ENVIRONMENTAL FATE OF FENOXYCARB

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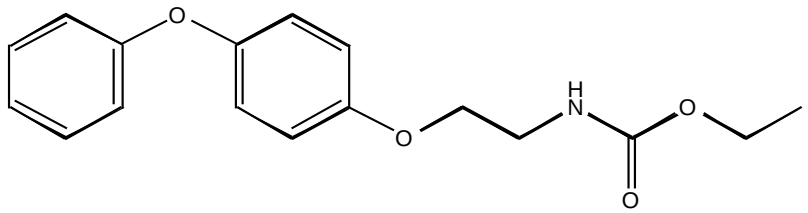
This document reviews the environmental fate and environmental effects of fenoxycarb (ethyl[2-(4-phenoxy-phenoxy)-ethyl]carbamate). Fenoxycarb ($C_{17}H_{19}NO_4$) was discovered in 1981 and was introduced by R Maag AG (The British Crop Protection Council, 1987). Fenoxycarb is a non-neurotoxic carbamate insect growth regulator used to control a wide variety of insect pests. This general use pesticide is useful for control of fire ants, fleas, mosquitoes, cockroaches, moths, scale insects, and insects attacking vines, olives, cotton and fruit (Extension Toxicology Network 1993; Miyamoto et al. 1993; The British Crop Protection Council, 1991). It is also used to control these pests on stored products, and is often formulated as a grit or corncob bait.



fenoxycarb
ethyl[2-(4-phenoxy-phenoxy)-ethyl]carbamate

Physico-Chemical Properties[a]

CAS Number:	79127-80-3
Molecular Weight:	301.30
Water Solubility:	6 mg/L @ 20º C
Melting Point:	53-54º C
Vapor Pressure:	7.8×10^{-3} mPa @ 20º C
Henry's Constant:	4.6×10^{-5} (Pa m^3/mol)
Octanol-water coefficient (Kow):	4.30

Adsorption Coefficient[b]:	1500
Environmental Fate[c]	
Hydrolysis Half-Life:	3136 days (pH 7)
Aqueous Photolysis	18-23 days (pH 7)
Soil Photolysis	6-14 days (primary) 73-1351 days (secondary)
Field Dissipation Half-life :	3-5 days (primary) 13-44 days (secondary)
Aerobic Aquatic Half-Life:	19 days
Aerobic Soil Half-Life (at field use rates):	6.7 hours (primary) 254 days (secondary)
Anaerobic Soil Half-Life:	113 days
Anaerobic Soil Half-Life (Aquatic):	1322 days
Toxicity[a]	
Acute Oral LD_{50} (Rat)[d]:	>10,000 mg/kg
Acute Dermal LD_{50} (Rabbit):	>2,000 mg/kg
Acute Inhalation LC_{50} (Rat):	>3.48 mg/l air - 4 hours
Ecological Effects[a]**:**	
Acute Toxicity:	
Rainbow Trout 96-hour LC_{50}[e]	1.6 ppm
Daphnia magna 48-hour LC_{50}	0.6 ppm
Mallard Oral LD_{50}	>3,000 mg/kg
Mallard 8-day Dietary LC_{50}	>20,000 ppm
Bluegill Sunfish 96-hour LC_{50}	0.74 ppm
Bobwhite Oral LD_{50}	>7,000 mg/kg
Bobwhite 8-day Dietary LC_{50}	>5,620 ppm
Chronic Toxicity:	
Invertebrate (*Daphnia*) Life Cycle MATC[f]	1.6 ppt

Mallard Reproduction NOEC:	48.0 ppb
Bobwhite Reproduction NOEC:	160 ppm
Fish (Fathead minnow) Early Life Stage	400 ppm

[a] Kidd and James, 1991
[b] Wauchope, et al., 1992
[c] Thede, 1995
[d] Keller, P. 1982
[e] Extension Toxicology Network. 1993.
[f] U.S. Environmental Protection Agency, 1986.

General Characteristics of Juvenile Hormones and Juvenile Hormone Analogs and Mode of Action of Fenoxycarb.

