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A Study of the Photodegradation Carbofuran and its Metabolites in Paddy Water Samples

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Degradation

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ABSTRACT

Rice fields are one of the agricultural sectors in Malaysia that are heavily pesticide-treated. This study aimed to determine how carbofuran degrades in paddy water and how carbofuran metabolites such as carbofuran-phenol and 3-keto carbofuran reacted during the degradation. The experiment was conducted in two distinct conditions: the first water sample was exposed to sunlight, while the second water sample remained in the dark. During the 56 days of observation, the study discovered carbofuran decomposed slowly in both conditions. The water sample exposed to sunlight showed a faster degradation rate (0.04/day carbofuran) than the water kept in the dark (0.0186/day). The results also demonstrated that photolysis and hydrolysis enhanced the carbofuran degradation in the water. Both 3-keto carbofuran and carbofuran-phenol were detected as metabolites with low concentration levels, ranging from 0.03±0.301 to 0.23±0.142 ppm. These metabolites are considered 'emerging pollutants' as they can be detected in the environment and may post-treat as much as the parent compounds themselves. Hence, this study is trying to fill the research gap to assess the route and rate of carbofuran and its transformation products.

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1 Introduction

Pesticides are chemical substances that are highly diverse. These are hazardous and non-biodegradable and have the potential to pollute our ecosystems. Pesticides are chemicals that prevent, eliminate, destroy, or minimize various pests such as insects, animals, fungi, and parasite plants (Hijosa-Valsero et al. 2016; Khalid et al. 2020). Among the total agricultural chemical expenditures in Malaysia, herbicides accounted for 70% (Tey et al. 2014; Foguesatto and Machado 2022; López-Felices et al. 2023), followed by insecticides (19%), fungicides (7%) and rodenticides (5%) (Shamsudin et al. 2010; Srivastava 2020). Malaysia's primary food crop is rice, and around 70% of pesticides are exclusively used in paddy fields (Bhattacharjee et al. 2012; Wang et al. 2021).

Carbofuran (2,3-dihydro-2,2-dimethyl benzofuran-7-yl-N-methyl carbamate) is a systemic acaricide, insecticide, and nematicide that belongs to the carbamate derivative pesticide family (Vithanage et al. 2016; Ćwieląg-Piasecka et al. 2021). In Malaysia, rats in rice fields and the rhinoceros beetle in oil palm plantations are controlled by using insecticides. Carbofuran is believed to be more long-lasting than other carbamate or organophosphate insecticides. Additionally, carbofuran's secondary metabolites, notably 3-keto carbofuran and 3-hydroxy carbofuran, are also fatal to human beings (Ferrari et al. 2023; Goh et al. 2021).

Pesticide mobility and degradation are determined by several indicators, including the country's climate and soil conditions, pH, humidity, soil type, organic matter, and clay content (Rasool et al. 2022). Furthermore, the environmental conditions under which pesticides were applied to plants and the physical-chemical characteristics of the pesticides also influence the pesticides movement and their environmental degradation (Arias-Estévez et al. 2008; Sharma et al. 2020). Pesticides can degrade and form metabolites in water, soil, and air. Degradation can occur through hydrolysis, photolysis, surface runoff, leaching, volatilization, oxidation or reduction, and microbial degradation (Lewis et al. 2016; Nieder et al. 2018).

Most studies agree that hydrolysis and photolysis are the most effective pathways for pollutant degradation. Further, transformation mechanisms are essential to understanding the pesticide's fate in water. Pesticide hydrolysis is a secondary reaction that involves nucleophilic substitution and follows the first-order reaction kinetics model (Chen et al. 2018). Furthermore, photolysis and hydrolysis of pesticides yield secondary pesticide compounds that are more polar and stable than the parent pesticides. Some pesticides remained for several months, contaminating the ecosystem (Sim et al. 2020; Tien et al. 2017). Besides pesticide degradation, reaction pathways are also crucial in determining the process, type of reactive intermediates, and end-products; all of these contribute to pesticide distribution in the environment (Chaudhari et al. 2023; Riyaz et al. 2023). The primary carbofuran metabolites discovered in different samples were 3-hydroxy carbofuran and 3-keto carbofuran. Both by-products are more polar but somewhat hazardous to specific and non-specific species (Osesua et al. 2017; Mishra et al. 2020).

