ASSESSING CARBOFURAN AND ITS METABOLITES IN THE PADDY FIELD WATER-SOIL COLUMN

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ASSESSING CARBOFURAN AND ITS METABOLITES IN THE PADDY FIELD WATER-SOIL COLUMN

by

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%	Percentage
°C	Degree Celsius
A	Initial residue concentration
b	Maximum adsorption capacity of the soil
C	Equilibrium concentration of carbofuran
C_e	Adsorbate concentration
C_0	Concentration at time, first day
C_t	Concentration at time, t
k	Rate of degradation
K_f	Freundlich constant
K_l	Langmuir constant
km	Kilometer
LC	Lethal Concentration
LD	Lethal Dose
mg/l	Miligram per litre
mg/kg	Milligram per kilogram
ml	Mililitre
min	Minute
m/s	Meter per second
ppb	Part per billion
ppm	Part per million
Pa	Pascal
R_2	Maximum correlation coefficient
R_{em}	Removal

q_e	Amount adsorb
t	Time
$t^{1/2}$	Half-life
x/m	Adsorbate concentration per unit amount of adsorbent
Y	Residue concentration at time, t
1/n	Freundlich coefficient

LIST OF ABBREVIATIONS

ACGIH	American Conference of Governmental Industrial Hygienists
ADI	Acceptable Daily Intake
APHA	American Public Health Association
BOD	Biochemical oxygen demand
CKB	Centre for Chemical Pesticides
CO_2	Carbon Dioxide
COD	Chemical oxygen demand
DBP	Dichlorobenzene
DI	Distilled water
DOM	Dissolved organic matter
EFSA	European Food Safety Authority
USEPA	United States Environmental Protection Agency
FAO	Food and Agriculture Organization
GC-ECD	Gas Chromatography-Electron Capture Detector
GCMS	Gas Chromatography–Mass Spectrometry
H_2O	Dihydrogen monoxide
LC/MS	Liquid Chromatography-Mass Spectrometry
LC/MS MS	Liquid Chromatography with Tandem Mass Spectrometry
MCPA	Malaysian Crop Care and Public Health Association
$MgSO_4$	Magnesium sulfate
MRL	Maximum Residue Limit
MW	Molecular weight
NaCl	Sodium chloride
ND	Not detected

NIOSH	National Institute for Occupational Safety and Health
OM	Organic Matter
OP	Organophosphorus
PADDY	Pesticide Paddy Field model
PCPF-1	Pesticide Concentrations in Paddy Field model
PFAM	Pesticide in Flooded Application Model
PMRA	Pest Management Regulatory Agency
QuEChERS	Quick, easy, cheap, effective, rugged, and safe
RICEWQ	Rice Water Quality model
SPE	Solid Phase Extraction
USDA	United States Department of Agriculture
US EPA	United States Environmental Protection Agency
UV	Ultraviolet
TSS	Total suspended solids
ZnO	Zinc Oxide
WHO	World Health Organization

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PENILAIAN CARBOFURAN DAN METABOLIT DI DALAM LAJUR AIR-TANAH DI SAWAH PADI

