ENVIRONMENTAL FATE OF CARBARYL

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The document reviews the environmental fate and environmental effect of carbaryl (1-naphthyl-N-methyl carbamate). Carbaryl is one of the most frequently used carbamate insecticides and widely used for the control of a variety of pests on fruit, vegetables, forage, cotton and many other crops, as well as on poultry, livestock and pets (Mathew et al., 1995). It is available as wettable powders, pellets, granules, dusts, suspensions and even solutions (U.S. EPA, 1988).

Physical and chemical properties
Common Name
Carbaryl

Chemical Name
1- naphthalenylmethylcarbamate

Trade Names
Arilat, Arilate, Arylam, Carbacine, Karbaryl, Menaphtam, Sevin, Vioxan

CAS Registry No.
63-25-2

Structural Formula
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\text{OCNCH}_3
\]

Empirical Formula
C_{12}H_{11}NO_2

Molecular Weight
201

Water Solubility
113 ppm at 22^0C (R&P, 1988)
40 ppm at 30^0C (Kidd and James, 1991)

Organic Solvents Solubility at 25^0C (R&P, 1988)
Methanol: 7960 ppm
Hexane: 214 ppm
Methylene Chloride: 242,600 ppm

Vapor pressure
1.17 x 10⁻⁶ mmHg @ 25°C (R&P, 1988)
4.1 x 10⁻² mPa @ 23.5°C (Kidd and James, 1991)

Octanol/water partition coefficient
70.8 (logK<sub>ow</sub> = 1.85) at 25°C (R&P, 1988)
logK<sub>ow</sub> = 2.36 (Kenaga and Goring, 1980)

Henry’s law constant (R&P, 1988)
2.7425 x 10⁻⁹ atm m³ g mol⁻¹ at 25°C

Environmental Fate

Hydrolysis Half-Life
>1500 days (pH = 5) (Wolfe et al., 1978)
12.1 days (pH = 7) (Carpenter, 1990)
3.2 hours (pH = 9) (Carpenter, 1990)

Soil Adsorption Coefficient (K<sub>oc</sub>)
251 (Sablijic, 1995)
100-600 (WHO, 1994a)

Photolysis Half-Life (Water, Artificial Light, pH = 5)
21 days (Das, 1990a)

Photolysis Half-Life (Soil, Artificial Light)
41 days (Das, 1990b)

Aerobic Soil Half-Life (WHO, 1994b)
4-17 days (sandy loam soil)
21-27 days (clay loam soil)
78 days (Miller, 1993a)

Anaerobic Half-life

Field Dissipation Half-life
0.76 – 10.9 days (Norris, 1991)

Toxicity and Ecological Effects
(Kidd and James, 1987):

Rat (oral, acute)
LD₅₀ 850 mg/kg (males)
LD₅₀ 500 mg/kg (females)