However, there are limited studies on carbofuran degradation and its transformation products in tropical paddy water, particularly in Malaysia, where the level of ultraviolet radiation (UV) and the existence of microorganisms may result in faster deterioration. Therefore, the purpose of this study is (i) to determine the degradation rate of carbofuran spiked into paddy water, (ii) to consider the potential pathways of degradation of carbofuran, and (iii) to determine the half-life of carbofuran and its by-products carbofuran-phenol and 3-keto carbofuran in paddy water samples. This study estimates the carbofuran degradation rate over 56 days in paddy field water in two environments, with and without sunlight.

2 Materials and Methods

2.1 Sampling site

Water samples were collected from a paddy field at Padang Tembusu Village in Penaga Mukim 5, Seberang Perai Utara, and Pulau Pinang, Malaysia. The study area has an annual average temperature of approximately 27ºC to 32ºC, a rainfall range of 100mm to 400mm, and a relative humidity range of 60 to 75%. The site of Padang Tembusu Village is portrayed in Figure 1.

2.2 Experimental Setup for the degradation study

100mL of paddy water was collected and placed in a glass container for the degradation study. The sample bottle is wrapped in aluminium foil and stored in the refrigerator before use in the batch study to slow down the reaction in the samples. From this, each 100mL of water was spiked with 0.1g of carbofuran, and the samples were stored in two conditions, including outdoors at ambient temperature which, exposed to sunlight (open location), and in the dark (in a drying cabinet set to 28ºC and 60% humidity). The bottles stored under dark conditions were wrapped in aluminium foil to protect the samples from sunlight. The degradation study was conducted for 56 days, and data were collected every seven days (0 - 56 days). The standard methodology estimated various physicochemical parameters, including pH, temperature, turbidity, BOD, COD, and TSS of collected paddy water samples. Samples were extracted using solid-phase extraction and analyzed using GC-ECD to determine carbofuran and its by-product concentrations (Figure 2).

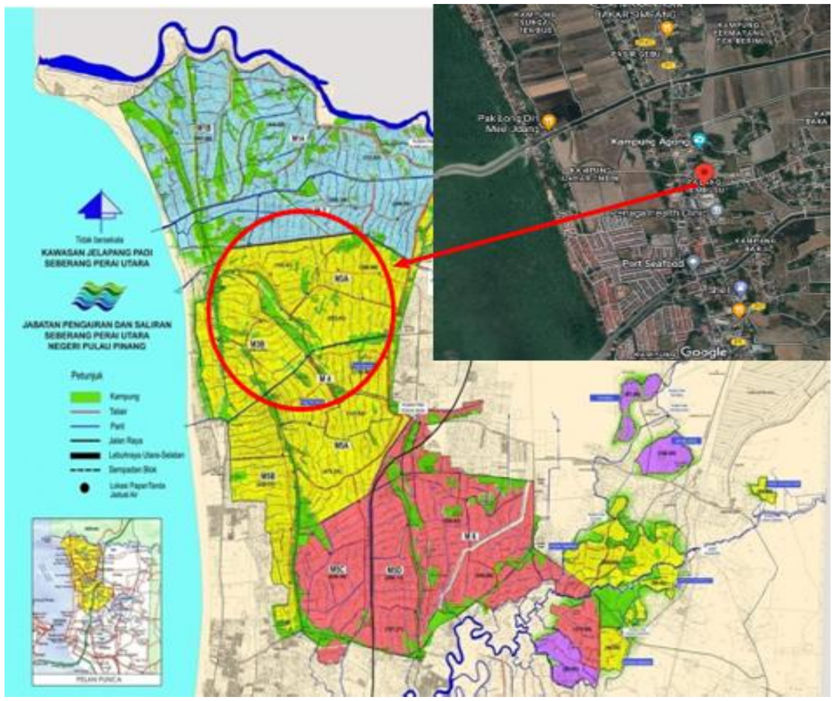
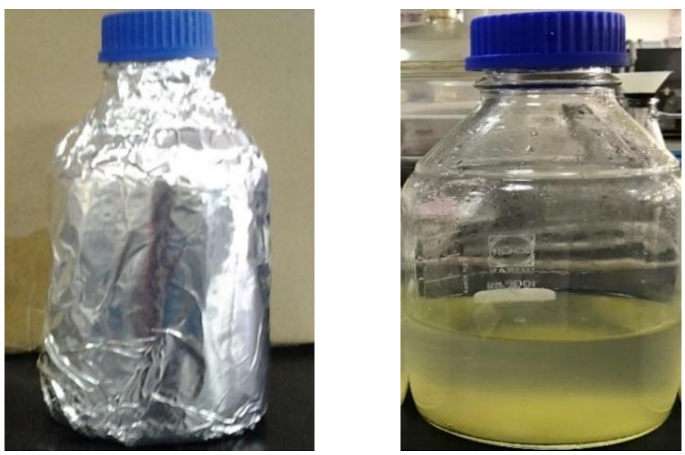