ABSTRAK

Dalam sektor pertanian Malaysia, sejumlah besar racun perosak digunakan pada sawah padi. Karbofuran ialah racun serangga yang diluluskan sehingga Malaysia mengharamkannya pada Mei 2023. Selain kepekatan dan kehadiran karbofuran, adalah penting untuk menyiasat metabolit aktif dan produk sampingannya. Di sebalik usaha ramai penyelidik menyiasat dan mendokumentasikan kesan alam sekitar dan persisten karbofuran, kajian yang memfokuskan kepada metabolit karbofuran di negara beriklim tropika seperti Malaysia masih sangat terhad dan kurang mendapat perhatian dalam penerbitan saintifik. Kajian ini bertujuan untuk menyiasat laluan karbofuran dan metabolit dalam turus air-tanah ekosistem sawah padi tropika. Penyelidikan dijalankan ke atas sawah padi dan saluran pengairan di Mukim 5 Penaga, Seberang Perai Utara, Pulau Pinang. Ia menilai kualiti air permukaan dan pengagihan sisa racun perosak dan degradasi di ladang padi berhampiran. Kajian ini bertujuan untuk meneroka degradasi karbofuran dalam air sawah padi dengan mengukur kandungannya dalam tempoh 0 hingga 56 hari di bawah keadaan terdedah dengan cahaya matahari dan sebaliknya. Kedua-dua 3-ketocarbofuran dan carbofuran-phenol dikesan dalam air sawah padi sebagai metabolit dengan tahap kepekatan rendah, antara 0.03 ± 0.301 hingga 0.23 ± 0.142 mg/L. Sisa karbofuran dikesan pada 8.53 µg/kg daripada degradasi karbofuran dalam tanah, dan kepekatannya menurun kepada 6.52 µg/g. Pemalar kadar tindak balas (k) untuk degradasi karbofuran dalam sampel tanah padi ialah 0.0036 dengan pekali korelasi (r^2) 0.9349. Separuh hayat carbofuran dalam tanah sawah padi pada suhu malar 30 °C ialah 147 hari. Dalam kajian awal penjerapan karbofuran, karbofuran mencapai keseimbangan optimum dalam tempoh 24 jam di dalam tanah sawah padi. Faktor kapasiti Freundlich (K_f) bagi karbofuran adalah lebih tinggi dalam tanah sawah padi, menandakan wujudnya interaksi yang kuat antara karbofuran dan komponen tanah. Selain itu, kapasiti penjerapan maksimum karbofuran yang direkodkan ialah 36.2318 mg/g, menunjukkan keupayaan penjerapan yang tinggi oleh tanah tersebut. Dalam kajian larut lesap turus, selepas 10 hari penyiraman air kepada tanah sawah padi (tanah liat) dan saluran pengairan (tanah liat berpasir), jumlah karbofuran dalam air larut resap untuk kedua-dua jenis tanah ialah 31.5 dan 40.2%. Tanah sawah padi mengandungi lebih banyak bahan organik dan tanah liat daripada tanah saluran pengairan (2.41 dan 8.55%), yang meningkatkan kapasiti penyerapannya. Kehadiran tanah berpasir dalam sistem pengairan didapati berpotensi meningkatkan mobiliti karbofuran, dengan peningkatan yang dicatatkan sebanyak 42.71%. Aplikasi model PADDY meramalkan kelakuan karbofuran dalam persekitaran sawah padi simulasi menunjukkan bahawa model ini berupaya untuk menganggarkan kepekatan racun perosak dalam air sawah dengan berkesan, berdasarkan kesesuaian yang tinggi antara nilai ramalan dan nilai sebenar yang diukur (pekali korelasi Pearson = 0.754–0.79). Ketepatan ramalan kepekatan dalam tanah adalah lebih rendah (pekali korelasi Pearson =0.21–0.357), mungkin disebabkan oleh faktor persekitaran seperti kelembapan, suhu, dan penyejatan yang tidak terkawal. Meskipun terdapat sedikit anggaran berlebihan terhadap sisa karbofuran dalam tanah, model PADDY terbukti berkesan untuk menilai karbofuran dalam air dan berpotensi digunakan untuk penilaian risiko dalam sistem sawah padi tropika, malah meramalkan kepekatan karbofuran dalam air dengan baik tetapi kurang tepat untuk tanah. Hasil kajian menegaskan keperluan pemantauan berterusan terhadap sisa racun perosak dan metabolitnya.

ASSESSING CARBOFURAN AND ITS METABOLITES IN THE PADDY FIELD WATER-SOIL COLUMN

ABSTRACT

In Malaysia's agricultural sector, a substantial amount of pesticides is used in paddy fields. Carbofuran was an approved insecticide until its ban in May 2023. In addition to the concentration and presence of carbofuran, it is important to investigate its active metabolites. Despite numerous researchers studying and documenting the environmental persistence of carbofuran, there is a significant lack of published studies focusing on its metabolites in tropical countries like Malaysia. This study aimed to investigate the pathway of carbofuran and its metabolites in the water–soil column of a tropical paddy field ecosystem. The research was conducted in paddy fields and irrigation channels in Mukim 5 Penaga, North Seberang Perai, Penang. It assessed surface water quality and the distribution and degradation of pesticide residues in nearby paddy farms. The study also explored carbofuran degradation in paddy water by measuring its content over 0 to 56 days under sunlight exposure and total darkness. Degradation of carbofuran in paddy water produced metabolites such as carbofuran-phenol and 3-ketocarbofuran. Results indicated that photolysis and hydrolysis enhanced the degradation of carbofuran in water. Both 3-ketocarbofuran and carbofuran-phenol were detected in paddy water at low concentrations, ranging from 0.03 ± 0.301 to 0.23 ± 0.142 mg/L. Carbofuran residues were detected at 8.53 µg/g from the degradation process in soil, decreasing rapidly to 6.52 µg/g. The concentration remained stable for weeks before declining by the fifth week. Two known oxidative metabolites, 3-hydroxycarbofuran and 3-ketocarbofuran, were only present in trace amounts in soil extracts and had short persistence. The rate constant (k) for carbofuran degradation in paddy soil samples was 0.0036, with a correlation

