

Review Article

Understanding the Degradation of Carbofuran in Agricultural Area: A Review of Fate, Metabolites, and Toxicity

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ABSTRACT

Pesticides are commonly applied in agriculture to manage pests, parasites, weeds, and other crop diseases to maximise product output value and minimise or reduce yield losses. Pesticides are widely and indiscriminately used in crop production in most countries. Carbofuran is a highly toxic insecticide commonly used to protect crops in agricultural areas. Exposure to carbofuran can cause harmful effects on both the ecological environment and human health, particularly on non-target species such as birds and aquatic organisms. Carbofuran continues to be used, although it has been banned in some countries. This review paper highlights carbofuran usage, its residue, toxicity, and mechanisms of degradation pathways in water, soil, and food, especially in agriculture. It has been shown that hydrolysis, photolysis, and microbial degradation are the main pathways for carbofuran degradation. Carbofuran phenol is significantly less toxic than all photo-metabolites, while 3-ketocarbofuran and 3-hydroxycarbofuran are practically as harmful as the parent compound. Hence, more study is needed on degradation pathways that may thoroughly minimise the toxicity of this deadly pesticide.

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INTRODUCTION

Pesticides are compounds or a mix of chemicals designed to kill, prevent, or control pests (Cossi et al., 2020). According to the terminology used in the agricultural

industry, “synthetic pesticide” refers to any pesticide manufactured and not found naturally. Synthetic pesticides are generally produced through chemical synthesis and are designed to be more potent and persistent than their natural counterparts (Ahmadi, 2019). Organochlorines, organophosphates, carbamates, and pyrethroids are classes of synthetic pesticides. In contrast to synthetic pesticides, pesticides derived from natural sources, such as plants or microbes, are often called “biopesticides” or “organic pesticides”. Biopesticides are derived from living organisms and their by-products, and they typically have low toxicity levels and little environmental impact (Ayilara et al., 2023).

Pesticides are used to control a wide range of pests, such as insects, plant pathogens, weeds, microbes, nematodes (roundworms), molluscs, mammals, birds, and fish, which cause massive losses in plantations and properties, spread infectious diseases, and act as disease vectors. Moreover, applying pesticides against pests and air-borne diseases improves the agricultural sector’s economic output and boosts crop yields (Idayu et al., 2014; Okoli et al., 2017). Despite having significant benefits, there are serious concerns regarding the effects of pesticides, such as their potential toxicity toward humans and other animals (Daliya et al., 2020).

Malaysia is an agriculture-based country with vast areas reserved for plantations and farming. 70% of the cropland is devoted to oil palm and rubber plantations, which occupy more than 3.8 million hectares (Fatah et al., 2017). Given the massive demand for plantation produce in recent years, pesticides have been extensively used. It has been reported that applying pesticides leads to ground and surface water contamination and causes many undesirable effects and problems in tropical countries with heavy rainfall, high humidity, and high temperatures (Farahani et al., 2007; Ismail et al., 2004). In Japan, China, and the Republic of Korea, more than 10 kg/ha of pesticide are applied, while most Asian countries are below 1 kg/ha (Figure 1).

It represents an average annual growth rate of 1.6% in the net value of agricultural pesticides used during the past 15 years. Recently, about two million metric tonnes of pesticides have been used annually: herbicides (50%), insecticides (30%), fungicides (18%), rodenticides (9%), and nematicides (Sharma et al., 2019). Their transport, transfer, and transformation mechanisms determine pesticides’ environmental fate. Herbicides in paddy fields, vegetable plantations in the Cameron Highlands, Pahang, Johor and tobacco-growing areas were studied (Boh & Yeang, 2002; Nashriyah & Azimahtol, 2002; Halimah et al., 2005; Ismail et al., 2015). It was also reported that surface and groundwater pollution due to pesticides had become a growing concern in tropical countries, including Malaysia (Sapari & Ismail, 2012).

Carbofuran is a highly hazardous pesticide that harms people, animals, and the environment. Due to its adverse effects, many countries, including Malaysia, have prohibited its use. However, as an alternative to chemical pesticides, there has been a recent

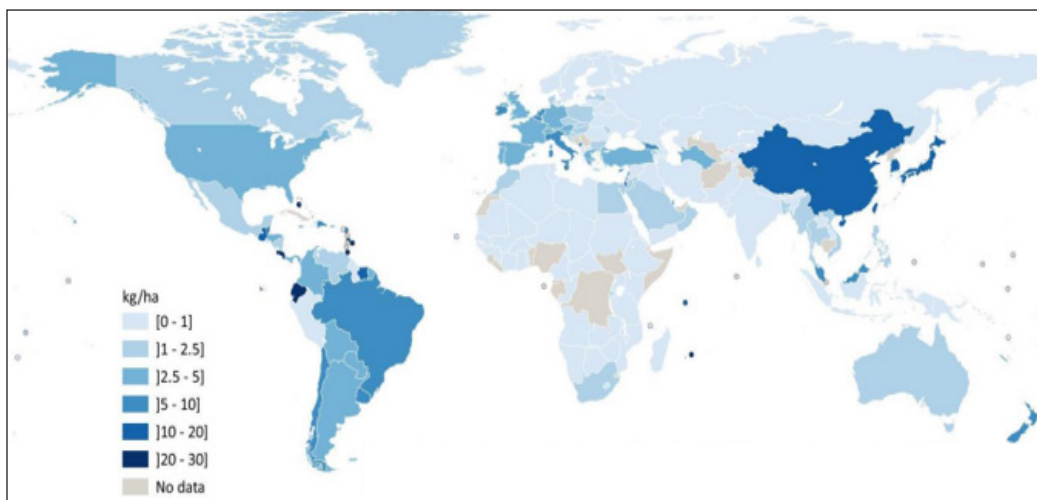


Figure 1. Pesticides use per cropland area, 2018 (FOA, 2020)

interest in using biological agents and natural pesticides. Natural pesticides are derived from natural sources such as plants, minerals, or microorganisms, whereas biological control agents are living organisms that feed on or parasitise pests (Yubak-Dhoj et al., 2021).

Biological control and natural pesticides are effective in pest control while posing the least risk to humans and the environment. They are frequently more specific and targeted than chemical pesticides, which can have unintended consequences for non-target organisms. Biological agents and natural pesticides are becoming more popular as safer and more sustainable alternatives to chemical pesticides such as carbofuran (Torres & Bueno, 2018).

In a study by Mustapha et al. (2019), 3-hydroxycarbofuran and 3-ketocarbofuran as carbofuran by-products are more polar but equally toxic to target and non-target organisms. Other known by-products of carbofuran include carbofuran phenol, 3-hydroxy-7-carbofuran phenol, and 3-keto-7-carbofuran phenol (through phenyl-ring oxidation/reduction and hydroxylation reactions), N-hydroxymethyl carbofuran, and 3-hydroxy-N-hydroxymethylcarbofuran (through methyl hydroxylation reactions). In plant tissue samples, 3-hydroxycarbofuran was higher and lasted longer than the parent compound (Ramasubramanian & Paramasivam, 2018; Ramesh et al., 2015).

The reaction pathways and breakdown of pesticides are crucial to determining the process involved, especially the nature of the reactive intermediates and their final products. In this way, proper management and control of the discharge of pesticides into the environment can be implemented (Fenner et al., 2013; Bose et al., 2021). For instance, water management is vital in rice production since the growth of the paddy field requires a large amount of water supply. Water from the main canal is channelled into each plot and retained for a certain period before being drained from the paddy field. Therefore,

the pesticides used in surface water would significantly affect the water quality and could threaten the lives of aquatic animals in the surrounding plantation.

This review aims to assess the reported concentrations of carbofuran residues and their effects on the environment and human health, as well as to discuss their insights on carbofuran usage, toxicity, and degradation, particularly in agriculture. Thus, we aim to emphasise the comprehensive mechanism of the carbofuran degradation pathway via hydrolysis, photolysis, and microbial degradation into its significant metabolites.

CARBOFURAN

Carbofuran (2,3-dihydro-2,2-dimethyl benzofuran-7-yl-N-methylcarbamate) is a broad-spectrum insecticide, acaricide, and nematicide. Carbofuran is classified under the general group of carbamate derivatives called furadan, curaterr, carbodan, carbosip, and chinufur, with its chemical structure shown in Figure 2 (Pyne, 2015; Mukaj et al., 2017).

It was during World War II that a lot of new methods were developed for dealing with pests. Many manufactured chemicals were tested for their insecticidal efficacy because of the pressing need to reduce human disease transmission by pests in tropical areas. Figure 3 displays a timeline of carbofuran usage throughout history. Carbamates, a third class of chemically synthesised insecticides, were identified by Swiss scientists in the 1940s. In the mid-1940s, the Geigy Chemical Company aimed to create an insect repellent and began working on carbofuran. A set of tests on carbamate compounds found that these compounds were ineffective insect repellents and poisonous to flies, mosquitoes, aphids, and other smaller pests. Geigy was prompted by this situation to explore the development of dimethyl carbamate insecticides instead of carbamate repellents (Mahindru, 2009).