Figure 1 Padang Tembusu Village, Penaga Mukim 5, SPU, and Pulau Pinang, Malaysia (jps.penang.gov.my)



(a) (b)

Figure 2 Experimental setup for (a) a sample kept in the dark and (b) a sample exposed to sunlight

2.3 Solid-phase extraction of water samples

The carbofuran and its products were extracted from water samples using solid-phase extraction (SPE) as described by Ismail et al. (2012). Before the separation procedure, water samples were pre-filtered. Before being connected to the manifold, the SPE cartridge was pre-washed with 10 mL acetone, 3 mL acetonitrile, and 3 mL distilled water. The cartridge was loaded with 100 mL of water, and the water sample flow rate of the disc was controlled at 1.5 mL/min pressure. After extracting the insecticide from the cartridge, it was eluted with 6 mL of acetonitrile. The extract was then dried using a rotary evaporator before injection into the GC-ECD.

2.4 Gas chromatographic-electron capture detector (GC-ECD) analysis

The analysis was done via a gas chromatography-electron capture detector (Shimadzu GC-ECD QP2010). The carrier gas nitrogen was employed at a 1 mL/min rate at 250°C in splitless mode. The detector's temperature was maintained at 280 °C, and the oven temperature was increased from 100°C to 250–280°C at a rate of 10°C per minute, then by 3°C per minute. A capillary column of 5% phenyl polysilphenylene-siloxane, BPX-5 (30 m×0.25 mm id×0.25 mm thickness) was used for sample uploading.

2.5 Recovery Study

The method's accuracy was determined by calculating carbofuran, carbofuran-phenol, and 3-keto carbofuran recovery rates at a few fortification levels as per the Lee et al. (2020) and Ripp (1996) method. The procedures were repeated three times for each blank sample in the recovery study. The analytical method of limit detection is calculated by multiplying the sample standard deviation by the correct student's t-value. Spike tests were used to conduct the recovery experiments. The concentration of the chosen compound was determined using an external calibration curve. A set of carbofuran standard solutions was prepared to produce the external calibration curve (0.5–15 ppm; n = 3).

3 Results and Discussion

3.1 Water quality analysis

Six physicochemical parameters, i.e., pH, temperature, turbidity, BOD, COD, and TSS of collected paddy water samples, were estimated by the standard methodology and shown in Table 1. The temperature during the study period ranged between 26 - 33ºC, and the test samples' pH value was 6 to 6.7, which is consistent with the pH of river water. These values are equivalent to what has been found in other rice fields in northern Malaysia. According to Aqmal-Naser and Ahmad (2018), the reasons that may affect the pH of the water are rainfall distribution, application of fertilizer, and decomposition of organic material like weeds and rice stalks.

The collected water samples' average BOD and COD values were 6 mg/L and 109.2 mg/L, respectively. Suratman et al. (2015) and Wu et al. (2018) indicate that concentrations of BOD and COD will remain high in the presence of significant organic contamination in the water. Further, paddy water has a high content of organic materials, including crop waste, fertilizer discharge faeces, and other waste, and bacteria use more oxygen to break down the organic material during oxidation. Total suspended solids are also crucial indicators for assessing water quality since they define residential wastewater concentration and influence water turbidity. The collected paddy water sample shows the low concentration of TSS (17.3 mg/L), which might be due to the dilution of water samples (Kamarudina et al. 2020).

