed to permethrin at the concentration 5 µg/L for 24 hours was > 168 hours, while the half-life in liver tissues was ~30 hours.

Schimmel et al. (1983) measured acute toxicity (96-hour lethality tests) to several species in seawater. Acute toxicity tests were conducted using a flow-through procedure. Animals were exposed to each concentration for 96 hours and mortality was recorded daily. For all species tested, permethrin was toxic at concentrations $\leq$ 7.8 µg/L. The species tested and their associated 96-hour LC_{50}'s (in µg/L) were: mysid shrimp, 0.02; pink shrimp, 0.22; sheepshead minnow, 7.8; Atlantic silverside, 2.2; and striped mullet, 5.5. All LC_{50} values were based on measured concentrations except for that of the mysid shrimp, which was based on nominal concentrations. A long-term bioconcentration study on permethrin with the eastern oyster (*Crassostrea virginica*) in seawater was also conducted. Experimental conditions included a temperature range of 22.5 to 30° C and a salinity range of 17.5 to 29 parts per thousand. The steady-state bioconcentration factor was determined to be 1900. In pesticide-free water, permethrin was depurated from tissues to nondetectable levels within 1 week.

The 48-hr LC_{50} for *Daphnia magna*, measured in filtered river water (20° C), ranges from 0.2 – 0.6 µg/L. Addition of alga *Chlorella pyrenoidosa* to waters spiked with permethrin at 0.5 µg/L, a value in the LC_{50} range, was found to cause a significant increase in the mortality of *D. magna*

within the first 24 hours compared to exposures without the addition of *C. pyrenoidosa.* After 48 hours, observed mortality was measured to be 70%. The addition of permethrin results in algal adhesion to *D. magna*, causing immobilization of the daphnids. The authors note that this phenomenon appears to be an important sublethal effect of permethrin on *D. magna* (Stratton and Corke, 1981).

Acute toxicity and behavioral effects of permethrin were measured for *Pteronarcys dorsata* (stonefly) and *Brachycentrus americanus* (caddisfly) in a study by R.L. Anderson (1982). Animals were exposed to permethrin in unfiltered lake water (pH=7.6-7.8) for 28 days by flow-through exposure at 15°C. A 21-day LC_{50} value of 0.17 µg/L was determined for the caddisfly. When exposed for less than 21 days at concentrations of 0.030 to 0.52 µg/L the caddisfly suffered some mortality, but mortality was always less than 50%. Therefore, an LC_{50} value was not calculated for times less than 21 days. The lethal concentration (LC_{50}) for the stonefly could not be determined, but altered behavior was observed. Both the caddisfly and stonefly experienced behaviors such as lack of feeding when exposed to permethrin at high concentrations or for long periods of time. Consequently acute toxicity LC_{50}s do not reflect potentially significant sub-lethal chronic effects of permethrin on stoneflies and caddisflies.

In some areas of the US, mosquito abatement and control agencies are beginning to replace traditional organophosphate insecticides with the use of a mixture of permethrin and piperonyl butoxide (PBO). The efficacy of permethrin is increased by the addition of PBO. The acute toxicity of a permethrin:PBO mixture (1:1) was measured, using two different tests, for juvenile striped bass hybrids (*Morone saxatilis* x *Morone chrysops*). In 24-hr acute toxicity tests, fish were exposed to the permethrin:PBO mixture at various concentrations for 24 hours and then moved to clean filtered water for an additional 72 hours. Toxic effects were measured after 96 hours and the estimated LC_{50} was 26.7 ppb. A 96-hr acute toxicity test was also conducted, with mortality measured every 24 hours. The estimated $LC_{50,}$ after 72 hours, was 16.1 ppb, with all mortality occurring before that time (Rebach, 1999).