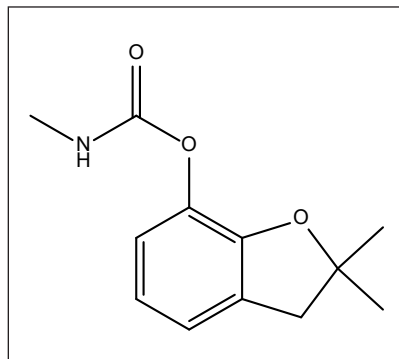


Figure 2. Carbofuran chemical structure

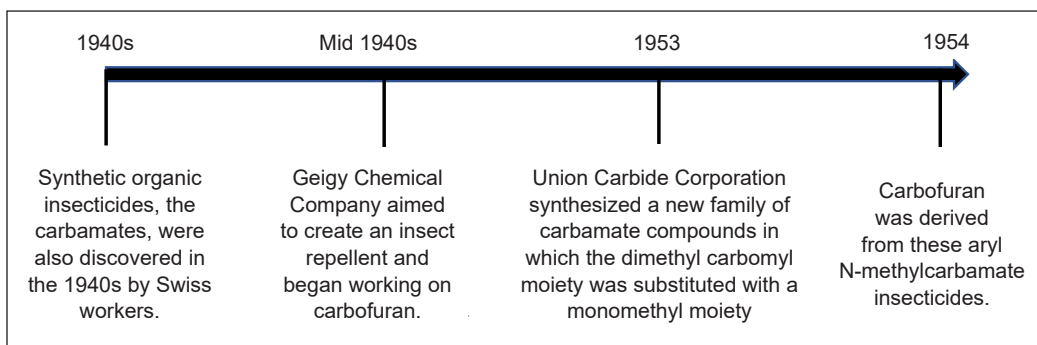


Figure 3. Timeline showing the history of the production of carbofuran

In 1953, Union Carbide Corporation synthesised a new family of carbamate compounds in which the dimethyl carbamoyl moiety was substituted with a monomethyl moiety. Compared to dimethyl carbamic acids, the insecticidal properties of aryl N-methylcarbamate were superior (Park et al., 2013). Carbofuran was derived from these aryl N-methylcarbamate insecticides.

Carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl-methylcarbamate) is a nematicide generally applied to soil or grassland. It is highly mobile and soluble in water (351 g/mL), posing a danger of environmental water pollution (Table 1) (Ćwieląg-Piasecka et al., 2021). The pesticide has moderate sorption to soil, based on organic matter and clay mineral composition, though it is unclear which soil element has the strongest affinity (Cáceres et al., 2019; Khairatul et al., 2013). Carbofuran degrades faster in an alkaline medium but is relatively stable in neutral or acidic environments. It is hydrophilic at concentrations up to 700 mg/L, while its solubility decreases in organic solvents at less than 30 mg/L (Brasel et al., 2007).

As with carbofuran, it has a low solubility in water but a high solubility in acetone, acetonitrile, benzene, and cyclohexane. It degrades at temperatures above 130°C and stimulates combustion when ignited. The substance is available as a powder, granules, and flowable formulation in a solvent (USEPA, 2006). It has a shorter environmental half-life than chlorinated hydrocarbon insecticides, degrades faster, and is excreted by nontarget organisms. Carbofuran may reach the aquatic environment by runoff from treatment plantation fields, direct application or broadcasting of granular formulations, or drift from sprayable mixtures (Valente-Campos et al., 2019).

CARBOFURAN USAGE/RESIDUE IN AGRICULTURAL PRODUCTS

Carbofuran is a pesticide that is commonly used to repel pests and nematodes on a wide range of crops, including rice, potatoes, corn, and soybeans, because of its broad-spectrum biological action and comparatively low persistence compared to organochlorine pesticides (Kuswandi et al., 2017; Bedair et al., 2022).

In Asia, Australia, and South America, its use is widespread. Meanwhile, Canada, Kenya, Brazil, the United States, and the European Union are among the countries that

Table 1
Carbofuran's physical and chemical characteristics (Otieno et al., 2010a)

Chemical formula	C ₁₂ H ₁₅ N O ₃
Molecular weight	221.6 g/mol
Physical state	White crystalline solid
Flammability	Not flammable
Melting point	15 to 154°C
Density	1.180 (20 °C)
Vapour pressure	2 × 10 ⁻⁵ mmHg (33°C) 1.1 × 10 ⁻⁴ mmHg (50°C)
Octanol/water partition coefficient	42.5
Water solubility	351 µg/ml (250°C)
K _{oc}	9–36 ml/g

have banned or restricted the use of carbofuran. Canada banned carbofuran-containing pesticides in 2009 when Health Canada's Pest Management Regulatory Agency (PMRA) cancelled all carbofuran registrations (Health Canada, 2020). In 2010, Kenya prohibited carbofuran import, distribution, and sale. Carbofuran's registration in Brazil was suspended in 2011, effectively banning its use there. In 2008, the European Union banned the use of carbofuran in all its member countries. The United States Environmental Protection Agency (EPA) banned all carbofuran uses in the country in 2009, claiming risks to human health and the environment (U.S. EPA, 2009).

Aubergines and other vegetables in Malaysia are often treated with carbofuran (Sim et al., 2019). It is an approved insecticide until May 2023, when it will be banned in agriculture (Pesticides Act 1974, 2021). The Pesticides Board of Malaysia, which oversees controlling pesticides in Malaysia, has said that carbofuran will be banned on April 20, 2021. The ban was put in place because the chemical was harmful to people and the environment, as well as to wildlife and organisms that were not its intended target.

About 1% of the earth's surface is used to grow paddy rice (*Oryza sativa*) because it is grown on every continent except Antarctica. Over half of the world's population uses rice as its primary food, which ranks second to wheat in global cultivation (Kumar et al., 2020). Given that rice is the only food crop cultivated during the rainy season in the tropical areas of Asia, the region has contributed over 90% of the world's rice production. Malaysia's land area used for rice cultivation has remained consistent since the 1980s at roughly 0.7 million ha. Nevertheless, rice productivity increased yearly, from 2.1 t/ha in 1961 to 3.6 t/ha in 2008. Similarly, total rice production has increased yearly since 1985, with an average annual increase of 28,000 metric tons (Ibitoye et al., 2014).

Table 2 summarises the amounts of carbofuran residues in water from the different agricultural industries. Carbofuran is a pesticide that can leave residues in treated products and is subject to maximum residue limits (MRL). However, it is important to note that MRLs for carbofuran may vary by country or region and are subject to periodic updates. Carbofuran levels in Canadian freshwater ranged from 0.03 to 158.5 mg/L, which is high. Carbofuran was discovered once (at 3.0 µg/L) in 678 samples from 1971 to 1986 (Health Canada, 2020). As for the USA, 1 µg/L of carbofuran was detected in streams (Papadakis et al., 2015), and 1 to 30 µg/L was discovered in groundwater (Conway & Pretty, 2013). For example, carbofuran has been heavily used in Kenya, increasing environmental contamination. (Otieno et al., 2011). Several samples of surface water from paddy fields were found to contain carbofuran at concentrations ranging from 0–3.395 µg/L, and those from lakes had carbofuran concentrations ranging from 0.949–1.671 µg/L, respectively (Chowdhury et al., 2012). It has been discovered that concentrations of carbamate insecticides in the environment that are higher than the limit set by the European Community (0.5 g/L) are unusual (Plese et al., 2005; Zhang et al., 2016).

Table 2

Concentration of carbofuran residues in water from the various matrixes

Concentration	Matrix	Reference
0.03–158.5 mg/L	Freshwater	Health Canada (2020)
1 µg/L	Streams	Papadakis et al. (2015)
1–30 µg/L	Groundwater	Conway and Pretty (2013)
0.18–14 µg/L	Drinking water	Howard (2017)
1–5 µg/L	Water table aquifers	Howard (2017)
0.1–0.5 µg/L	Rainwater	Howard (2017)
0.005–0.495 mg/L	Rivers	Otieno et al. (2011)
2.301 mg/L	Ponds and dams	Otieno et al. (2011)
0.949–1.671 µg/L	Lake's water	Chowdhury et al. (2012)
0–3.395 µg/L	Paddy water	Chowdhury et al. (2012)
233 µg/L	Paddy water	Clasen et al. (2014)
16–28 µg/L	Runoff water	Larson et al. (2019)
4.3 µg/L	Ground water	Moreira et al. (2015)

The highest values found in the paddy water exceed the values approved by the American Environmental Protection Agency (EPA) (40.0 g/L) and the European Community (<0.10 µg/L). The concentration of paddy water, 0–3.395 µg/L reported by Chowdhury et al. (2012), was below both MRL, but Clasen et al. (2014) showed carbofuran concentration exceeded the MRL with 233 µg/L. The United States Environmental Protection Agency (EPA) has set a Maximum Residual Disinfectant Level (MRDL) of carbofuran in drinking water at 0.04 parts per million (ppm), which is the highest level of a disinfectant allowed in drinking water, while the World Health Organization (WHO) recommends a detection limit of 0.9 µg/litre for carbofuran in water and provides analytical methods to measure its concentration (Edzwald, 2011; World Health Organization, 2020).

