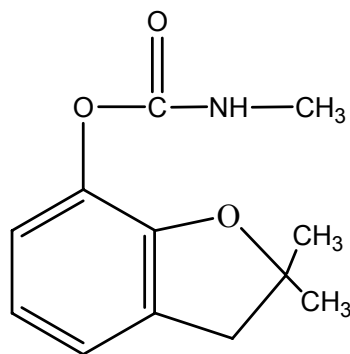


# Environmental Fate of Carbofuran

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This document reviews the environmental fate of carbofuran, IUPAC name 2,3-dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate. Products containing the active ingredient carbofuran include Furadan, Curaterr, Yaltox, Bay 70143, Carbodan, and ENT 27164 (Trotter et al., 1991). Its CAS registry number is 1563-66-2.



Carbofuran

## General Information and Mode of Action

Carbofuran is a broad-spectrum carbamate insecticide, acaricide, and nematicide. It is applied in granular form or aerially, though the granular form is currently restricted in the U.S. It may be used on a variety of crops, the most common including strawberries, alfalfa, corn, grapes, soybeans, and wheat. Carbofuran is used to control soil-dwelling and foliar-feeding insects such as corn rootworm, wireworms, boll weevils, mosquitoes, alfalfa weevil, aphids, and white grubs (Trotter et al., 1991). Working on contact or ingestion, carbofuran is a cholinesterase inhibitor, but the short-term effects on the nervous system are reversible (EXTOXNET, 2001).

Carbofuran is formulated as a flowable or wettable powder, while pure carbofuran is an odorless to mildly aromatic white crystalline solid (Farm Chemicals Handbook, 2001). It is stable in acidic and neutral media, but hydrolyzes under alkaline conditions. Thermal breakdown may release toxic fumes (WHO, 1996a, 1996b).

According to the Department of Pesticide Regulation's Pesticide Use Report, more than 130,000 pounds of active ingredient was used in California in 1999, and again in 2000. In 2000, approximately half of this was used on alfalfa alone, with cotton and grapes making up a majority of the remainder (DPR 2002).

Granular carbofuran products are no longer federally registered for use because carbofuran generally displays high avian toxicity. The formulated granules look very similar to seeds certain birds incorporate into their diet. Mistaking the granules for food, they seize and die upon ingestion, leading to bird-kill incidents. Secondary poisoning of raptors feeding on contaminated birds has also been reported (Erwin, 1991).

Table 1. Physical-Chemical Properties

Molecular Weight	221. 26
Molecular Formula <sup>b</sup>	C <sub>12</sub> H <sub>15</sub> NO <sub>3</sub>
Water Solubility <sup>a</sup>	351ppm (at 25°C)
Vapor Pressure <sup>b</sup>	8.3 x 10 <sup>-6</sup> mmHg (25°C)
Octanol-Water Partition Coefficient (K <sub>ow</sub> ) <sup>a</sup>	17 - 26
Henry's Law Constant <sup>b</sup>	3.9 x 10 <sup>-9</sup> atm m <sup>3</sup> /mol
Hydrolysis Half-Lives (days) <sup>a</sup>	27.7 (pH 7, 25°C)
	2.73 (pH 8, 25°C)
	0.54 (pH9, 25°C)
Aqueous Photolysis Half-Life (days) <sup>a</sup>	7.95 x 10 <sup>3</sup> (pH 7, 28°C)
Soil Photolysis Half-Life (days) <sup>a</sup>	138 (27°C, pH 5.7, sandy-loam, 2.1% organic carbon, 21% moisture)

Aerobic Degradation Half-Life (days) <sup>a</sup>	22 (25°C, pH 5.7, sandy-loam, 2.1% organic carbon, 21% moisture)
Anaerobic Degradation Half-Life (in days) <sup>a</sup>	30.0 (25°C, pH 5.7, sandy-loam, 2.1% organic carbon, 21% moisture)
Field Dissipation Half-Life (in days) <sup>a</sup>	13.0 (pH 7.3, sandy-loam, .38% organic carbon)
Adsorption coefficient (Koc) <sup>c</sup>	22

<sup>a</sup>. DPR Pesticide Chemistry Database (2002)

<sup>b</sup>. Handbook of Environmental Fate and Exposure Data, Vol. 3 (1991)

<sup>c</sup>. EXTTOXNET (2001)

Table 2. Ecological Toxicity Data<sup>a</sup>.