LD₅₀ 710 mg/kg

Rabbit (oral, acute)
LC₅₀ >206.1 mg/l air

Pigeons (oral, acute)
LD₅₀ >2000 mg/kg

LD₅₀ 2230 mg/kg

LD₅₀ 1000-3000 mg/kg
Channel Catfish (96 hrs)  $\text{LC}_{50}$ 15.8 ppm (Tucker, 1970)
Asellus (96 hrs)  $\text{LC}_{50}$ 280 ppb (Tucker, 1970)
Daphnia Magna (48 hrs)  $\text{LC}_{50}$ 18.6 ppb (Li and Yang, 2000)
Daphnia Magna (48 hrs)  $\text{EC}_{50}$ 0.26 ppb (Rawash et al. 1975)
Daphnia Magna (Surprenant, 1985)  21-day MATC 1.5–3.3 ppb
                           21-day NOEC 6.0 ppb
Fathead Minnow (96 hrs)  $\text{LC}_{50}$ 5.29 – 10.4 ppm (Brooke, 1984)
Brine Shrimp (Barahona and Sanchez-Fortun, 1999)  $\text{LC}_{50}$ 27.5 ppm
                          (24 hrs)  $\text{LC}_{50}$ 5.90 ppm
                          (48 hrs)  $\text{LC}_{50}$ 0.35 ppm
                          (72 hrs)  $\text{LC}_{50}$ 4.38 ppm
Rainbow Trout (96 hrs)  $\text{LC}_{50}$ 6.76 ppm
Bluegill Sunfish (96 hrs)  $\text{LC}_{50}$ 13.2 ppm
Goldfish (96 hrs)  $\text{LC}_{50}$ 280 ppb (Johnson and Finley, 1980)
Sow Bug (Asellus Brevicaudus) (96 hrs)  $\text{LC}_{50}$ 5.6 ppb (Johnson and Finley, 1980)
Glass Shrimp (Palaemonetes) (96 hrs)  $\text{LC}_{50}$ 120 ppb (Chaiyarach et al., 1975)
(Kadiakensis)  $\text{LC}_{50}$ 320 ppb (Mayer, 1987)
Blue Crab (48 hrs)  $\text{LC}_{50}$ 1.5 ppb (Mayer, 1987)
Brown Shrimp (48 hrs)  $\text{LC}_{50}$ 28 ppb (Mayer, 1987)
Grass Shrimp (48 hrs)  $\text{LC}_{50}$ > 7.7 ppb (Nimmo et al., 1981)
Mysid shrimp (96 hrs)  $\text{LD}_{50}$ 1.54 – 26.5 μg a.i/bee (Union Carbide, 1983)
Honey Bee

**Mode of Action**

Carbaryl is a member of the widely used carbamate pesticides. Like most carbamates, carbaryl acts as an inhibitor to cholinesterase, one of many important enzymes in the nervous systems of humans, vertebrates and insects (Extoxnet, 2000). A specific cholinesterase enzyme, acetylcholinesterase (AChE), plays an important role in breaking down the acetylcholine (Ach), which is the synaptic mediator of nerve impulses in the
nervous systems of mammals and insects (WHO, 1994d). The presence of cholinesterase inhibiting pesticides, such as carbaryl, prevents AChE from breaking down acetylcholine and results in high concentration of Ach in the nervous system. As a result, the continuous stimulation of the muscle leads to uncontrolled, rapid movement of some muscles, paralysis, convulsions and even death.

Environmental Fate

Air: Carbaryl has a low vapor pressure, $1.17 \times 10^{-6}$ mmHg, and is not readily volatilized into the air. A low Henry’s law constant, $2.74 \times 10^{-9}$ atm m$^3$ g mol$^{-1}$, suggests that carbaryl has low potential to volatilize from aqueous solution (Lyman et al., 1982). It might be found in the atmosphere associated with air-borne particulates or as spray drift but should not be over a large area. If existing in air, carbaryl tends to react with hydroxyl radical in the ambient atmosphere (Kao, 1994). Carbaryl in air was monitored after being applied to a large area of forest in Maine for the control of spruce budworm, and the concentrations ranged from 0.0035 to 0.107 µg/m$^3$ (Shehata et al., 1984).

Water: Hydrolysis is the primary degradation pathway for carbaryl at pH 7 or above. The compound degrades rapidly at pH 7 and 9 at 25°C, with half-lives of approximately 10-17 days and 3 hours, respectively (Aly & El-Dib, 1971; Carpenter, 1990). In acidic water, carbaryl is rather stable with a half-life of more than 1500 days at 27°C (Wolfe et al., 1978). The identified degradation products are 1-napthol, methylamine and CO$_2$ (Aly and ElDib, 1971; Larkin and Day, 1986). In natural water, carbaryl is expected to degrade faster due to the presence of microorganisms. The half-lives of carbaryl in steams, rivers and brooks as a result of forest spraying are 25, 28 and 23 hours, respectively (Stanley et al., 1980).