3.2 Degradation of carbofuran in paddy water samples

The presence of carbofuran and its transformation products in the water will be monitored under two conditions (with and without sunlight). Samples were taken, extracted, and the concentrations of the samples were measured with external standard solutions. Throughout the experiment, carbofuran degradation was observed faster for the first 28 days than the subsequent 28 to 56 days. Figure 3 illustrates the declining concentration of carbofuran in paddy water, implying that carbofuran rapidly disappeared in the first week and generally continued to decline slowly until day 56.

The intermediates products were also reviewed to understand the major degradation mechanisms involved in carbofuran photodegradation. Only two carbofuran by-products, i.e. 3-keto carbofuran and carbofuran-phenol, were recorded using GC-ECD analysis compared to genuine analytical standards. Degradation started on day 7 for both 3-keto carbofuran and carbofuran-phenol,

Table 1 Water quality of paddy water sample

pH	Temp (°C)	Turbidity (NTU)	BOD(mg/L)	COD(mg/L)	TSS(mg/L)
6.5	33.8	23.7	6	109.2	17.3

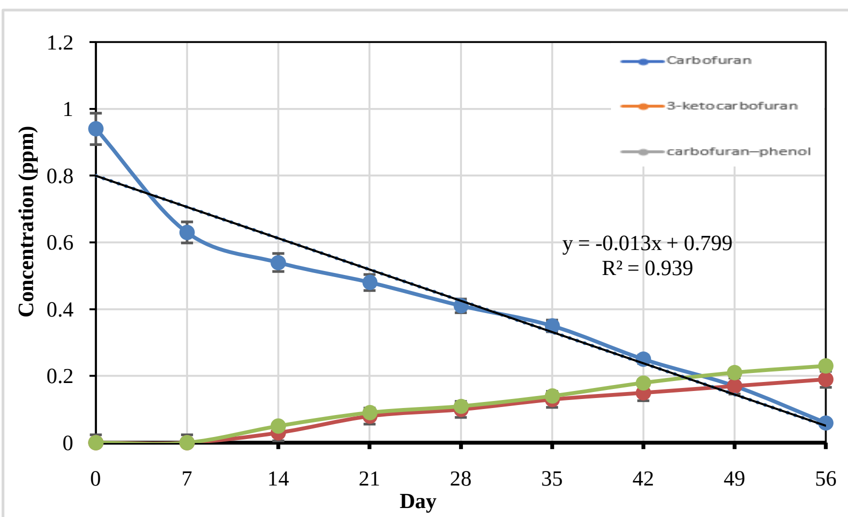


Figure 3 The concentrations of carbofuran and its transformation products in water samples exposed to sunlight

and their concentrations were increased from 0.03±0.301 to 0.23±0.142 ppm.

Similarly, Siddaramappa et al. (1978) recorded that carbofuran was rapidly hydrolyzed to carbofuran-phenol after five days of its application to paddy water. The turbidity of the sample began to decrease with time increased, which may lead to a faster rate in the first half of the study period. With fewer suspended solids, sunlight may permeate the solution more efficiently, allowing photodegradation to occur more rapidly (Seiber and Cahill, 2022). There is no evidence of algal growth in the collected water sample throughout the study period; it might be due to nutrient deficiency or pesticide toxicity.

Results presented in Figure 4 show the trends of carbofuran degradation in water without sunlight (dark). The study's results also revealed that carbofuran degradation began on day 1 and persisted until day 56. The trends of carbofuran degradation showed a similar trend to the water samples exposed to sunlight. However, on day 56, the carbofuran concentrations in the dark remained significantly higher (0.32±0.447ppm) than the samples exposed to the light (0.03±0.301 ppm).

The trends of carbofuran degradation decreased in both conditions and are shown in Figures 3 and 4, and it was recorded between R^2 0.9397 and 0.9572. The possible mechanism of carbofuran degradation was hydrolysis and oxidation in the water sample. Further, 3-keto carbofuran and carbofuran-phenol were detected in the water extract simultaneously. 3-keto carbofuran reached a maximal concentration after day 35 and was subsequently stable, whereas there was a slow increase in concentration for carbofuran-phenol between days 28 and 56.