Mallard Duck LD <sub>50</sub>	0.4 mg/kg
Mallard Duck 8-Day LC <sub>50</sub>	190 ppm
Bobwhite Quail LD <sub>50</sub>	5 mg/kg
Bluegill Sunfish 96-hr LC <sub>50</sub>	0.24 ppm (BCF 2-12X)
Rainbow Trout 96-hr LC <sub>50</sub>	0.28 ppm
Daphnia Magna 48-hr LC <sub>50</sub>	38.6 ppb
Honeybee 48-hr LD <sub>50</sub>	0.16 µg/bee

<sup>a</sup>. DPR Ecotox database (2002)

## Environmental Fate

### Air

Carbofuran's low vapor pressure and low Henry's Law constant (Table 1) indicates it has a low tendency to volatilize from water or moist soils (Duel et al., 1979). Low concentrations of carbofuran were found in air when samplers were placed 20 yards from the edge of an agricultural field in Imperial County, California. Reported concentrations ranging from .03 to .66 ug/m<sup>3</sup> were observed after a 44-hour sampling period following an application of 44% active ingredient carbofuran (Shibamoto et al., 1993).

Once in the air, carbofuran is subject to vapor-phase photooxidation by reacting with hydroxyl radicals. The half-life under this reaction is estimated to be 4.6 hours in a typical atmosphere (Handbook of Environmental Fate and Exposure Data, 1991).

### Water

Base-catalyzed hydrolysis to carbofuran phenol is the major degradation pathway of carbofuran in both water and sediment (Yu et al. 1974, Seiber et al. 1978, Brahma Prakash et al., 1987, Talebi and Walker, 1993). Other degradation products can include 3-hydroxy-7-phenolcarbofuran (Chiron et al. 1996), carbofuranphenol, *N*-methylcarbamic acid via hydroxylation of the benzofuranyl moiety (Yu et al., 1974). The aqueous hydrolysis rate of carbofuran increases dramatically with increasing pH. One laboratory study reported 80-95% recoveries of initial carbofuran spikes at pH 3 after 1, 3, and 6 hours (25°C). In contrast, at pH 10 only 65% of the original amount was recovered after 1 hour, 35% remained after 3 hours, and 10% remained after 6 hours (Bailey et al., 1996).

Seiber et al. (1978) found that the hydrolysis of carbofuran was more than 700 times faster at pH 10 than at pH 7; the reported half-lives were 1.2 hours and 864 hours, respectively. The foregoing data were obtained using rice paddy water treated with the granular formulation. Hydrolysis was also observed to be much more rapid in natural paddy water than in deionized (DI) water. Half-lives at pH 7 were 240 hours in paddy water and 864 hours in DI water, whereas at pH 8.7 half-lives were 13.9 hours in paddy water and 19.4 hours in DI water. Overall, the mean laboratory half-life in paddy water was 40 hours at pH 8. This agreed well with the 57-hour average observed in the field at the same pH, considering factors such as slight variations in sunlight, pH, temperature, and microbial degradation (Seiber et al., 1978).

Photolysis of carbofuran is a less important degradation pathway. Photometabolites include 2,3-dihydro-2,2 dimethyl benzofuran-4,7-diol, and 2,3-dihydro-3 keto-2,2 dimethyl benzofuran-7-yl carbamate (or 3-ketocarbofuran) (Raha and Das, 1990). One study compared recovery of carbofuran in DI water exposed to summer sunlight for 96

hours to carbofuran/DI water exposed only to laboratory light. The mean recovery was 75.6% for the natural sunlight-exposed carbofuran, while the mean recovery from carbofuran exposed to artificial light was 93.3%. This difference suggests that aqueous photodecomposition of carbofuran may be significant (Deuel et al., 1979). However, Seiber et al. reported only a slight difference in carbofuran half-lives obtained in DI water and paddy water (pH 7), both under exposure to laboratory UV light and no light. The half lives were found to be: DI water- light, 660 hours; DI water- dark, 753 hours; paddy water- light, 173 hours; paddy water- dark, 224 hours (Seiber et al., 1978). Bachman and Patterson (1999) suggested that the rate of carbofuran photolysis decreases with increasing amounts of dissolved organic matter (DOM). They proposed that the degree of inhibition was “directly proportional to the binding capacity of a particular DOM sample.” By binding to the DOM, they hypothesized that photolysis was slowed, making carbofuran slightly more persistent.