coefficient (r^2) of 0.9349. The half-life of carbofuran in paddy soil at a constant temperature of 30 °C was 147 days. In preliminary adsorption studies, carbofuran reached optimal equilibrium within 24 hours in paddy soil. The Freundlich adsorption coefficient (K_f) for carbofuran was higher in paddy soil, indicating strong interactions between carbofuran and soil components. The maximum recorded adsorption capacity was 36.2318 mg/g, demonstrating high sorption capacity by the soil. In leaching column studies, after 10 days of water irrigation through paddy (clay) and irrigation channel (sandy clay) soils, the amount of leached carbofuran in both soil types was 31.5% and 40.2%, respectively. Leachate from irrigation channel soil contained more carbofuran than from paddy soil, indicating higher mobility in irrigation soil. In both soils, clay, sand, and organic content influenced mobility. Paddy soil had higher organic matter and clay content (2.41% and 8.55%), enhancing its sorption capacity. The presence of sandy soil in irrigation systems increased carbofuran mobility by up to 42.71%. Application of the PADDY model to predict carbofuran behavior in simulated paddy field environments showed that the model effectively estimated pesticide concentrations in paddy water, based on a strong fit between predicted and measured values (Pearson correlation coefficient = 0.754–0.79). The model's accuracy in predicting soil concentrations was lower (Pearson correlation = 0.21–0.357), likely due to environmental factors such as moisture, temperature, and evaporation. Despite minor overestimation of soil residues, the PADDY model proved effective in assessing carbofuran dynamics in water and is potentially useful for risk assessment in tropical paddy systems. The PADDY model predicts carbofuran concentrations in water accurately but is less reliable for soil estimates. The findings highlight the need for continuous monitoring of pesticide residues and their metabolites.

CHAPTER 1

INTRODUCTION

1.1 Overview

Pesticides are commonly applied in agricultural production to eliminate or manage pests, diseases, weeds, and other plant pathogens, with the purpose of reducing or minimising yield losses while achieving higher output quality (Cossi et al., 2020). Even though pesticides are beneficial in producing high crop yields and controlling disease-borne pests, the negative impacts of their residues in water, soil, and plants are manifestly harmful. The sprayed pesticide will travel and be released into the ecosystem via water, wind, and soil absorption. Some residues can remain for hours, weeks, months, or even years (Daliya et al., 2020). Kamaruzaman et al. (2020) reported that as of 2016, Malaysia used approximately 49,199 tonnes of active pesticide ingredients, averaging 5.9 kg per hectare of cropland. Pesticides are widely applied across various crops, including paddy, vegetables, fruits, rubber, and oil palm plantations.

Numerous researchers on a local and global scale have found carbofuran residue concentrations in agricultural fields, rivers, and estuaries. However, the common understanding of carbofuran and its by-products is limited solely to the original compounds, with little attention paid to its derivative products. Pesticide transformation products are considered “emerging pollutants” since most of them are identified in the environment and can pose as much of a threat as the original substances, if not more (Arman et al., 2021; Suman et al., 2022).

Carbofuran is a systemic carbamate insecticide, nematicide, and acaricide with a wide range of activities. Carbofuran can easily get into water bodies near rice fields through runoff because it is broadly used in agriculture and dissolves well in water with a solubility of 320 mg/L at 20°C, which makes it particularly prone to movement through aquatic pathways (Cáceres et al., 2019; Clasen et al., 2014). Despite its effectiveness in pest control and crop management, carbofuran is highly toxic and has been linked to animal deaths in many countries. In fact, carbofuran use has been prohibited in some countries (Khuntong et al., 2010; Vithanage et al., 2016). Carbofuran dissipates in the environment via both abiotic and biotic processes, whereas its biomineralization completely detoxifies a polluted area (Jemutai-Kimosop et al., 2014; Prudnikova et al., 2021).

Monitoring the active metabolites and by-products of the administered pesticide is vital. The presence of transformation products may indicate that the degradation process has occurred, not to mention that they may be potentially more hazardous than their parent substance. The most common carbofuran metabolites are 3-hydroxycarbofuran and 3-ketocarbofuran, which are more polar but harmful to specific and non-specific species (Mishra et al., 2020; Osesua et al., 2017). Other carbofuran by-products include carbofuran phenol, 3-hydroxy-7-carbofuran phenol, 3-keto-7-carbofuran phenol, N-hydroxymethylcarbofuran, and 3-hydroxy-N-hydroxymethylcarbofuran (Ramesh et al., 2015; Suman et al., 2022).

The climate and soil conditions of a country, as well as the pH, humidity, soil type, organic matter, and clay content, all have an impact on pesticide mobility and degradation. Additionally, the environmental conditions under which pesticides were administered to plants and the physical-chemical characteristics of the pesticides affect how pesticides move and degrade in the surroundings (Arias-Estévez et al., 2008; Sharma et al., 2020). When a pesticide is introduced into the water, soil, and air, it can decay via several degradation processes or dissipation mechanisms and transform into several types of metabolites. Degradation can occur through hydrolysis, photolysis, surface runoff, leaching, volatilization, oxidation or reduction, and microbial degradation (Lewis et al., 2016; Nieder et al., 2018).