Results presented in Table 2 revealed that most of the carbofuran exposed to sunlight was degraded up to 93.62%, whereas the percentage of carbofuran degradation was only 67.01% in the

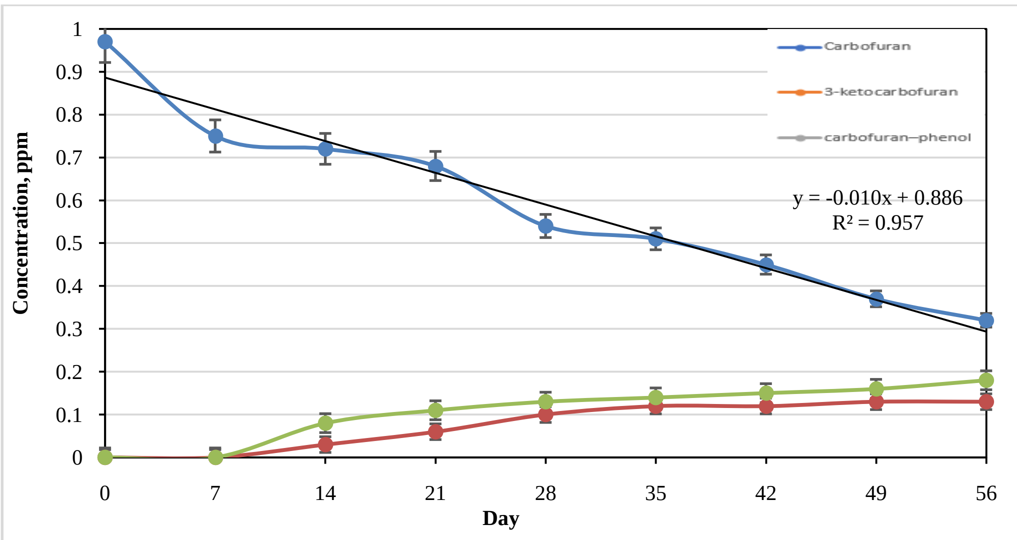


Figure 4 The concentrations of carbofuran and its transformation products in dark

Table 2 Percentage of carbofuran and its metabolites' degradation in collected paddy water sample

	Paddy water exposed to the sunlight			Paddy water in the dark		
Day	Carbofuran (%)	3-keto carbofuran (%)	Carbofuran phenol (%)	Carbofuran (%)	3-keto carbofuran (%)	Carbofuran-phenol (%)
7	32.98	0	0	22.68	0	0
14	42.55	3	5	25.77	3	8
21	48.94	8	9	29.90	6	11
28	56.38	10	11	44.33	10	13
35	62.77	13	14	47.42	12	14
42	73.40	15	18	53.61	12	15
49	81.91	17	21	61.86	13	16
56	93.62	19	23	67.01	13	18

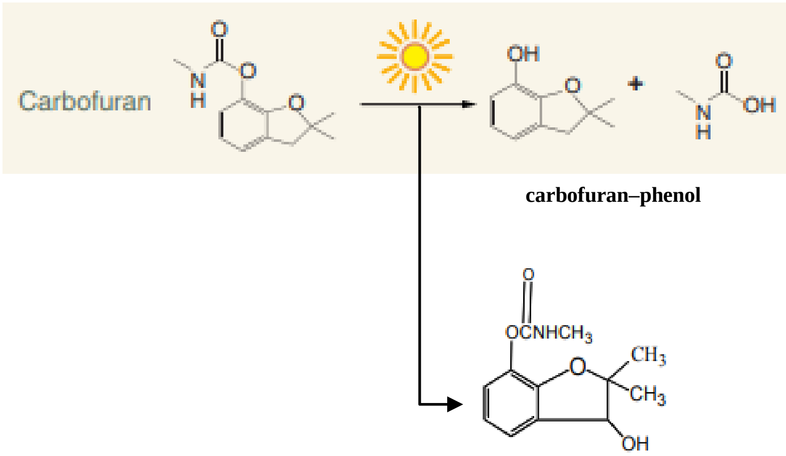


Figure 5 Reaction pathways of carbofuran (direct photodegradation)

paddy water samples kept in the dark. Here carbofuran degradation is slow, and it might be due to only two main degradation pathways, i.e., hydrolysis and oxidation. Throughout the experiment, 3-keto carbofuran and carbofuran-phenol were detected and varied greatly as per the time duration and storage conditions.