Also, Farahani et al. (2007) and Khuntong et al. (2010) measured the amount of carbofuran residue in agricultural fields, rivers, and estuaries worldwide. However, understanding the breakdown of carbofuran and its transformation products is limited solely to the parent compounds. To date, researchers have not considered the potential hazards of its derivative products. Carbofuran pollution in rice-field waterways, mainly contributed through runoff, is plausible due to its widespread use in paddy cultivation and relatively good solubility in water (320 mg/L at 20°C) (Clasen et al., 2014).

Table 3 shows carbofuran concentrations in surface soil. Even though soil residue levels were low, water contamination by runoff and secondary transfer to smaller birds were still feasible. Carbofuran concentrations were relatively higher in the rainy season than in the dry season, indicating that it dissolves quickly and can be detected in the soil soon after application. Moreover, Otieno et al. (2012) reported that pesticide residues, including

Table 3

Carbofuran concentration residues in soil from various agricultural areas

Concentration	Soil type	Region	Reference
0.146 mg/kg	Farm soil	Isiolo	Otieno et al. (2011)
0.176 mg/kg	Farm soil	Laikipia	Otieno et al. (2011)
4.9 mg/dm	Sandy soil	Netherland	Leistra and Boesten (2008)
0.01–0.54 µg/kg	Polish soil	Poland	Ukalska-Jaruga et al. (2020)
0.2479 mg/L	Paddy soil	Brazil	de Melo Plese et al. (2005)
2.35 µg/g	Sandy clay soil	N. Sembilan	Farahani et al. (2008)
5.80 µg/g	Clay soil	Perak	Farahani et al. (2008)
148 µg/g	Alluvial soil	Orissa	Ripley and Chau (2020)
202 µg/g	Laterite soil	Kerala	Ripley and Chau (2020)
0.178 ± 0.01 mg/kg	Paddy soil	Bangkok	Khuntong et al. (2010)
0.01–1.08 mg/g	Clay soil	Kenya	Jemutai-Kimosop et al. (2014)

carbofuran were elevated during the monsoon season due to increased agricultural runoff that discharged large amounts of pesticide residues into waterways.

In addition, carbofuran is known to be more resistant to insecticides than other organophosphorus (OP) or carbamate insecticides. Since 0.15–0.33 mg/kg of carbofuran was found in milk products, hens' tissues, and eggs (World Health Organization, 2020), carbofuran has been banned in several countries (Mishra et al., 2020). Plants are more tolerant to carbofuran than animals. Migratory waterflow risks can be decreased by restricting granular formulations with more than 3% active components.

Trevisan et al. (2004) found more carbofuran traces in the bagasse than in the whole fruit, but they decreased quickly during the sampling time. This insecticide was found to stay in the bagasse for at least 28 days, and there was evidence that it tended to build up when treated with multiple sprays and went down more slowly during this time. It shows that carbofurans are degraded quickly into their metabolites. Also, 3-hydroxy-carbofuran was found in a few bagasse samples from the treatment with the double rate (20 g a.i. 100 L⁻¹ water), but only in very small amounts (0.05–0.09 mg/kg). The summary of concentrations of carbofuran residues in vegetables, fruits, and food from the various agricultural industries is shown in Table 4.

Food safety is a major public concern worldwide, and most governments, private companies, and international organisations have established MRLs for food commodities to control an unacceptable risk of human toxicity. To avoid unacceptable health risks, pesticide residues in food commodities such as fruits and vegetables must be below MRLs. In developing countries, more cases of pesticide poisoning were reported than in developed countries (Azam et al., 2020; Latif et al., 2011). Carbamate concentrations significantly exceeded MRLs in many samples; carbofuran concentrations exceeded MRLs in 80 samples, respectively. Carbamates, like OPs, are acetylcholinesterase enzyme system

Table 4

Concentration of carbofuran residues in vegetables, fruits, and food from various agricultural products

Concentration	Vegetable, fruit, and food	Reference
0.15–0.33 mg/kg	Milk product & eggs	Health Canada (2020)
48.3±5.3 µg/g	Long bean	Lan et al. (2019)
73.7±4.9 µg/g	Chives	Lan et al. (2019)
22.6±3.2 µg/g	Mango	Lan et al. (2019)
51.9±6.1 µg/g	Watermelon	Lan et al. (2019)
0.001 mg/kg	Apples	EFSA (2014)
0.001 mg/kg	Potato	EFSA (2014)
0.002 mg/kg	Lettuce	EFSA (2014)
0.01 mg/kg	Citrus fruit	EFSA (2014)
8–17 µg/kg	Tobacco	USEPA (2006)
19–36 µg/kg	Corn	USEPA (2006)
14–18 µg/kg	Cotton	USEPA (2006)
0.075 mg/kg	Sugarcane	Kabir et al. (2007)
0.86 ± 0.10 mg/kg	Orange (bagasse)	Trevisan et al. (2004)
0.07 ± 0.02 mg/kg	Orange (Whole fruit)	Trevisan et al. (2004)

inhibitors, but because of their high mammalian toxicity and the even greater toxicity of their intermediates, carbamates are a potential environmental concern (Liu et al., 2019; Syed et al., 2014).

TOXICITY OF CARBOFURAN

The acute toxicity level of carbofuran differs between organisms. The toxicity of carbofuran to mammals is higher through the oral and inhalation routes than the dermal route. Furthermore, carbofuran effects in humans are associated with reproductive disorders, endocrine-disrupting activity, and cytotoxic and genotoxic abnormalities (Mishra et al., 2020). In past years, carbofuran has emerged as a global contaminant that can harm health and the environment (Figure 4). Massive carbofuran use can significantly affect non-target species via many pathways.

The World Health Organization (2020) classified carbofuran as a highly hazardous class 1b pesticide (rat oral [lethal dose 50%] LD50 ranging from 5 to 50 mg/kg). Despite the decision by WHO, the classification does not take into consideration the fact that the technical product provided a safer profile through the dermal route (LD50 > 1,000 mg/kg and LD50 > 2,000 mg/kg in rats and rabbits, respectively), which should have classified carbofuran as class II or III (moderately or slightly hazardous) under WHO guidelines (Numan et al., 2018). Although such classifications help standardise the comparison of technical products, the information becomes less relevant under practical field applications as pesticide users are in direct contact with the formulations and not the technical product.

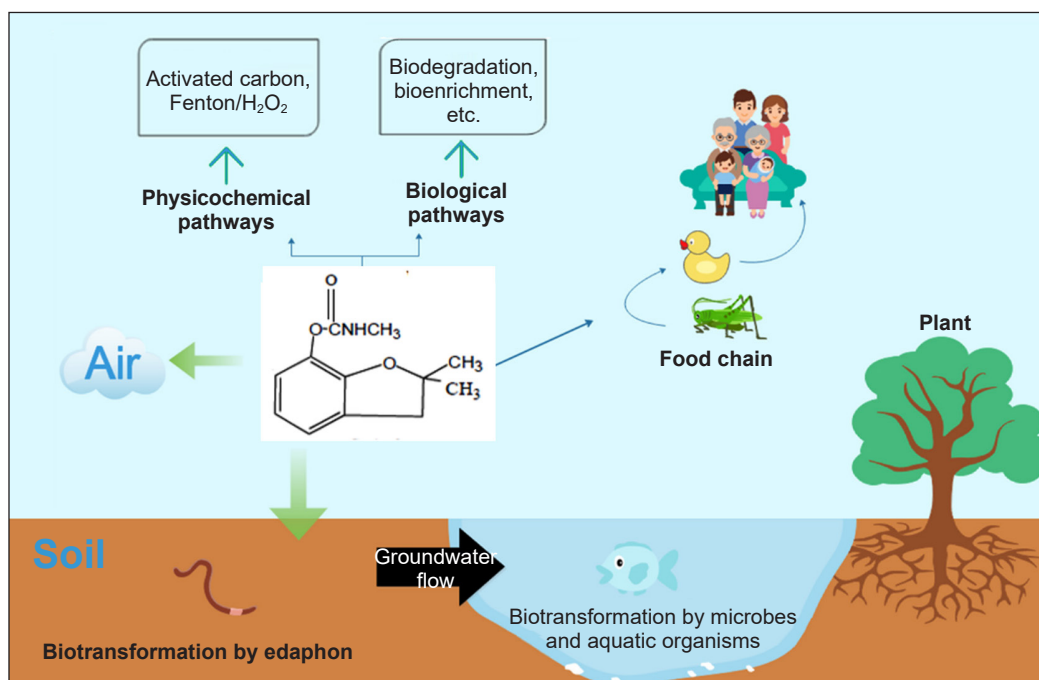


Figure 4. Contamination and degradation of carbofuran from the natural environment (Zhang et al., 2021)

Hence, the information regarding the toxicity of the end-use formulation only serves as a guideline to establish relevant warnings for users.