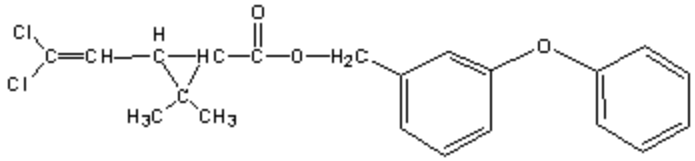
Kreutzaeiser and Wood (1991) measured the bioconcentration factors for Brook trout, Atlantic salmon, and Slimy sculpin exposed to experimental applications of permethrin in forest streams. The measured bioconcentration factors for each species were as follows: Brook trout, 39-113; Atlantic salmon, 97-613; Slimy sculpin, 154.

The bioconcentration factor of permethrin was determined for the protozoan *Tetrahymena pyriformis* in a study by Bhatnagar et al. (1988). The *Tetrahymena* cultures were maintained on a sterile medium (pH=7) and incubated in the dark at 27°C for 72 hours before exposure to permethrin. Cultures were treated with permethrin at concentrations of 0.1, 0.5, and 1 µg/mL. After exposure, cultures were sampled every 2 hours for a 12-hour period. The threshold bioconcentration factors were determined to be as follows: 1110 (0.1 µg/mL), 349 (0.5 µg/mL), 1056 (1 µg/mL). The author noted that accumulation of permethrin by *T. pyriformis* could allow permethrin to enter the aquatic food chain and therefore higher trophic levels, if environmental levels reached 1 µg/mL.

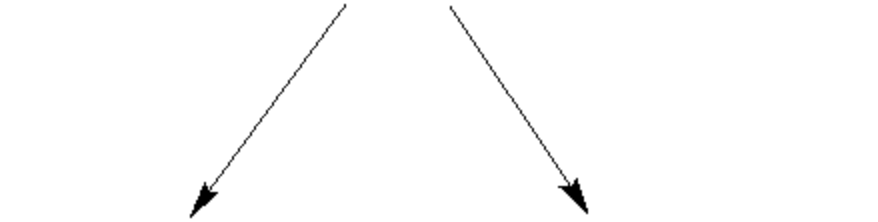
Summary

The environmental fate of permethrin is strongly influenced by its extreme hydrophobicity, low solubility, and high tendency to adsorb to soil. Thus, permethrin is largely associated with sediment in aquatic systems and immobile in soil making it unlikely to leach to ground water. Microbial degradation and photolyisis are important degradation routes while volatilization and hydrolysis are relatively unimportant dissipation routes. Permethrin has a relatively low mammalian and avian toxicity, but is potentially very toxic to aquatic organisms, especially invertebrates. The highest risk for aquatic toxicity in the water column is immediately after application. Due to its hydrophobic behavior, after application to water permethrin binds quickly to sediment and becomes less bioavailable to organisms. While permethrin does have a tendency to bioconcentrate, aquatic organisms have demonstrated the ability to depurate permethrin through excretion in some studies.

Permethrin Degradation



Permethrin



Phenoxybenzyl alcohol

Phenoxybenzoic acid

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DPR Pesticide Ecotoxicity Database. The DPR Pesticide Ecotoxicity Database contains information on the biological activity of pesticide active ingredients: acute and dietary toxicity to avian species, avian reproduction effects, acute toxicity to warmwater and coldwater fish, toxicity to marine fish species, fish bioconcentration values, marine and freshwater aquatic invertebrate toxicity, honeybee and earthworm toxicity and marine and freshwater plant toxicity. This information is extracted from wildlife and aquatic organisms studies conducted by pesticide manufacturers in compliance with the requirements of California's pesticide registration process.

DPR Pesticide Chemistry Database. The Pesticide Chemistry Database contains information on the physical and chemical properties of pesticide active ingredients: solubility, vapor pressure, hydrolysis half-life, Henry's Law constant, anaerobic soil metabolism half-life, aerobic soil metabolism half-life, field dissipation half-life, soil adsorption coefficient, and the octanol-water partition coefficient. This information is extracted from environmental fate studies conducted by pesticide manufacturers and formulators in compliance with the requirements of California's pesticide registration process.

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