The results of the study showed that degradation of the carbofuran is faster in the first week. Similarly, Ecobichon (2019) also reported that carbofuran was degraded entirely in one week. Furthermore, the rate of carbofuran degradation in the dark was slightly slower than in the sunlight. Many pesticides are altered by 'oxidizers generated by sunlight' rather than directly absorbing sunlight (Field 2013; Temgoua et al. 2023). Carbofuran is a water-insoluble compound that accumulates in water over time, so many countries have prohibited its usage (Lan et al. 2020). Figure 5 shows the degradation mechanism (photodegradation) and reaction pathways of carbofuran and its metabolites, carbofuran–phenol and 3-keto carbofuran, in the water samples exposed to sunlight.

The study's results agree with the findings of Howard (2017) and Remucal (2014), who suggested that sunlight directly degraded the carbofuran and its by-products. The pesticide's photodegradation rate is substantially faster in seawater, pond water, and humic acid solutions than in distilled water at the same pH values, implying that dissolved organic matter is indirectly sensitized in photodegradation, a critical loss mechanism. While carbofuran degrades more rapidly in river water than in seawater, adding humic acids has been shown to lower the carbofuran by direct photolysis (Campbell et al. 2004; Iwafune 2018; Atwan et al. 2020).

Insecticides are commonly applied to manage various insects and have a long residual effect on the environment (Gaur et al. 2018). Hydrolysis of carbofuran produces less hazardous metabolite endosulfan diol in certain bacteria (*Pseudomonas aeruginosa*, *Burkholderia cepacia*). Carbofuran degradation was associated with the development of carbofuran-phenol, carbofuran hydrolysis product, and its formation in paddy water, and it can also be proven by thin-layer chromatography (Parte et al. 2017; Mudhoo et al. 2019; Seiber and Cahill 2022). The analysis of carbofuran by-products is essential because they might be more stable and prevalent than the parent pesticides. This is especially important in tropical environments, where carbofuran breakdown at the application site can be relatively fast (Aisha et al. 2022; Mustaffha and Sabran 2020).

3.3 Determination of rate of degradation, k, and half-life of carbofuran

According to Farahani et al. (2012), chemical degradation can be defined by a first-order degradation curve ($C = C_o e^{-kt}$) or ($\ln C = \ln C_o - kt$), where C is the compound's concentration at time t, C_0 is the compound's initial concentration, and k is the rate constant. A pesticide's half-life is described as the time it takes for the pesticide concentration to be half that of its initial concentration, as defined by $t_{1/2}$ = ln 2/k. A straight line may be formed by plotting the ln of concentration vs. time, from which the rate constant (k) and half-life ($t_{1/2}$) can be calculated. Table 3 presents the degradation rate and different half-lives of carbofuran insecticide when exposed to sunlight and kept in the dark in the previous study.

Table 3 shows that this study's half-life of carbofuran was double that of most previous studies. This can be due to the low pH of paddy water as compared to other previous studies where the pH was higher and the soil was more alkaline. The ability of carbofuran to remain stable in water decreases gradually as the pH of the water increases (Howard 2017; Khan et al. 2020). During

Table 3 Rate constant of degradation (k) and half-life ($t_{1/2}$) of carbofuran in paddy water samples exposed to sunlight and kept in dark

Degradation of Carbofuran	This study		Farahani et al. 2012	Cromlab 2010	Kim and Kim 2002	Seiber et al. 1978; Campbell et al. 2004
	Rate constant (day^{-1})	Half-life (day)	Half-life (day)	Half-life (day)	Half-life (day)	Half-life (day)
Exposed to sunlight	0.040	17.33	6.6	6.25	9.7	7.2
Kept in the dark	0.0186	37.27	8.6	-	-	9.3

photolysis, rice plants take up carbon dioxide from the water and release oxygen, which can increase the pH of the water. As it occurs mainly during daylight hours, the pH of paddy water tends to increase during the day and decrease at night (Aisha et al. 2022; Mustaffha and Sabran 2020). Further, this degradation pattern is more prominent in the early growing season before the canopy blocks sunlight from reaching the paddy water. Additionally, colloidal matter in paddy soils may absorb ultraviolet light, drastically lowering the energy available for photodegradation. It shows that the fast dissipation seen in rice paddies is caused by hydrolysis at high pH (Katagi 2016; Davenport et al. 2022; Southwell et al. 2023).