Carbofuran has caused the deaths of irregular fish, animals, and invertebrates recommended application rates and compositions. In short-term laboratory studies, sensitive aquatic biota died at 200 ppb carbofuran (in water), 238 ppb (acute oral), 190,000 ppb for birds, 2,000 ppb (acute oral) and 100,000 ppb (dietary) for mammals. Carbofuran is toxic and often life-threatening to fish at > 15 ppb and aquatic invertebrates at > 2.5 ppb. A level of 10 to 50 ppb in food and 1,000 ppb in drinking water is toxic to birds and mammals (Eisler, 1985; Kanedi, 2017). “Safe” carbofuran levels in beef are 50 ppb. The current allowable carbofuran aerosol levels of 0.05 ppb (50.0 g/m³) appear sufficient to preserve animals, but data suggests they should never exceed 2 ppb (Eisler, 1985; Otieno et al., 2010b).

According to the National Centre for Biotechnology Information (2023), carbofuran has one of the highest acute toxicities to humans of any insecticide widely used on field crops, and it is stated that 1 ml (1/4 teaspoon) of carbofuran can be fatal to humans. This statement is supported by the National Oceanic and Atmospheric Administration’s Chemical Emergency Response Tool, which indicates that a lethal oral dose for humans is 5 to 50 mg/kg or 7 drops to 1 teaspoon for a 150 lb. person (Alexeeff, 2000). It is important to note that carbofuran can cause serious effects on the maternal-placental foetal unit, and its toxicity can be potentiated by simultaneous exposure to other cholinesterase inhibitors.

The acceptable daily intake (ADI) estimates the amount of a substance that can be ingested daily over a lifetime without posing an appreciable health risk. The Food and Agriculture Organization (FAO) and the World Health Organization (WHO) have derived the ADI of carbofuran as 1.0 mg/kg bw per day (Ostergaard & Knudsen, 1998). The National Institute for Occupational Safety and Health (NIOSH) and American Conference of Governmental Industrial Hygienists (ACGIH) stated that the recommended airborne exposure limit for carbofuran is 0.1 mg/m³ averaged over an 8 or 10-hour work shift (Satar et al., 2005).

In rats, mice, and lactating cows, carbofuran metabolism and excretion have been the subject of significant research. Absorption, degradation, and elimination from the oral dosage occur very quickly. Mixed-function oxidases are mammals' main enzymes responsible for metabolism, as 3-hydroxycarbofuran and 3-ketocarbofuran are the most prevalent carbamate metabolites. The toxicological effects of the carbofuran range on various matrixes are shown in Table 5.

A recent study (Mishra et al., 2020) found that grain farmers exposed to a low dose of carbofuran through the skin and the air for four days had carbofuran in their urine. Even though none of the farmers showed outward signs of being poisoned, the blood cholinesterase was significantly slowed down. Moreover, another study thoroughly discussed the metabolic

Table 5
Toxicological effects of carbofuran range on various matrixes

Study Sample	Concentration/Median Lethal Concentration (LC50)/Median Lethal Dose (LD50)	Reference
Cattle	3–19 mg/kg	Choez and Evaristo (2018)
Chickens	2.5 mg/kg	Lehel et al. (2010)
Hamster	5–100 mg/mL	Soloneski et al. (2008)
Rat	75 mg/kg	Gammon et al. (2012)
Rat	1 mg/kg mg/kg	Islam et al. (2008)
Rat	1.2×10^{-8} mg/kg	Ferguson et al. (1984)
Human	4.6×10^{-8} mg/kg	Soreq and Zakut (1989)
Fly	2.5×10^{-8} µg/kg	Metcalf et al. (1968)
Birds	238 µg/kg	Eisler (1985)
Mammals	2000 µg/kg	Eisler (1985)
Catfish	23 µg/kg	Liong (1988)
Fish fillets	10.50 µg/kg	Tejada (1995)
Cat	2.5–3.5 mg/kg	Daul et al. (2012)
Guinea pig	9.2 mg/kg	Daul et al. (2012)
Dog	15.38 mg/k	Daul et al. (2012)
Rabbit	7.5 mg/kg	Daul et al. (2012)
Honeybees	0.16 µg/bee	USEPA (2006)
Japanese quail	1.7–1.9 mg/kg	Daul et al. (2012)
Pheasant	4.15 mg/kg	Smith (1992)

activity of carbofuran since the metabolites pose a substantial effect on the general toxicity of carbofuran (Ruíz-Hidalgo et al., 2016). Due to frequent reports of bird poisoning, carbofuran has been prohibited in several countries, particularly the United States, Canada, and the European Union (Sparling, 2016). The Royal Society for the Protection of Birds reported 316 incidents of bird poisoning due to carbofuran in the United Kingdom between 2002 and 2011 (Vincent, 2014). In addition, 3-ketocarbofuran and 3-hydroxycarbofuran, secondary metabolites of carbofuran, were also identified as poisonous. It was recorded that 187 vultures and hyenas died in 2004 after they scavenged bird carcasses containing carbofuran residue and its by-products (Plaza et al., 2019). Regardless of its severe effects, carbofuran is still broadly applied in Asia, South America, Australia, and Malaysia, which registered carbofuran as a legal pesticide (Sim et al., 2019).

CARBOFURAN DEGRADATION PATHWAYS IN THE ENVIRONMENT

Pesticide degradation breaks down pesticides into less toxic derivatives or their original elements (Sidhu et al., 2019). The degradation occurs through various processes or dissipation mechanisms once the pesticide enters the water and soil. Pesticides from the soil usually migrate into surface water, such as rivers, lakes, streams, and estuaries. Once in the water, it degrades according to the pseudo-first-order rate equation (Villaverde et al., 2018). The half-life of carbofuran in the environment is 30–120 days, based on where it is, the temperature, the pH of the soil or water, and medium humidity. The most common ways carbofuran and its by-products degrade are through hydrolysis, sunlight exposure, and biodegradation (Morales et al., 2012).

Various factors have been identified to influence the dispersion and degradation of pesticides, including the country's climate and the properties of the water and soil. In addition, the physical-chemical properties of the pesticides also determine how they disperse and degrade in the environment (Kumar et al., 2015). Because of its widespread use in agriculture, Carbofuran can react with water to form C–N bonds and break C–X bonds (X representing –OH group) (Jaiswal et al., 2017). Biodegradation regulates the fate and transformation of carbofuran use in nature. Research into the degradation of pesticides is widespread. Generally, carbofuran is degraded by hydrolysis, photolysis, microbial degradation and oxidation, as described in Figure 5 (Prosen, 2012; Elbashir & Aboul-Enein, 2015).

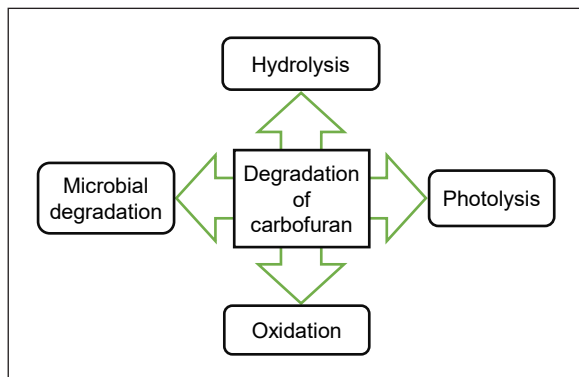


Figure 5. Degradation pathways for carbofuran

Hydrolysis Degradation

Most studies have concluded that hydrolysis and photolysis are the two most important degradation pathways for pollutants. Understanding the fate of a pesticide in water requires knowledge of the transformation mechanisms. Pesticide hydrolysis is a secondary and nucleophilic substitution reaction and fits first-order reaction kinetics (Singh et al., 2017). Morrica et al. (2001) state that temperature and pH are common hydrolysis factors. The degradation pathway takes place in both water and sediment through base-catalysed hydrolysis, which generates carbofuran phenol as well as other degradation products, such as 3-hydroxy-7-phenolcarbofuran and N-methylcarbamic acid via hydroxylation of the benzofuranyl moiety (Evert, 2002; Howard, 2017; Nafeesa et al., 2017; Sandín-España & Sevilla-Morán, 2012). The carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranol methylcarbamate) molecule degrades when it reacts with water to form a new C–N bond and break a C–X bond in the parent molecule. The net reaction is a direct removal of X by OH (Plese et al., 2005; Ripley & Chau, 2020).

Carbofuran is generally stable in water at acidic and neutral pH, but the hydrolysis rate increases rapidly with increasing pH. The chemical degradation controls the environmental persistence of carbofuran, as shown in Figure 6. Hydrolysis is an effective alternative degradation route, with average lifetimes in waters ranging from 2 days at pH = 9.5 to 1,700 days at pH = 5.2 (Marine, 1999). Besides the pH, the temperature directly influences the degradation rate in hydrolysis.