Two major insect-hormones act to control metamorphosis: the molting hormone and the juvenile hormone (JH). High concentrations of JH and low concentrations of molting hormone cause molting larva to continue growing as larval instars (a stage of an insect or other arthropod between molts). Presence of the molting hormone coupled with the absence of JH in insect circulation results in larvae which change into adults. Insects often go through a number of instars however when the JH secretion stops metamorphosis follows (Staal 1972). JH maintains the "youthful character" of the insect and prevents the insect from becoming an adult before it is fully grown. Abnormal amounts of JH often result in the eventual death of the larva.

The search to apply knowledge of JHs to the development of effective insecticides has since been limited to the area of JH analogs (JHAs) (Matolcsy et al., 1988). JHAs act in the same manner as JHs but are much more chemically stable. JHAs are said to be active mimics of JHs (Matolcsy et al., 1988).

Fenoxycarb was the first JHA compound introduced to control agricultural pests (Miyamoto et al., 1993). Fenoxycarb and pyriproxyfen, a fenoxycarb derivative in which part of the aliphatic chain has been replaced by pyridyl oxyethylene, are the JHAs with high insecticidal activities (Riddiford 1994). Fenoxycarb mimics the action of the juvenile hormones on a number of physiological processes, such as molting and reproduction. Fenoxycarb kills eggs and larvae of numerous insect species (Masner et al., 1987). Since the egg is not usually exposed to high levels of JH until about halfway through embryonic development, its development is halted and the egg will not hatch. High levels of JHAs, when applied to later instars, cause the adult insect

to maintain larval characteristics and these insects generally cannot reproduce. Another property of these compounds is that, in adults, they disrupt normal reproductive physiology and act as a method of birth control.

Environmental Fate of Fenoxycarb

Air: The vapor pressure of fenoxycarb is low (4.6×10^{-5} Pa m^3/mol), which indicates that it does not have a strong tendency to volatilize into the atmosphere. Aside from drift that may occur with spray applications, fenoxycarb is not expected to be found in the air.

Soil: Fenoxycarb has relatively low water solubility and readily adsorbs to soil surfaces. The compound has a low potential for leaching from the soil and has a moderate to strong tendency for soil binding (U.S. EPA, 1986). These characteristics of fenoxycarb in soil indicate that it is unlikely to contaminate groundwater. It is relatively quickly degraded in soil by microbial action, and has an overall reported field dissipation half-life of 14-45 days However, fenoxycarb is stable to photodegradation in most viable soil types (ARS Pesticide Properties Database, 1995). The photolysis half-life for fenoxycarb in soil under artificial light was determined to follow biphasic kinetics with a primary half-life ranging from 6 to 14 days and a secondary half-life ranging from 73 to 1351 days (Thede 1995).

Thede (1995) conducted a field study for twelve months at two doses of ^{14}C-A ring fenoxycarb to determine metabolic degradation rates in a Maryland limekiln sandy loam soil. Aerobic kinetic incubations were dosed at 0.122 ppm and the bulk incubations were dosed at 9.16 ppm. Degradation of fenoxycarb for the aerobic and anaerobic kinetic phases followed biphasic kinetics. The primary half-life for the aerobic biphasic kinetic incubation was determined to be 6.7 hrs and the secondary half-life value was calculated to be 8.2 months. The aerobic/anaerobic half-life was calculated to be 113.6 days. By the twelfth month, volatiles (CO_2) accounted for around 42.5% of total dose in the aerobic incubations and 32.1% of total dose in the aerobic/anaerobic kinetic incubations. Multiple degradation pathways appear to contribute to the conversion of fenoxycarb to CO_2 and there was evidence that some radiolabeled carbon from the fenoxycarb was incorporated into the soil biomass. Evidence indicates that fenoxycarb rapidly degrades to several minor components that do not accumulate over time. The degradates in turn rapidly degrade into CO_2 (Thede, Amendment 1, 1995).

Terrestrial field studies of ^{14}C-fenoxycarb on bare ground soil in California show that most residues remain in the first 3 inches of soil. Degradation of parent followed biphasic kinetics with primary and secondary half-lives ranging from 3.07-5.11 days and 13.7-44.9 days, respectively (McDonald 1995). Schuster and Goff (1995) determined that fenoxycarb was immobile and dissipate rapidly and no residues were found in any other soil layer beyond the zero to 6-inch soil horizon.