Oxidation and volatilization are generally considered insignificant dissipation pathways for carbofuran in water (Seiber et al., 1978; Raha and Das, 1990).

### Soil

Because of its high water solubility (351 ppm at 25° C) and low adsorption coefficient ( $K_{oc}= 22$ , Table 1), carbofuran is relatively mobile in soil and in surface runoff. Consequently carbofuran has the potential to contaminate lakes, streams, and groundwater. Carbofuran has been detected in the Sacramento River (Nicosia et al., 1991), although concentrations were below U.S. Health Advisory Levels (HALs) and Maximum Contaminant Levels (MCLs) (Cohen, 1996).

A study done by Kumari, Singh, and Saxena (1987) on the movement of carbofuran found a slight difference between adsorption coefficients in 2 soil types. In clay loam (OC content .53%, pH 8.6), carbofuran was found to have a  $K_d$  value of 22.4, while in silt loam (OC content .18%, pH 8.4) it had a  $K_d$  value of 19.9. Apparently less movement, and therefore higher adsorption, was seen in the clay loam, because of the presence of a greater organic matter and/or clay content. Leaching studies similarly demonstrated

increased sorption and lesser mobility in the clay soil (Kumari et al., 1987). Sharom et al. (1980) compared leachability of carbofuran from sand (OC content .7%, pH 7.0) and organic soil (OC content 75.3%, pH 6.1) with 10 successive rinses with 200 ml of distilled water. Carbofuran was almost completely leached out of the sand within the first two rinses (1<sup>st</sup> rinse recovered 94.8%, 2<sup>nd</sup> rinse recovered 4.1%). Amounts recovered from organic soil were less, with 73.8% from the 1<sup>st</sup> rinse, and 16.3% from the 2<sup>nd</sup> (Sharom et al., 1980).

According to Johnson and Lavy (1995), carbofuran is expected to partition into the water from soil. Immediately following granular application to paddy soil, 54% of the carbofuran was found in the water while 46% was found remaining in soil. The study done by Nicosia et al. (1991) disagreed with this data. They found the mass recovered from paddy soil was 5 times greater than mass recovered in paddy water immediately after application. 70 days after flooding, the mass recovered in soil was 98 times greater than the mass recovered in water. They noted low pH levels in soil compared to the water pH may have contributed to persistence in the soil (organic carbon content in this study ranged from 2.2% to 2.8%).

Similar to pH effects on aqueous hydrolysis rates, carbofuran degradation is much quicker in alkaline soils than in acidic soils. Getzin (1973) reported a 10-fold difference in DT<sub>50</sub> (time required for 50% breakdown) between soils at pHs 4.3 and 7.8. He concluded that while hydrolysis was the major route of degradation in alkaline soils, the slower degradation in acidic and neutral soils was dominated by microbial and chemical mechanisms. Breakdown products in soil include carbofuran phenol (Getzin, 1973), 3-hydroxycarbofuran, and 3-ketocarbofuran (Johnson and Lavy, 1995).

Other studies indicate that microbial degradation is an important route of carbofuran degradation in neutral soils. Miles et al. (1981) compared dissipation rates in two soils, a sandy loam (organic matter 3.3%, pH 7.3) and a muck (organic matter 36%, pH 7.3) under sterile and nonsterile conditions. Carbofuran was persistent in sterile soils, with 77% remaining in sterile muck and 50% in sterile sandy loam after 8 weeks. In contrast,

25% remained in the nonsterile muck while carbofuran was undetectable in the nonsterile sandy loam after 8 weeks (Miles et al, 1981). Carbofuran's metabolites also dissipated relatively rapidly in the nonsterile soils as well, and so are also suspected of degradation by microbes in the soil. Miles et al. (1981) observed disappearance of 90% of 3-hydroxycarbofuran within 1 week in both the nonsterile soils, while 3-ketocarbofuran disappeared from nonsterile loam in 1 week, and from nonsterile muck in 2 weeks.

A study using soil previously treated with carbofuran granules found a dissipation half-life of 58 days in one field (2.4% organic carbon), and 43 in another (2.2% organic carbon) (Nicosia et al.1991). Persistence of carbofuran in soil has also been reported. Szeto and Price (1991) found 78 ug/g of carbofuran in Canadian silt loam soils nearly a year after the application of granular material. The pH of similar soils from this area in the Fraser Delta of British Columbia, Canada, has been reported as between 5.0 and 5.9 (Mineau, 1993). Caro et al. (1973) reported a soil dissipation half-life of 117 days in a cornfield. Low soil pH (5.3) and lower soil moisture content may explain the relatively slow rate of dissipation.