It was reported that the hydrolysis half-life, $t^{1/2}$, of carbofuran was 35 days at pH 7.0 and 350 days at pH 6.0 (Gammon et al., 2012). Acidic hydrolysis occurs under acidic conditions, which degrades slower than in alkaline conditions. For carbofuran, hydrolysis involves the cleavage of the carbamate bond in the compound, resulting in the formation of 3-hydroxy-carbofuran, which is less toxic than the original compound. Another previous study reported that carbofuran spikes recovered between 80% and 95% after 1, 3, and 6 hours at 25 °C and pH 8. On the contrary, the original amount of carbofuran recovered at pH 10 after 1, 3, and 6 hours was only 65, 35, and 10%, respectively (Bailey et al., 1996;

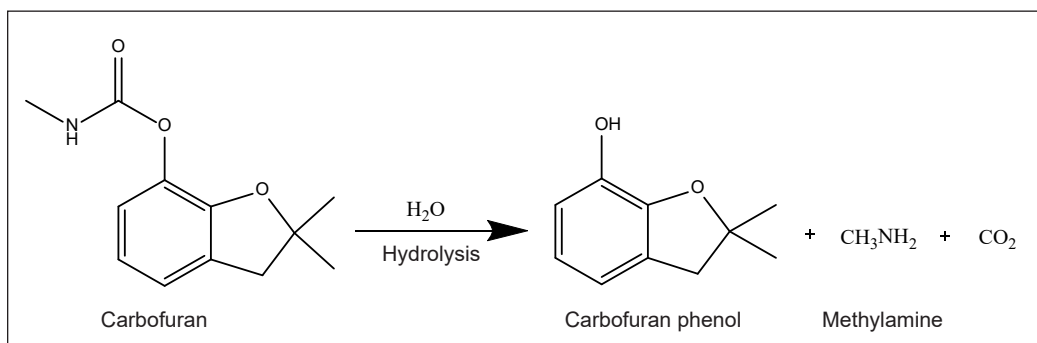


Figure 6. Hydrolysis mechanism of carbofuran (Filik and Çekiç, 2011)

Cycoń et al., 2017). The measured half-lives of carbofuran under acidic and alkaline conditions were 320 days and 150 days, respectively (Pinakini & Kumar, 2006).

Seiber and colleagues demonstrated that at pH 10, carbofuran hydrolysed 700 times faster than at pH 7, with half-lives of 1.2 and 864 hours, respectively. These results were collected from granule-treated paddy water. In addition, paddy water was hydrolysed faster than deionised water. At pH 7, paddy water half-lives were 240 and DI water 864 hours. At pH 8.7, paddy water and deionised water each had half-lives of 13.9 hours. Based on the results, the carbofuran half-life in paddy water (laboratory) at pH 8 was 40 hours, which was similar to the 57-hour half-life recorded from field samples at the same pH level, given slight variations in several factors, such as the source of light, pH level, the surrounding temperature, and the rate of microbial degradation (Howard, 2017; Mackay et al., 2006; Seiber et al., 1978).

Moreover, a higher rate of carbofuran hydrolysis was reported in anaerobic conditions. The hydrolysis rate of carbofuran under aerobic environments was compared to that in stable and undisturbed flooded conditions. Nevertheless, the degradation products, consisting of carbofuran phenol and 3-hydroxycarbofuran, were stable under anaerobic conditions, while further degradation was only observed under aerobic conditions. So, it was thought that the rapid hydrolysis of carbofuran was caused by cycles of flooding and drying that led to alternating anaerobic conditions (Venkateswarlu & Sethunathan, 1978; Ramakrishnan et al., 2019; Mohamed et al., 2021).

Hydrolysis was considered the most important degradation pathway, with a half-life ranging from 0.2 days at pH 9.5 to 1,700 days at pH 5.2. The rate of carbofuran hydrolysis in aqueous solutions accelerates significantly as the pH of the solution increases. The hydrolysis half-lives of carbofuran in water at 25°C is 690, 8.2, and 1.0 weeks at pH values of 6.0, 7.0, and 8.0, respectively. Hydrolysis reactions involve adding water to a large molecule to break it into multiple smaller molecules (Bailey et al., 1996).

The degradation pathways of carbofuran in water systems are shown in Figure 7. Hydrolysis was reported as the main mechanism leading to degradation in alkaline soils. On the other hand, acidic and neutral soils were dominated by microbial and chemical mechanisms, which led to slower degradation. Carbofuran phenol, 3-hydroxycarbofuran, and 3-ketocarbofuran are among the transformation products of carbofuran degradation that can be detected in soil (Acharid et al., 2006; Achik & Schiavon, 1989; Katagi, 2016).

One factor that reduces the effectiveness of insecticides in controlling the infestation of the brown planthopper *Nilaparvata lugens*, a significant pest of rice plants, is the rapid chemical hydrolysis of carbofuran in paddy water (Hayasaka et al., 2012). It was revealed that carbofuran phenol production from carbofuran degradation took only 5 days under alkaline paddy water conditions.

Furthermore, the effect of paddy water pH on carbofuran persistence was demonstrated in another study in which less than 5% of carbofuran remained after 5 days of application

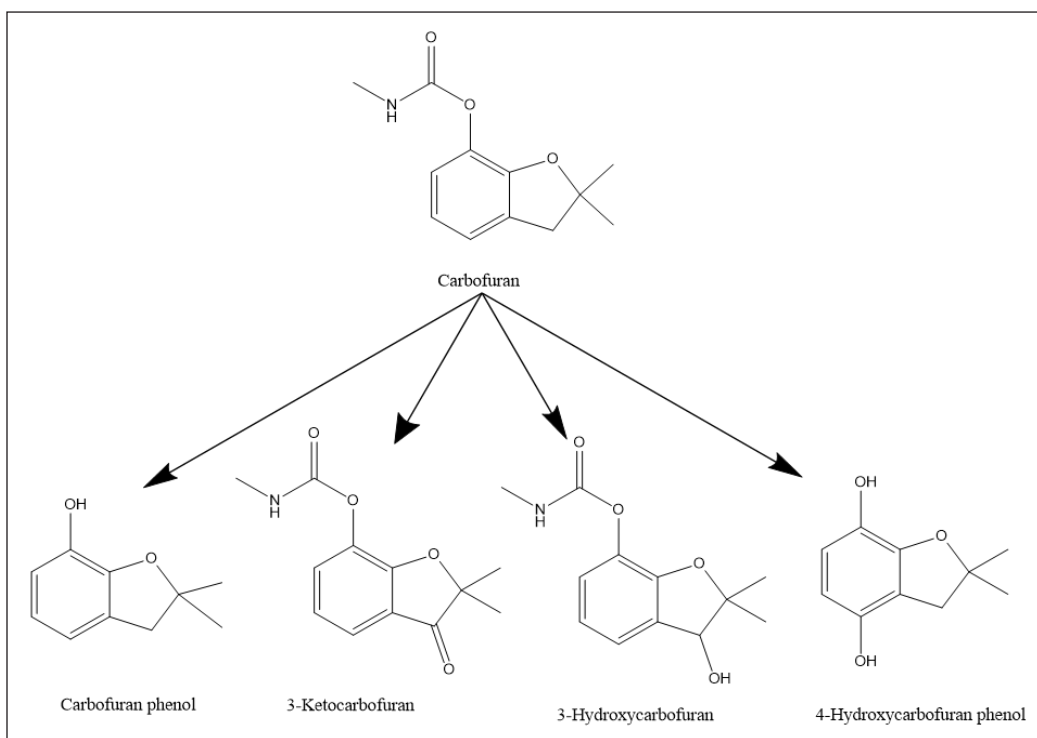


Figure 7. Environmental fate of carbofuran in water (Evert, 2002)

at pH 8. In contrast, the remaining amount of intact carbofuran after 10 days was 70% and 14% at pH 6 or lower and pH 7.1, respectively (Siddaramappa & Seiber, 1979; Roger & Bhuiyan, 2012; Xu et al., 2014). Other studies have also shown that hydrolysis and photochemical degradation are the major degradation pathways for carbofuran in water (Farahani et al., 2012; Tien et al., 2017). The biodegradation and pH of the water were among the main factors influencing the degradation of carbofuran.

Photolysis Degradation

Photolysis of pesticides leads to chemical changes in pesticides by absorbing light radiation directly and indirectly. In direct photolysis, the pesticide molecules absorb the photons directly, whereas in indirect photolysis, a carrier and other photochemical processes (photosensitizers) are involved (Fang et al., 2022). Photolysis and hydrolysis produce more polar and stable pesticides than the parent compounds. Some pesticides persist for several months, polluting the environment (Tien et al., 2017; Sim et al., 2019). There is, thus, a need for research into the by-products of carbofuran.