Water: Fenoxycarb is stable to hydrolysis in water at pH 3-9 and temperatures up to 50 ºC. Thede (1995) reported that the half-life of fenoxycarb in aqueous buffer was 1,406 days, 3,136 days, and 4,101 days at pH 5, 7, and 9, respectively. Based on these data, hydrolysis would not be expected to be a major degradation pathway for fenoxycarb. Fenoxycarb is thus much less stable to photolysis than it is to hydrolysis in water at environmental pH's. The aqueous photodegradation of fenoxycarb was determined to be 18-23 days at 25ºC under artificial sunlight at approximately 1 ppm and at a hydrolytically stable aqueous buffered pH of 7. (Thede 1995).

Aerobic metabolism studies suggest that fenoxycarb rapidly partition from the aqueous layer and into sediment under aerobic aquatic conditions. The half-life of ^{14}C-fenoxycarb was found to be 3.89 days in aqueous media and 18.80 days overall under aerobic aquatic conditions (Burton, 1995).

Fenoxycarb readily sorbs to organic matter, which may limit its persistence in water. To estimate the potential loss of fenoxycarb from water onto organic matter, Schaefer et al. (1987) performed a laboratory study in which duplicate sets of six 600-ml water samples were fortified with 0.02-ppm fenoxycarb and various quantities of straw. One set was held for 24 hours and the other set was held for 48 hours, after which they were filtered and analyzed via HPLC. Results show a steady loss of fenoxycarb onto straw as either the amount of straw or holding time increased. In this same study, residues in the water could be detected for only two days following an aerial treatment of ponds with fenoxycarb for the control of mosquitoes. Since fenoxycarb is stable in water over a range of temperature (10-38 ºC) and pH (6.5-10), the author suggests that observed reduced field recoveries may be due to adsorption of fenoxycarb from water onto indigenous organic matter.

Biota: Fenoxycarb is expected to break down relatively quickly in plants (Kidd and James, 1991). Fenoxycarb has very low toxicity to mammals via ingestion. The oral LD_{50} of the compound is greater than 10,000 mg/kg in rats (Keller, 1982). It is slightly to practically nontoxic via the dermal route, with a reported dermal LD_{50} in the rat of greater than 2000 mg/kg. Fenoxycarb is not a skin sensitizer in guinea pigs and causes only minimal eye irritation when applied to rabbits. The inhalation toxicity of fenoxycarb is moderate, with an acute inhalation LC_{50} in rats of greater than 0.480 mg/L (Kidd and James, 1991). Fenoxycarb exhibits low toxicity to birds. The compound has LD_{50} values greater than 3000 mg/kg and 7000 mg/kg in mallard ducks and bobwhite quail, respectively (Kidd and James, 1991). The dietary LC_{50} value for bobwhite quail is about 11,000 ppm (US EPA, 1986).

Fenoxycarb is considered moderately to highly toxic to fish with LC_{50} values ranging from 1.6 mg/L in rainbow trout to 10.3 mg/L in carp (Kidd and James, 1991). Fenoxycarb is also considered highly toxic to the aquatic invertebrate *Daphnia* and affects growth and reproduction after chronic exposures to >1.6 ng/L (US EPA, 1986). However, when fenoxycarb was applied at rates ranging from 0.015 to 0.03 lbs/acre to ponds, the compound had no effect on a number of different invertebrates including cladocerans, copepods, ostracods, and mayfly nymphs (Miura, et al., 1986). In one study, bluegill sunfish accumulated 20 times the amount of the compound's

concentration in the water. Tissue residues of the pesticide quickly declined after the fish were placed in pesticide-free water (Schaefer et al., 1987). In laboratory tests, contradictory results are obtained with the mosquito fish *Gambusia affinis*. Miura, et al. (1986) found no mortality with fenoxycarb doses from 0.0001 to 1.0 ppm; while Tietze et al. (1991) reported an LC50 value of 1.05 ppm after 24 hour exposure. Miura and Takahashi (1987) also reported that fenoxycarb treatment rates of 0.03 kg AI/ha had no deleterious effects on planktonic organisms and aquatic beetles regularly found in mosquito breeding habitats.