There is a general consensus among researchers that repeated application of carbofuran to soils can result in enhanced rates of microbial degradation (Harris et al, 1984; Turco and Konopka, 1990; Scow et al. 1990). Enhanced degradation of a soil-applied pesticide may occur when a population of soil microorganisms is repeatedly exposed to a chemical and adapts by developing the ability to catabolize the chemical (Parkin and Shelton, 1994). Singh and Sethunathan (1999) found that when recoveries of applied carbofuran were compared between soils that are previously treated with carbofuran and soils untreated, the previously treated soils had a much lower recovery rate. The authors examined this theory using standing water from previously treated *Azolla* plots. After 2 days, 89.4% of the applied carbofuran was recovered in the uninoculated plot, while only 55.5% was recovered in the previously treated plot. After 5 days, 87.3% was recovered in the uninoculated plot, while only 29.8% was recovered from previously treated plot (Singh and Sethunathan, 1999). Getzin and Shanks (1990) found that enhanced degradation could develop with as little as one or two applications of carbofuran.

Volatilization is not as important as microbial degradation to carbofuran dissipation, but is a contributing dissipation process. In a controlled laboratory study examining volatilization, amounts of carbofuran evolved after 20, 40, and 60 days in sandy loam were, in  $\mu\text{g}$ , were 4.4, 10.3, and 14.4, respectively (initial concentration applied was 7.3 ppm, 5.8% water). In sand, amounts of carbofuran evolved (in  $\mu\text{g}$ ) were 216, 466, and 842 (initial concentration applied was 5.8 ppm, .7% water) (Caro et al., 1976). It has been reported that carbofuran volatilization rates are much more rapid under flooded soil conditions than under non-flooded soil conditions. The authors state that this is most likely due to co-evaporation with the water on the surface of the soil (Lalah et al., 1996).

Photodegradation is generally considered a minor route of carbofuran degradation. One study found that carbofuran adsorbed onto silt loam had a half-life of 13.6 days when exposed to  $2400 \mu\text{W}/\text{cm}^2$  and  $26^\circ\text{C}$  (National Resource Council of Canada, 1979). The rate of dissipation in soil is also strongly affected by temperature (Yen et al., 1997). One laboratory study found that carbofuran's half-life in silty clay loam (pH 6.7, organic matter 2.9%) was 105 days and 35 days at  $15^\circ\text{C}$  and  $35^\circ\text{C}$ , respectively (Yen et al., 1997).

### Biota

In 1991, the EPA and the FMC Corporation (carbofuran's manufacturer) agreed to ban granular formations of the chemical (although use was permitted on rice until August of 1999, U.S. EPA, 2002). The primary factor in this decision was the toxicity of the granular form to birds. Numerous reports of bird kills are documented as the result of direct ingestion of carbofuran after applications in fields. It seems the granular form is mistaken by birds as grit or food, and can easily be ingested by waterfowl while sifting sediments (Erwin, 1991). Over 80 separate bird kills have been reported, involving more than 40 species of birds, including robins, larks, sparrows, cardinals, goldfinches, bluebirds, blackbirds, and doves. Secondary poisoning (poisoning resulting from ingestion of poisoned insects and small birds) has been reported in owls, hawks, and eagles (Erwin, 1991). It should be noted that flowable carbofuran is as toxic to birds as the granular form, but exposure to the flowable form is less likely.



It is well documented that the principal metabolite of carbofuran in plants is 3-hydroxycarbofuran (National Resource Council of Canada, 1979). It subsequently oxidized to 3-ketocarbofuran, which is then rapidly hydrolyzed to the much less toxic 3-ketocarbofuran-7-phenol. This terminal residue is not likely to be detected in plants above trace levels (Eisler, 1985). Caro, Taylor, and Freeman (1976) found that carbofuran is readily absorbed by roots and is transported via plant fluids to areas of greatest transpiration, such as leaves. In corn, they discovered concentrations were highest in the leaves, less in the stalks, and very small amounts in the ears. It was estimated that .14% of the applied carbofuran was taken up by the crop (Caro, Taylor, Freeman 1976).