A less significant degradation pathway of carbofuran is through the photolysis reaction. Carbofuran is not likely to accumulate in sunlight-exposed water and does not bioaccumulate (Baumart et al., 2011). The metabolic product of photolysis includes

2,3-dihydro-2,2 dimethyl benzofuran-4,7-diol and 2,3-dihydro-3 keto-2,2 dimethyl benzofuran-7-yl carbamate (3-ketocarbofuran) (Mahalakshmi et al., 2007; Remucal, 2014). A comparison was made between the rate of carbofuran recovery in deionized water exposed to sunlight and laboratory light for 96 hours. According to the results, the average recovery of carbofuran was 75.6% for the sunlight-exposed samples and 93.3% for the artificial light-exposed samples, respectively. The large difference suggested the significant photolytic aqueous decomposition of carbofuran (de Melo Plese et al., 2005; Gunther & Gunther, 2013).

Carbofuran photolyzes directly, producing photoproducts. At the same pH level, photolysis occurs more rapidly in pesticides in seawater, freshwater, and humic acid solutions than in distilled water. Meanwhile, although no control was used, carbofuran in freshwater photolyzes faster than seawater. In one case, adding humic acids decreased carbofuran's direct photolysis rate (Raha & Das, 1990; Mahalakshmi et al., 2007). Figure 8 shows the metabolites' chemical structure. The transformation of carbofuran generated

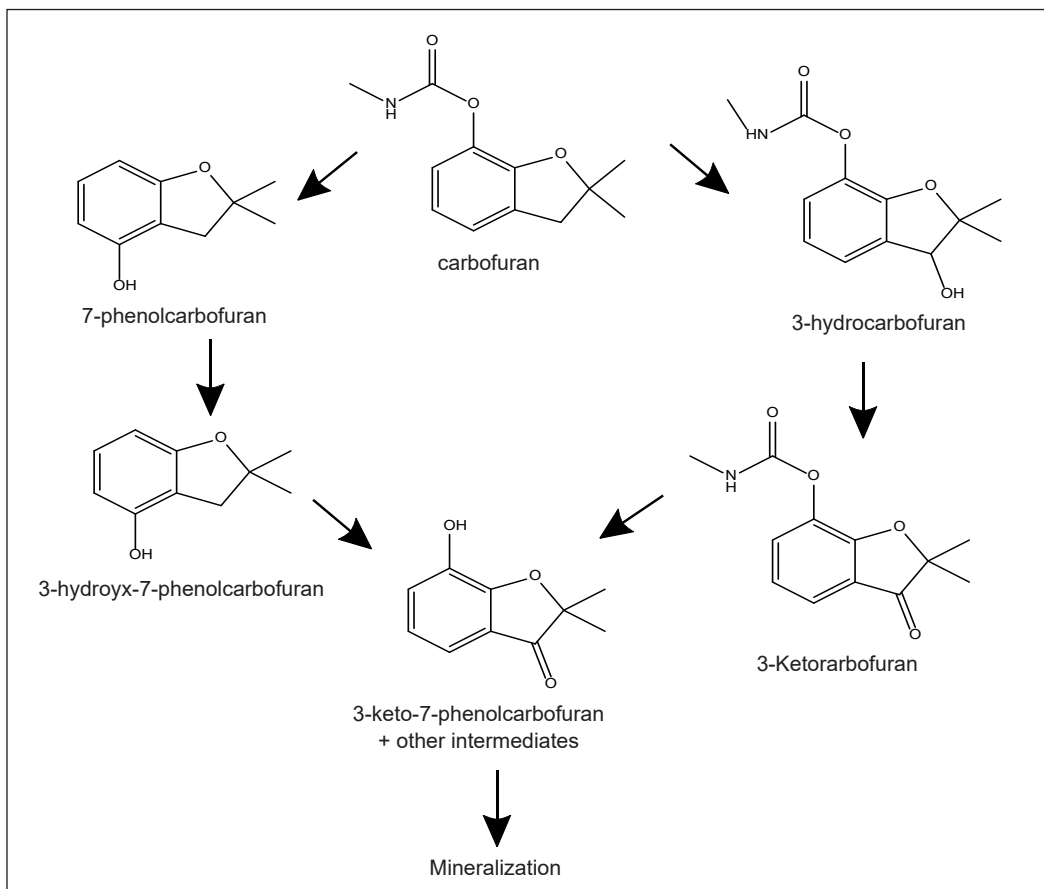


Figure 8. The chemical structure for the detected by-products of carbofuran (Mishra et al., 2020)

7-phenolcarbofuran, 3-hydroxycarbofuran, and 3-ketocarbofuran in all cases, while ZnO formed 3-keto-7-phenolcarbofuran.

Meanwhile, the vapour pressure and Henry's Law constant of carbofuran in the air are low, indicating that carbofuran has a low potential to volatilise from moist soils or water (Cid et al., 2011). Once carbofuran vaporises into the air, it is subjected to vapour-phase photooxidation by reacting with hydroxyl radicals. The half-life of this reaction at standard atmospheric conditions was estimated to be 4.6 hours (Howard, 2017). However, the oxidation and volatilisation of carbofuran in water were considered insignificant dissipation pathways (Wijesinghe et al., 2011).

As demonstrated in Table 6, the carbofuran half-lives in the Laysan and Ottawa sands were comparable (40–41 days), according to Campbell et al. (2004). In comparison, Seiber et al. (1978) found that the half-lives of carbofuran in DI water and paddy water (pH 7) were only slightly different when both were exposed to ultraviolet (UV) light and darkness in the lab. Bachman and Patterson (1999) suggested that the increase in the amount of dissolved organic matter (DOM) inversely reduced the photolysis rate of carbofuran. The assumption was made that the level of inhibition is proportional to the binding capacity of a specific DOM sample. Therefore, the binding of DOM reduced the rate of photolysis and slightly improved the persistence of carbofuran (Bolan et al., 2011).

It is interesting to highlight that the rate constant for the degradation of carbofuran in sunlight-exposed seawater was higher than in sunlight-exposed fresh water. Consequently, the half-life of carbofuran in sunlight-exposed fresh water was longer than that in sunlight-exposed seawater, in line with a similar trend observed by others (Farahani et al., 2012). Campbell et al. (2004) observed that the half-life of carbofuran in sunlight-exposed seawater (7.5 hours) was approximately 6 times faster than in sunlight-exposed DI water (41.6 hours), with the same rate of degradation in seawater (0.1 hours) as in DI water (3.1 hours) under a light intensity of 300 nm. This difference (6–31 folds) and the differences

Table 6
Carbofuran half-lives and photodegradation constants, k

Matrix	Light source	-k	Half-life
Ottawa sand	Dark	0.0151/day	39.7 day
Laysan sand	Dark	0.0182/day	40.9 day
Distilled deionised water	300 nm	0.1941/h	3.1 h
Seawater	300 nm	0.328/h	0.1 h
Distilled deionised water	Sunlight	0.0162/h	41.6 h
Seawater	Sunlight	0.1284/h	7.5 h
Distilled deionised water	Ultraviolet (UV) light	0.105×10^{-2}	27.5 day
Paddy water	Ultraviolet (UV) light	0.04	7.2 day
Distilled deionised water	Dark	0.092	31.4 day
Paddy water	Dark	0.41	9.3 day

observed in the present research were presumably due to differences in water composition (Campbell et al., 2004; Remucal, 2014; Mishra et al., 2020; Maksuk, 2021). Carbofuran's photodegradation may be aided by the existence of organic compounds, ions, and chemical sensitizers (Wang et al., 1998; Huang & Mabury, 2000; Seo et al., 2012; Wols & Hofman-Caris, 2012).

The degradation rate of pesticides also varies between countries with tropical and temperate climates. Among the main climate elements that affect the rate of pesticide degradation are the mean temperature in the region, the mean amount of rainfall, the average amount of sunlight emitted, and the existence of microbes (Daam et al., 2008). Tropical countries generally experience more rainfall than temperate-climate countries. According to past studies, the pesticide contamination of soil and water can be influenced by rainfalls through the dilution of the concentration of pesticides in the environment or by leading to pesticide runoffs that could flow into the watersheds and irrigation channels (Abdullah et al., 1997; Daam & Van den Brink, 2010).

Microbial Degradation

Microbial degradation mainly occurs in water and soil when microorganisms are present. Microbial degradation includes complex biological processes. Therefore, it requires ideal conditions such as pH, temperature, and nutrient availability (Grandclément et al., 2017). The pH level and microorganism types in the water determine the rate of microbial degradation in a flooded rice field (Hayasaka et al., 2012). Depending on the metabolic pathways of microbes, microbial degradation can occur under either aerobic or anaerobic conditions, depending on oxygen availability.

Aerobic metabolism is the process of converting organic compounds into energy using oxygen. This reaction occurs in the presence of oxygen, and the end products are typically carbon dioxide and water. Aerobic microorganisms are commonly used to degrade organic pollutants in the environment in bioremediation processes. These microorganisms use enzymes such as monooxygenases and dioxygenases to oxidise and degrade organic compounds (Diale et al., 2022).