The aqueous photolysis of carbaryl was determined to be 21 days in sterile distilled water under artificial sunlight at a concentration of 10.1 ppm and pH 5 (Das, Y.T., 1990a). The intensity of artificial light was comparable to that of the natural sunlight, at 510.5 and 548.8 watts/m$^2$, respectively. Other reported aqueous photolysis half-lives are much
shorter than that obtained from sterile water. Wolfe et al. (1978) has reported that photolysis half-life of carbaryl is 6.6 days, and Zepp et al. (1977) as 50 hours near water surface. The aqueous photolysis rates increase as intensity of sunlight increases; therefore, the rate of hydrolysis is much faster in summer than that in winter. Wolfe et al. (1976) has calculated aqueous photolysis half-lives of carbaryl in surface water (in < 10 cm water) at latitude 40 degrees North in different seasons: 64 hours in spring, 52 hours in summer, 102 hours in fall and 200 hours in winter. The major photolysis product is 1-naphthol, which will further photooxidize to 2-hydroxy-1,4-naphtho-quinone in basic condition (Wauchope and Haque, 1973).

The soil sorption coefficients ($K_{oc} = 100 \sim 600$), octanol/water partition coefficients ($\log K_{ow} = 1.85 \sim 2.36$) and water solubility indicate that carbaryl moderately binds to soils and sediments. Thus, suspended particulates or mud in natural water may remove some carbaryl from the aqueous phase. Karinen et al. (1967) reported that 50% of initial carbaryl disappeared from estuarine water after 38 days at $8^\circ$C in the absence of mud; in the presence of mud, 90% of initial applied carbaryl was withdrawn from the water after 10 days at the same temperature due to significant removal of carbaryl by mud.

Carbaryl may enter marine system resulting from the control of oyster pests and predators (Haven et al., 1966). Carbaryl is believed to be more persistence in seawater than in freshwater (WHO, 1994c). Armbrust et al. (1991) reported that hydrolysis half-lives of carbaryl in filtered and sterilized seawater at pH 7.9 and 8.2 at $24^\circ$C were 24 and 23 hours, respectively, and the major degradation product was 1-naphthol. Naphthol was not degraded in dark sterile seawater but was undetected within 96 hours in raw seawater. When exposed to artificial sunlight, carbaryl had a half-life of 5 hours and naphthol was completely degraded in 2 hours.

**Soil:** Overall, carbaryl is not persistent in soil. It can be degraded through hydrolysis, photolysis as well as by microorganisms. The photodegradation of carbaryl was investigated on soil under artificial sunlight for a total of 30 days (Das, 1990b). In this
case, carbaryl was applied on 1-mm soil layers at a concentration of 9.8 ppm. The estimated half-life was approximately 41 days with no findings of major metabolites.

Microbes play a significant role in the degradation of carbaryl in soil. Quite a few bacteria can use carbaryl as their sole source of carbon and nitrogen. Chapalamadugu et al. (1991) revealed that two Pseudomonas spp, which were isolated from soil, can metabolize either carbaryl or 1-naphthol. A bacterial consortium, constructed by two isolates, is able to completely catabolize carbaryl to CO₂ within 36 hours. The mechanism of the metabolism of 1-naphthol by Pseudomonas spp is proposed as via salicylic acid (Larkin and Day, 1986).

In aerobic soil, carbaryl was quickly degraded with an approximate half-life of 4 days (Miller, 1993a). A significant amount of CO₂ was produced, ranging from 0.1% at day 1 to 59.7% at day 14. Another major degrade is 1-naphthol. Carbaryl degrades more slowly in anaerobic aquatic soil with an estimated half-life of 72 days (Miller, 1993b). 1-naphthol is the major degrade with minor compounds of 1,4-naphthoquinone, 5-hydroxy-1-naphthyl methylcarbamate and 1-naphthyl-(hydroxymethyl) carbamate. None of these minor degradates accounted for more than 2.5% of total applied dose. CO₂ was generated slowly, ranging from none at day 3 to 4% at day 94. At day 126, CO₂ reached the maximum of 23.6%.