Because of its high water solubility and low  $K_{ow}$ , carbofuran is not expected to bioaccumulate to any great extent. This is also indicated by carbofuran's low measured bioconcentration factors in bluegill sunfish (Table 1). Metabolites include carbofuran phenol, 3-hydroxycarbofuran-7-phenol, *N*-hydroxymethyl carbofuran, 3-ketocarbofuran, and 3-ketocarbofuran phenol (Eisler, 1985). These compounds all become conjugated and excreted in the urine and bile.

Carbofuran has not been observed to accumulate significantly in aquatic systems. While carbofuran disrupts enzyme and lipid metabolism in fish, the effects are reversible with no observable permanent damage (Eisler, 1985).  $LC_{50}$  values ranged from 130 ppb to 1,420 ppb in tests of 72 to 96 hours, with yellow perch (*Perca flavescens*), green sunfish (*Lepomis cyanellus*), and lake trout (*Salvelinus namaycush*) being among the most sensitive, and channel catfish (*Ictalurus punctatus*) and fathead minnow (*Pimephales promelas*) among the most resistant (Eisler, 1985). When compared with the toxicities of other aquatic species, marine worms seemed to be the most resistant to the pesticide, while fish were the most sensitive (National Resource Council of Canada, 1979).

For terrestrial species, honeybees are extremely sensitive to carbofuran ( $LD_{50}$  is 0.16 $\mu$ g/bee, Eisler, 1985). Earthworms (*Lumbricus herculeus*) are also particularly susceptible, with an  $LC_{50}$  value in soil of 0.5 ppm at 5 hours. Earthworm mortality could result in an increased likelihood of secondary poisoning in many species (Eisler, 1985).

There have been no confirmed detections of carbofuran in California's groundwater (DPR Ground Water Database, 2002). However, carbofuran has been detected in surface water every year from 1991 through 1998, with a total of 279 detections out of 3007 samples taken as of December 2002 (DRP Surface Water Database, 2002). When carbofuran was still registered for use on rice, the majority of detections were associated with rice production; most detections occurred in rice-growing areas of Northern California during the months of April-June (DPR Surface Water Database, 2002).

### Conclusion

Carbofuran is a broad-spectrum carbamate insecticide, acaricide, and nematicide. It is used to control soil-dwelling and foliar-feeding insects, and works on contact or ingestion as a cholinesterase inhibitor.

The low vapor pressure and low Henry's Law Constant of carbofuran indicates that volatilization is a minor dissipation route for carbofuran. The small amounts that do volatilize react with hydroxyl radicals, giving carbofuran an estimated half-life of 4.6 hours in a typical atmosphere.

Hydrolysis is the main degradation pathway of carbofuran under alkaline conditions. Base-catalyzed decomposition products include 3-hydroxy-7-phenolcarbofuran, carbofuran phenol, and *N*-methylcarbamic acid. Carbofuran's hydrolysis rate is highest under alkaline conditions, being 700 times faster in water with pH 10 than in water with pH 7.

Microbial degradation is an important degradation route in neutral and acidic conditions. Microbial adaptation has been observed; repeat applications may result in lesser persistence.

Photolysis is not generally considered a significant degradation pathway in either water or soil. Photo-degradates include 2,3-dihydro-2,2 dimethyl benzofuran-4,7-diol and 2,3-dihydro-3-keto-2,2 dimethyl benzofuran-7-yl carbamate. Oxidation and volatilization are generally considered as minor dissipation pathways.

Carbofuran's high water solubility and low soil sorption coefficient render carbofuran relatively mobile in soils. It partitions weakly to soil and sediment from water. Consequently, carbofuran has the potential to contaminate lakes, streams, and groundwater via percolation and runoff. Degradation is more rapid in alkaline soils than in acidic soils. Breakdown products in soil include carbofuran phenol, 3-hydroxycarbofuran, and 3-ketocarbofuran, all of which appear to be relatively non-persistent.

Carbofuran does not bioaccumulate to any noteworthy extent. One of the more significant metabolites is 3-ketocarbofuran. In fish, carbofuran disrupts enzyme and lipid metabolism, but effects seem to be reversible. Honeybees and earthworms are particularly sensitive to this pesticide. In plants, carbofuran is readily absorbed by roots and is transported to areas of greatest transpiration.

Granular carbofuran is currently banned in the U.S. because it is highly toxic to birds. Numerous bird kills have been linked to direct ingestion of carbofuran by birds, as they may accidentally consume carbofuran while sifting sediments.

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