Breaking down organic compounds without using oxygen is known as anaerobic metabolism. This process occurs without oxygen and can be carried out by microorganisms such as bacteria and fungi. In terms of energy production, anaerobic metabolism is less efficient than aerobic metabolism, and the end products vary depending on the metabolic pathway. Some anaerobic bacteria, for example, use sulphate or nitrate as a final electron acceptor, producing hydrogen sulphide or nitrogen gas.

Fungi are also essential in microbial degradation, particularly in the breakdown of lignin, a complex polymer found in plant cell walls. Fungi use enzymes like lignin peroxidase and manganese peroxidase to break down lignin into simpler compounds that

other microorganisms in the environment can use. The fungal metabolism of carbofuran is a new area of study, and it has been shown that different fungal strains from the genera *Trichoderma*, *Pichia*, *Trametes*, *Aspergillus*, *Aschochyta*, *Xylaria*, *Acremonium*, *Gliocladium*, and *Mucor* can degrade carbamate pesticides (Mustapha et al., 2019).

Carbofuran was metabolised by *Mucor ramannian* to produce carbofuran phenol, which was then metabolised to yield 2-hydroxy-3-(3-methylpropan-2-ol) phenol, also known as 7a-(hydroxymethyl)-2,2-dimethylhexahydro-6H-furo[2,3-b]pyran-6-one and 3-hydroxy carbofuran-7-phenol (Sun et al., 2022). Among the pyrethroid pesticides, *Trametes versicolor* has been found to degrade carbofuran, imiprothrin, and cypermethrin. In the spent media analysis, 3-hydroxycarbofuran was the only intermediate of carbofuran degradation. It has been reported that the non-specific *monoxygenase cytochrome-P450* plays a significant role in carbofuran metabolism in this strain. (Mir-Tutusaus et al., 2014).

Pesticides degraded by microorganisms serve as a food supply for growth and energy. Based on recent studies, microbes are responsible for the breakdown of natural organic materials and the degradation of numerous xenobiotic chemicals such as petroleum hydrocarbons, pesticides, and organic solvents (Ariffin & Rahman, 2020). Strachan et al. (2018) reported that microorganisms used s-triazine herbicide as an energy source during their degradation. The conversion of contaminants into less harmful substances via microbial degradation is likely in the case of mineralisation, while in certain situations, mostly under anaerobic transformation, toxic products can also be produced (Onunga et al., 2015).

Bacteria capable of efficiently degrading carbofuran have been discovered in soil, sludge, and water contaminated with carbofuran (Mishra et al., 2020). *Pseudomonas*, *Flavobacterium*, *Achromobacterium* sp., *Sphingomonas* sp., *Arthrobacter* sp., *Enterobacter* sp., *Burkholderia* sp. PLC3, *Cupriavidus* sp. ISTL7 and *Bacillus* sp. were isolated and characterised to determine their mechanisms for degrading pesticides. *Sphingomonads* (*Sphingomonas*, *Novosphingobium*, *Sphingopyxis*, and *Sphingobium*) may be the ideal carbofuran-degrading bacteria. These bacteria degrade carbofuran and carbofuran-phenol better than others (Nguyen et al., 2015; Yan et al., 2007). So far, numerous bacterial strains from the genera *Stenotrophomonas*, *Achromobacter*, *Flavobacterium*, *Pseudomonas*, *Sphingomonas*, *Novosphingobium*, *Paracoccus*, *Aminobacter*, and *Cupriavidus* can degrade carbamate insecticides (Gupta et al., 2019; Jiang, Zhang, et al., 2020).

Microbial degradation can benefit the environment by using microorganisms to break down and transform pollutants into less harmful substances. Microbes play key roles in biodegradation, which recycles biologically essential elements within the earth's biogeochemical cycles (Jørgensen, 2008). Microbial degradation is a possible and environmentally friendly way to degrade carbofuran. However, most prior studies on carbofuran degradation have focused on bacterial degradation, and the degradation rates remain slow (Mishra et al., 2020).

In general, the use of microbial degradation for environmental remediation can have several advantages over other methods, such as physical or chemical treatments. For example, microbial degradation can be a cost-effective and environmentally friendly approach, as it can occur naturally and may not require additional chemicals or energy (Liu et al., 2021). Continuous exposure to pollutants and synergy with other strains make microbial consortiums more suitable for environmental remediation. Microbial consortiums or mixed cultures degrade carbofuran residues on a large scale. Tondon et al. (2018) discovered four carbofuran-degrading bacterial strains from contaminated soil samples: *Arthrobacter globiformis*, *Bhargavaea indica*, *Bacillus beijingensis*, and *Streptomyces* sp. Table 7 shows an overview of the microbial species studied for carbofuran biodegradation. Several strains of bacteria and fungi from different sources have been studied.

Microbial degradation completely mineralizes carbofuran into non-toxic substances and CO₂. As a result, microbial carbofuran degradation is an effective and practical method. Microbes mostly use oxidative and hydrolytic mechanisms to eliminate carbofuran. Figure 9 illustrates carbofuran's comprehensive microbial degradation pathway and describes carbofuran's microbial degradation into its significant metabolites: carbofuran phenol, methylamine, and CO₂. Carbofuran and carbofuran phenol are formed in *Sphingomonas* sp, but the bacterium cannot grow on them. The hydroxylase-reductase pair CfdCX and *Novosphingobium* sp conduct carbofuran phenol production. (Malhotra et al., 2021).

Table 7
Microbial degradation of carbofuran in soil by different microbes

Microbial species, Strain or Community	Sample sources	Reference
<i>Sphingomonas</i> sp.	Soil	Park et al. (2006)
<i>Mucor ramannianus</i>	Soil	Seo et al. (2007)
<i>Novosphingobium</i> sp. FND-3	Sludge	Yan et al. (2007)
<i>Paracoccus</i> sp. YM3	Sludge	Peng et al. (2008)
<i>Enterobacter</i> sp.	Soil	Mohanta et al. (2012)
<i>Pseudomonas</i> and <i>Alcaligenes</i>	Soil	Omolo et al. (2012)
<i>Burkholderia</i> sp. PLC3	Soil	Plangklang and Reungsang (2012)
<i>Novosphingobium</i> sp	Soil	Nguyen et al. (2014)
<i>Bacillus</i> sp.	Soil	Onunga et al. (2015)
<i>Consortia</i>	Soil	Tien et al. (2017)
<i>Pseudomonas</i> sp.	Soil	Devi et al. (2017)
<i>Aspergillus</i> sp.	Soil	Devi et al. (2017)
<i>Enterobacter cloacae</i> strain TA7	Soil	Fareed et al. (2017)
<i>Arthobater globiformes</i>	Soil	Tondon et al. (2018)
<i>Streptomyces</i> sp.	Soil	Tondon et al. (2018)
<i>Cupriavidus</i> sp. ISTL7	Landfills	Gupta et al. (2019)
<i>Sphingbium</i> sp. CFD-1	Sludge	Jiang et al. (2020)

Carbofuran phenol is further degraded into novel metabolites by carbofuran-degrading microorganisms and their hydrolase enzymes. In *Novosphingobium* sp. In KN65.2, the initial step involves hydrolysis of the carbamate linkage to form carbofuran phenol, methylamine, and CO₂ (Duc, 2022; Yan et al., 2018).

The hydrolytic pathway is more uncomplicated and produces fewer toxic by-products than the oxidative pathway (Kim et al., 2004; Nguyen et al., 2014). Hydrolase enzymes break methyl and N-methyl carbamic acid's amide and ester bonds to yield carbofuran 7-phenol, CO₂, and methylamine. The inducible oxidative enzyme hydroxylase transformed carbofuran to 4-hydroxycarbofuran. (Malhotra et al., 2021).

According to Garcia-Saavedra et al. (2018), a bacterial consortium degraded 34.99% of carbofuran in soil samples. Advances in biochemical, molecular, and biotechnological techniques have increased the potential of carbofuran-degrading microorganisms. Catabolic genes, enzymes, plasmids, mobile elements, and transposons all play essential roles in catalysing novel biochemical pathways during microbial degradation (Mishra et al., 2020). However, dehydrogenase and alkaline phosphatase activities in fertilised soil were greatly decreased by increasing carbofuran dosage (0.02–1.0 kg/ha to 5.0 kg/ha) compared to control soils (Singh et al., 2012).

The degradation process involves microbes (biodegradation), chemical reactions (chemical degradation), or light (photodegradation) (Tiryaki & Temur, 2010). The process relies on the pesticide's chemical composition and environmental conditions. Degradation of herbicides by soil bacteria and fungi can take hours to years. The degradation rate by 11 microorganisms increased under warm temperatures, ideal soil pH, appropriate oxygen, soil moisture, and good soil fertility and decreased under less favourable conditions (Meftaul et al., 2020). Pesticides degrade when they react with soil chemicals like water or oxygen. As soil pH becomes more alkaline or acidic, chemical degradation increases because microbial activity decreases (Tiryaki, 2017). In aerobic conditions, microorganisms convert organic contaminants to CO₂ and H₂O. On the contrary, anaerobic metabolic reactions occur without molecular oxygen (Furmanczyk et al., 2018; Kaida et al., 2018; Chaudhary & Kim, 2019).