Murthy et al. (1989) studied the metabolism of ¹⁴C-carbaryl and 1-naphthol in moist and flooded soils over a 28-day period. More CO₂ was generated from carbaryl treated moist soil than from flooded soil. Most radio-activities existed as soil bound materials and only less than 1 percent of parent was present in extractable radiocarbon. The major degradation was 5-hydroxyl carbaryl in moist soil and 4- and 5-hydroxyl carbaryl in flooded soil.

The adsorption coefficient values (Kₜₐ) of carbaryl range from 100 to 600 (WHO, 1994a; Jana and Das, 1997), indicating carbaryl moderately binds to soil. Sorption experiments
were implemented on two types of soils, Red Bay (AB) and Astatula (AS), which were further separated into two layers, topsoil (0-30 cm) and subsoil (31-60 cm) (Nkedi-Kizza and Brown, 1998). The properties of individual soil are: AB top (pH 6.3, OM 15.2%), AB sub (pH 5.3, OM 3.9%), AS top (pH 5.6, OM 8.0%) and AS sub (pH 4.8, OM 2%). The sorption coefficient values (Koc) of carbaryl on soils are: 338, 144, 590 and 671 mg/kg on AB topsoil, AB subsoil, AS topsoil and AS subsoil, respectively. The half-lives of carbaryl on the four soils ranged from 8 to 18 days. Given a same soil, carbaryl degraded much faster in topsoil than in subsoil.

Terrestrial field dissipation studies were conducted at two locations, one in California and one in North Carolina (Norris, 1991). Data showed that most residues remain in the first 0-0.15 meters of soil, with only one finding in the layer of 0.3 –0.45 meter. The dissipation half-lives of carbaryl were estimated as from 0.76 to 10.9 days.

**Biota:** The efficacy of carbaryl for the control of pests is attributed to its ability to inhibit acetylcholinesterase (Ache) in the nervous systems (Barabona and Sanchez-Fortun, 1999). Given the same mode of action, carbaryl also poses risks to other non-target animals, including human beings. Carbaryl can penetrate the skin, mucous membranes, respiratory tract and gastrointestinal tract of mammals. However, it can be rapidly metabolized by various animals, and excreted especially in the urine as glucuronides or sulfates (Dorough and Casida, 1964; Fukuto, 1972). The following metabolites have also been identified: 1-naphtyl N-hydroxymethylcarbamate, 4-hydroxy-1-naphthyl-N-methylcarbamate, 5-hydroxyl-1-naphthyl-N-methyl-carbamate and 5,6-dihydroxy-1-naphthylmethylcarbamate.

Carbaryl is relatively safe to mammals although it can temporarily inhibit AchE. Rats given a single oral dose of 560 mg/kg body weight showed a decrease of 42% erythrocyte- and 30% brain-ChE activity within 5 minutes (Carpenter et al., 1961). However, the activity recovered to normal level after 24 hours.
Carbaryl and its major degradate, 1-naphthol, are toxic to some ecologically beneficial soil microorganisms such as *Chlorella vulgaris*, *Nostoc linckia*, and *Synechococcus elongates* (Megharaj et al., 1990). Obulakondaiah et al. (1993) reported that carbaryl and 1-naphthol resulted in toxicity at concentrations of 50-100 ppm and 25-100 ppm, respectively. In this case, 1-naphthol was found to be more toxic than its parent compound since it inhibits nitrogen cycling mediated by tested microorganisms. Under other circumstances, carbaryl presented more toxic effect on different microbes than 1-naphthol (Megharaj et al., 1990).

Carbaryl is considered moderately to highly toxic to fish with LC$_{50}$ values ranging from 4 ppm to 13 ppm (Beyers et al., 1994; McKim, 1987; Sinha et al., 1991). The chemical is especially toxic to the aquatic invertebrate *Daphnia magna* with LC$_{50}$ values at 48 hours less than 18.6 ppb (Li and Yang, 2000). Weis et al. (1974) reported that 0.1-ppm carbaryl water solution is able to disrupt the schooling habit for juvenile *Menida medidia*. 1-naphthol is believed to be the major factor instead of the parent compound. However, schooling behavior was recovered within 3 days.