Fenoxycarb is practically nontoxic to honeybees (Kidd and James, 1991). The oral LC50 (24 hour) for adult honeybees is greater than 1000 ppm. Young bumble bee (*Bombus terrestris*) colonies treated with 1:1 sucrose solution containing 0.20, 2.0, and 20 ppm fenoxycarb and pyriproxyfen exhibited no larval mortality and the brood developed normally (De Wael et al., 1995.). Bee hazard is decreased when the pesticide is formulated as grit or corncob bait. However, it is recommended (Grenier and Grenier, 1993) that more care be taken by avoiding application during blossoming periods, cutting the grass on the ground under trees to remove all the flowers before treatment, and making applications outside normal flight hours of bees.

Conclusions

Fenoxycarb (ethyl[2-(4-phenoxy-phenoxy)-ethyl]carbamate) is a broad spectrum insect growth regulator. Although fenoxycarb is a carbamate insecticide, it exhibits no anti-cholineasterase activity and is thus considered non-neurotoxic. It is useful for control of fire ants, fleas, mosquitoes, cockroaches, moths, scale insects, and insects attacking vines, olives, cotton and fruit. It is also used to control these pests on stored products, and is often formulated as a grit or corncob bait.

Fenoxycarb mimics the action of the juvenile hormones (JH) on a number of physiological processes, such as molting and reproduction. Because of its ability to imitate the physiological effects of juvenile hormones, it is often called a juvenile hormone analog (JHA). It exhibits ovicidal and ovolarvicidal activity against numerous insect species and affects its target species by exposing newly deposited eggs or very early instars to high levels of simulated JH. Fenoxycarb binds to juvenile hormone receptor, but is not broken down by juvenile hormone esterases in insect larvae. Since the insect is not usually exposed to high levels of JH until about halfway through embryonic development, its development is halted and the eggs will not hatch. High levels of JHAs such as fenoxycarb, when applied to later instars, cause the final adult insect to maintain larval characteristics and these insects generally cannot reproduce.

Because of its low vapor pressure and Henry's Law constant, fenoxycarb is not expected to be found in the air, except possibly from drift that may occur with spray applications. Fenoxycarb has low water solubility, low potential for leaching from the soil, and has a moderate to strong tendency for soil binding. Consequently, it is unlikely to contaminate groundwater. In soils, fenoxycarb is readily degraded by hydrolysis and by microbial action but is very stable to photodegradation.

Aerobic metabolism studies suggest that fenoxycarb rapidly partition from the aqueous layer into sediment under aerobic aquatic conditions. In sandy loam soil, aerobic and anaerobic degradation of fenoxycarb was found to follow biphasic kinetics (variable rate laws). The primary half-life for aerobic degradation was determined to be 6.7 hrs and the secondary half-life value was calculated to be 8.2 months. The primary anaerobic half-life was calculated to be 16 days and the secondary half-life value was calculated to be 8.5 months. Of the multiple degradates present in the extraction fractions the only component present in significant quantities was un-degraded fenoxycarb. There was no evidence of accumulation of any single degradate during the incubation period. Evidence indicates that fenoxycarb rapidly degrades to several minor components which do not accumulate over time but which rapidly degrade into CO_2

Fenoxycarb is stable to hydrolysis in water at pH 3-9 and temperatures up to 50 ºC. The half-life of fenoxycarb in aqueous buffer was determined to be 1,406 days, 3,136 days, and 4,101 days at pH 5, 7, and 9, respectively. Hydrolysis would thus not be expected to be a major degradative pathway. However, fenoxycarb photodegrades rapidly in pure and natural water, with half of the initial amount of the compound broken down within 5 hours (US EPA, 1986). In addition, fenoxycarb readily sorbs to organic matter, which may limit its persistence in water.

Fenoxycarb is expected to break down relatively quickly in plants and has low toxicity to mammals, bees, and birds. Fenoxycarb is considered moderately to highly toxic to fish and *Daphnia* and affects growth and reproduction after chronic exposures. However, when fenoxycarb was applied to ponds, the compound had no effect on a number of different invertebrates including cladocerans, copepods, ostracods, and mayfly nymphs. Numerous studies suggest that it is of low likelihood that the compound would pose a threat to aquatic organisms or to other organisms that consumed the fish because of the low acute toxicity of fenoxycarb to these groups at the low use-rates.

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