Oxidation and Volatilization

Carbofuran is a commonly used carbamate derivative pesticide and a priority pollutant. Several studies have been conducted on the degradation of carbofuran by oxidation and volatilization processes. Considering that biological treatment methods involve lengthy residence times and thermal treatment can generate secondary pollutants, oxidative reactions are favoured for the rapid degradation of contaminants (Zheng et al., 2022). Therefore, a variety of effective treatment techniques, such as ultrasonic process, UV + Fe(III), UV/TiO₂ and UV/O₃, have been applied for carbofuran removal from aqueous samples (S. Lu et al., 2021; Oliveira et al., 2006).

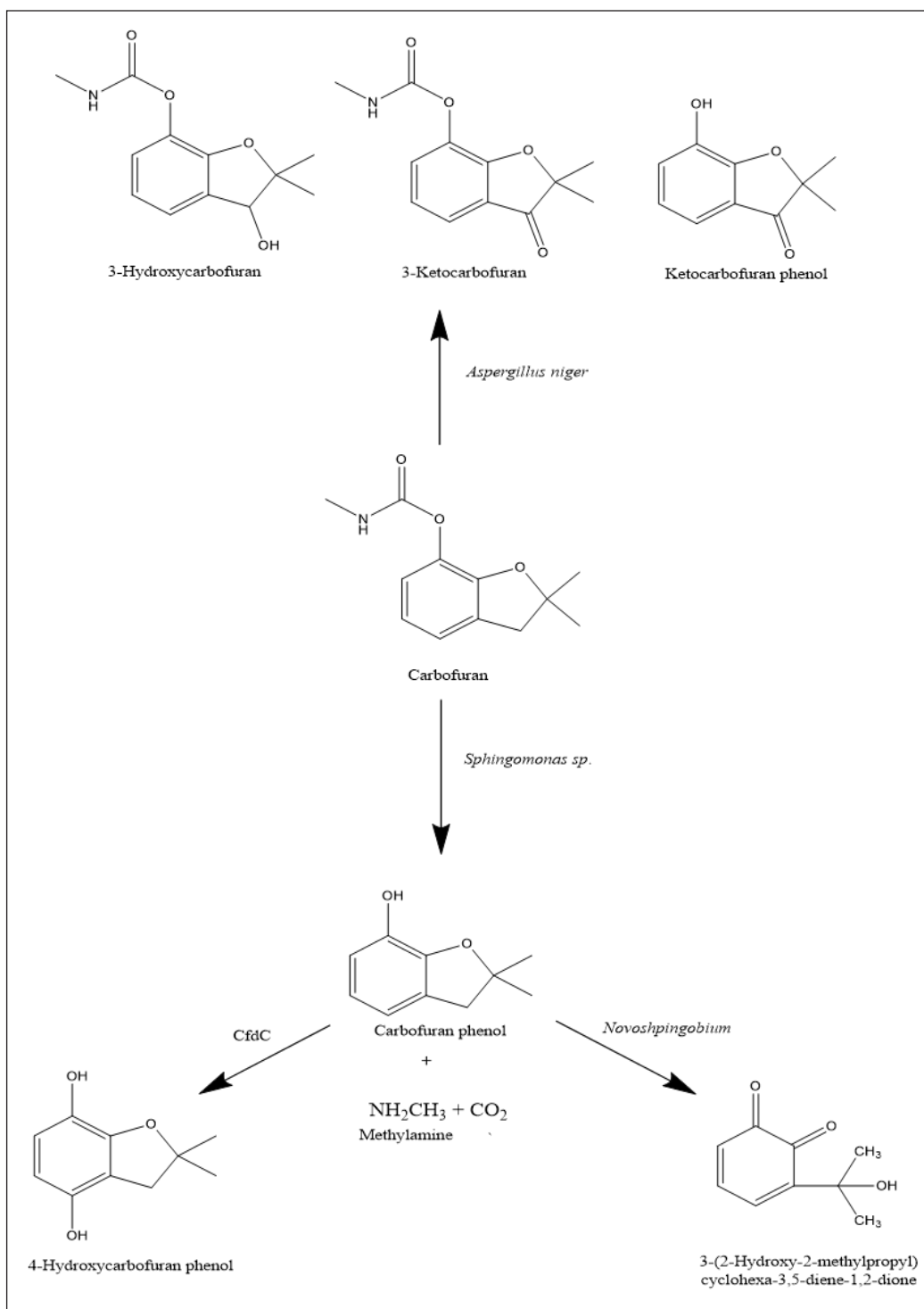


Figure 9. The microbial metabolic mechanisms for the carbofuran degradation in *Aspergillus niger*, *Sphingomonas sp.*, and *Novosphingobium sp.* (Jiang, Gao et al., 2020; Mishra et al., 2021)

Ma et al. (2009) analysed four degradation products that produced three intermediates, including 1,4-benzenedicarboxaldehyde anion, 7-benzofuranol, 2,3-dihydro-2,2-dimethyl (also known as 2,3-dihydro-2,2-dimethyl-benzofuran-7-ol), and 7-hydroxy-2,2-dimethyl-benzofuran-3-one, using GC/MS at retention times of 3.6 min, 7.44 min, and 13.8 min, respectively. The experimental results show that the Fenton process is an effective method for degrading carbofuran-contaminated water.

Javier Benitez et al. (2002) investigated how ozonation affects the breakdown of carbofuran. The research concluded that pseudo-first-order kinetics could be used to explain the global ozonation reaction. Temperature and partial ozone pressure significantly influence the removal rate of carbofuran. In contrast, similar degradation rates are obtained for pH 2 and 9 experiments, indicating a negligible contribution of the reaction with hydroxyl radicals generated by ozone self-decomposition at pH 9. The apparent pseudo-first-order rate constants for the ozonation reaction are calculated and found to be in the 5.1×10^{-4} to $19.5 \times 10^{-4} \text{ s}^{-1}$ range. A kinetic competition model was used to calculate the actual rate constant for the reaction between ozone and carbofuran at 20°C, which was 1108 l/mols (Bhat & Gogate, 2021; Javier Benitez et al., 2002).

In addition to these studies, advanced oxidation processes (AOP)s, which include ultraviolet radiation, ozone, and hydrogen peroxide, are the most effective at degrading carbofuran. Several studies have proven that AOPs are promising and attractive alternatives in treating organic pollutants that are either toxic or refractory to biological treatments (Pignatello et al., 2006; M. Zhang et al., 2019). AOPs mainly generate highly oxidative free radicals, mostly the hydroxyl radical ($\bullet\text{OH}$) with an E° of 2.8 V/SHE (L.-A. Lu et al., 2011; Thomas et al., 2021).

In a separate investigation by Ma et al. (2010), the degrading of carbofuran was investigated using three different processes: ultrasound, the Fenton reaction, and a combination of the two. The researchers monitored the effects of various factors on the kinetics of carbofuran's degradation, including the dosages of H_2O_2 and Fe_2^+ as well as the initial concentrations of carbofuran. After 30 minutes of reaction time with an initial carbofuran concentration of 20 mg/L and H_2O_2 and Fe_2^+ dosages of 100 mg/L and 20 mg/L, more than 99% carbofuran degradation efficiency and 46% mineralization were achieved, all at pH 3, respectively. Increases in the Fenton reagents H_2O_2 and Fe_2^+ improved degradation efficiency, but increases in the initial carbofuran concentration had the opposite effect (Anandan et al., 2020; Bhat & Gogate, 2021; Ma et al., 2010).

CONCLUSION

This review focused on carbofuran usage, toxicity, and degradation pathways for agricultural purposes. Hydrolysis and photolysis were suggested as the major degradation routes of carbofuran, followed by microbial degradation and oxidation. This process

generally reduces aqueous carbofuran concentrations when combined with microbial activity.

Several metabolites are formed during the breakdown of carbofuran. These include 3-hydroxy-carbofuran, 3-ketocarbofuran, carbofuran-phenol, and 3-hydroxy-5-nitrophenol. These metabolites vary in toxicity and persistence in the environment, with some being more lethal than the parent compound. The detailed pathways and mechanisms of their formation are determined by the degradation method involved. For example, microbial degradation can involve hydrolysis, oxidation, or reduction pathways, while photolysis can generate various metabolites via direct or indirect light reactions.

Based on the current research on carbofuran degradation, there are a few recommendations for future studies, such as bioremediation, advanced oxidation processes (AOPs), enzymes, and phytoremediation. Combining these methods can be an effective strategy for remediating soil and water bodies contaminated with carbofuran. Further studies are needed to enhance the conditions and increase the efficacy of these methods, not only on a laboratory level but also on a wide scale in field applications to benefit the community.

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