Carbaryl is slightly or practically non-toxic to birds, with LD$_{50}$ for young mallard ducks, young pheasants and pigeons of >2179, 2000, 1000-3000 mg/kg, respectively. The effect of low concentration carbaryl (1.68 kg/ha) on nontarget birds, mammals and insects have been investigated in western North Dakota (George et al., 1992). No evidence was found to conclude that carbaryl depressed brain AChE in birds or small mammals collected from the treated area after 2, 10, 21 days or 1 year.

Carbaryl is highly toxic to honey bees, with LD$_{50}$ values ranging from 1.5 to 26.5 ug a.i. per bee (Union Carbide, 1983). Study revealed that adjusting the application time and formulation of carbaryl could significantly reduce the toxicity of carbaryl to honey bee. To minimize the death of honey bee, applications could be made during early morning or late evening when bees are not actively foraging.

The metabolism of carbaryl in plants is similar to that in animals. Several water-soluble metabolites were recovered from crops treated with $^{14}$C-carbaryl, including 5,6-hydroxy-
5,6-dihydrocarbaryl, N-hydroxymethylcarbaryl, 4- and 5-hydroxycarbaryl and 1-naphthol
(Kuhr, 1967; Kuhr and Casida, 1967; Kuhr, 1970). Both hydrolytic and oxidative
reactions contributed equally to the metabolism of carbaryl.
The persistence of carbaryl on plants have been investigated by several research groups
(Choudhary, et. al., 1988; Galhotra, et. al., 1985; Iwata, et. al., 1979, Rao and
Ramasubbaiah, 1988). Sevin 80W were applied on mature orange and lemon trees at the
rate of 11.5 lb a.i. (1200 gal)⁻¹ acre⁻¹ in Orange County and Riverside County California,
respectively (Iwata, et al., 1979). After 5 days, foliar residues for orange were 5.6 ug/cm²
and lemon 2.4 ug/cm². The residues after 60 days were 0.36 and 0.41 ug/cm² on orange
and lemon, respectively. The half-lives of carbaryl on oranges and lemons were reported
as 14 and 22 days, respectively. In other experiments, the dissipation half-lives of
carbaryl were 1.80-1.94 days in sesame plant and less than 1.25 days in tomato
(Choudhary, et. al., 1988 and Galhotra, et. al., 1985). Galhotra (1985) reported the
carbaryl residues in potato foliage and tuber, 64-94 days after application at the rates of 1
– 5 kg a.i./ha, were below detectable level (0.03 – 0.10 ppm).
The side effects of carbaryl on the growth of plants have been well documented (Murthy
and Raghu, 1990; Jones et al., 1991). Undesirable thinning of apples have been observed
after paclobutrazol and carbaryl were applied to apple trees within an interval of seven
days in a period over 20-30 days after full bloom Carbaryl with a concentration of 2.5
ppm in clay and sandy loam soils had no effect on the growth of barley. However, higher
concentration of carbaryl, 25 and 100 ppm, demonstrated the inhibitory effects (Murthy
and Raghu, 1990). The phototoxic effects of carbaryl only lasted for a few days after the
application of carbaryl in soil.

Conclusion

Carbaryl is a contact and respiratory poison, functioning as a reversible inhibitor of
cholinesterase (ChE) activity. In general carbaryl is slightly toxic to mammals,
moderately to highly toxic to aquatic organisms and honeybees. Carbaryl is degraded
rapidly in plants.
Carbaryl does not readily volatize into the atmosphere and it is unlikely to volatize from water to air. Carbaryl moderately binds to soil and has potential to leach to groundwater (Guo, 2000). It is not persistent in soil since it can be hydrolyzed, photodegraded, oxidized, degraded by microbes.

In alkaline or neutral water, hydrolysis is the major degradation route for carbaryl, with half-lives ranging from a few hours to a few days. It is also subject to microbial degradation in natural water. Photolysis plays a role in the degradation process, significantly reducing degradation half-life of carbaryl. The major degradation product is 1-naphthol.

References


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