Photolysis may enhance the degradation process in the water. The UV radiation from the sun, which makes up around 10% of the sun's overall electromagnetic radiation output, can break specific chemical bonds, creating transformation products. Bachman and Patterson (1999) developed a pathway for the UV degradation of carbofuran that involves the Fries' rearrangement, which produces a by-product consistent with the hydrolysis of the ethereal moiety of the 2,3-dihydrofuran ring. The results of this study were established by the findings of Elsheikh (2020) and Harmoko et al. (2023), who reported that carbofuran degradation was faster under sun exposure compared to the dark. From the results of this study, it can be concluded that the water sample exposed to sunlight had a faster rate of carbofuran degradation than the water sample kept in the dark (0.04/day with a correlation coefficient R^2 = 0.8758 compared to the water that was kept in the dark at 0.0186/day with a correlation coefficient R^2 = 0.9771). The half-life, $t_{1/2}$ period for the samples exposed to sunlight was 17.33 days, whereas it was reported to be 37.27 days for the samples stored in the dark. de-Azeredo Morgado et al. (2023) and Maqueda et al. (2017) suggested that the half-life of glyphosate in water is 10.0 days, less than the carbofuran, indicating that the carbofuran is more stable in water as compared the glyphosate. The half-life period of the carbofuran is approximately 30–120 days under natural conditions, and this degradation rate depends on location, temperature, soil types, water pH, and the surrounding medium's moisture content. The major routes of carbofuran degradation are hydrolysis and biodegradation (Vishnuganth et al. 2017; Cid et al. 2018). Carbofuran is more mobile in soil than other insecticides, and its degradation is faster in water than in soil (Matthies and Beulke 2017; Chae and An 2018; Jain 2021). Further, ions, organic molecules, and chemical sensitizers may have facilitated carbamate pesticide photodegradation. The prolonged half-life of carbofuran observed when it is stored in the dark might be due to the slow photodegradation (Remucal 2014; Kaur et al. 2021). Since many pesticides do not absorb sunlight directly, they are transformed by 'oxidizers formed by sunlight'. Photochemical breakdown, as a rule, is not complete and leads to the formation of breakdown products (Peña et al. 2020). Many countries have prohibited its use due to its persistence in water and its transformation into other products, which allowed it to remain in the water longer.

Few studies have been conducted on identifying and analyzing the route of carbofuran degradation and its major degradation products, which can be long-lasting and toxic compared to their parent substances (Nollet and Rathore 2016). This study demonstrated that sunlight can enhance the photodegradation of carbofuran in water, and hydrolysis is the main route for carbofuran degradation in water. Findings of previous studies suggested that 3-keto carbofuran and 3-hydroxy carbofuran are the most stable carbofuran metabolites (Ramasubramanian and Paramasivam 2018; Mohamed et al. 2021; Boonkhao et al. 2022). In the current study, the recovery for carbofuran, 3-hydroxy carbofuran, and 3-keto carbofuran is within the acceptable range (83–94%). As previously reported by Martínez Vidal et al. (2000), the best recovery range for pesticides found in water samples is between 76% and 122%. The detection limits for all pesticides were in the range of 0.005 and 0.3 g/mL (Hladik et al. 2008; Masoner et al. 2019).

Conclusion

In conclusion, this study demonstrated that paddy water exposed to sunlight degraded approximately two times faster than water in the dark. The results also showed that sunlight helps in the faster degradation of carbofuran. Both 3-keto carbofuran and carbofuran-phenol were detected as metabolites as their concentration increased at low levels, ranging from 0.03±0.301 to 0.23±0.142 ppm. Therefore, with a rising number of pesticide by-products in diverse environmental media, a more thorough understanding of the ecological threat of pesticide by-products is required for future risk assessments and regulatory policy-making on pesticide restriction.

Acknowledgments

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Conflict of Interest

The authors declare that they have no conflict of interest concerning this work.

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