A significant amount of research indicates that hydrolysis and photolysis are the primary mechanisms by which pollutants undergo degradation. Comprehending the fate of pesticides in water necessitates a thorough understanding of the transformation mechanisms. Pesticide hydrolysis is a secondary and nucleophilic substitution reaction and fits first-order reaction kinetics (Singh et al., 2017). Fang et al. (2022) state that temperature and pH are common factors affecting hydrolysis. In Malaysia, Zakaria et al. (2012) have reported on carbofuran stability in river, sea, and ground waters. It was discovered that carbofuran is more stable in groundwater. On the other hand, prior researchers have also examined the downward transport of carbofuran in disturbed and undisturbed soil columns of two different soil types (Farahani et al., 2008; Khairatul et al., 2013).

The understanding of carbofuran degradation and its transformation products focuses only on the parent compounds. To date, many researchers have not considered the potential hazards of its derivative products. Therefore, the present study aims to address the existing research gaps by evaluating the pathway and rate of carbofuran and its metabolites. This study also assesses water-soil column uptake in selected paddy field soil samples, which are hypothesised to be affected by both tropical climate and field conditions. The study's findings will contribute to a better understanding of the fate of carbofuran in the water and soil as well as provide beneficial information towards more sustainable pesticide practices while minimising their negative impacts on humans and the environment.

1.2 Carbofuran Usage in Agricultural Areas

Carbofuran is a pesticide 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).

According to FAO (2019), carbofuran is primarily used for seed treatment, at-plant soil application, and directed or foliar applications in agricultural settings. However, the use of carbamate insecticides, including carbofuran, has decreased in agricultural applications over the years, with pyrethroid and other insecticides being used as replacements.

In Malaysia, it is commonly used on aubergines and other vegetables (Sim et al., 2019). Previous studies by Farahani et al. (2007) and Khuntong et al. (2010) reported that the concentration of carbofuran residue in agricultural fields, rivers, and estuaries has been quantified locally and globally.

1.3 Impact of Carbofuran on Humans and the Ecosystem

The impact of carbofuran on humans and the ecosystem has been a subject of concern due to its use as an insecticide, nematicide, and acaricide in agricultural practice. Carbofuran is highly toxic to mammals, birds, fish, and wildlife due to its anticholinesterase activity, which inhibits acetylcholinesterase and butyryl cholinesterase activities (Mohanta et al., 2012). Exposure to carbofuran can occur through various routes, including inhalation, ingestion, and dermal absorption. Human exposure to carbofuran can lead to adverse health effects such as endocrine disruption, reproductive disorders, cytotoxicity, and genotoxic abnormalities. Overall toxicity has been linked to carbofuran and its main metabolites, 3-hydroxycarbofuran and 3-ketocarbofuran (Mohamed et al., 2021).

A recent study (Mishra et al., 2020) found that grain farmers who were 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, a comprehensive study extensively examined the metabolic activity of carbofuran in relation to its overall toxicity, specifically focusing on the significant impact of carbofuran metabolites (Ruíz-Hidalgo et al., 2016).

To date, carbofuran has been prohibited in several countries, particularly the United States, Canada, and the European Union, due to frequent reports of bird poisoning (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 (Harper, 2011). In addition, 3-ketocarbofuran and 3-hydroxycarbofuran, which are secondary metabolites of carbofuran, were also identified as being poisonous. Approximately 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, and Australia, which registered carbofuran as a legal pesticide (Sim et al., 2019).

1.4 Banning Carbofuran in the Agricultural Industry

In Asia, Australia, and South America, carbofuran use is widespread. Meanwhile, Canada, Kenya, Brazil, the United States, and the European Union are among the countries that have banned or restricted carbofuran use. Canada banned the use of carbofuran-containing pesticides in 2009, when Health Canada's Pest Management Regulatory Agency (PMRA) cancelled all carbofuran registrations in the country (Health Canada, 2020). In 2010, Kenya prohibited the importation, distribution, and sale of carbofuran. Carbofuran registration in Brazil was suspended in 2011, effectively banning its use in the country. In 2008, the European Union banned the carbofuran use in all of its member countries. The United States Environmental Protection Agency (EPA) declared a ban on all carbofuran uses in the country in 2009, claiming risks to human health and the environment (USEPA, 2009).

Carbofuran was an approved insecticide until it was banned in the agriculture sector effective May 2023 (Pesticides Act 1974, 2021). The Pesticides Board of Malaysia, which is the regulatory authority responsible for the control of pesticides in Malaysia, announced the ban on carbofuran in April 2021 (Figure 1.1).

Figure 1.1 Banning of carbofuran in the agriculture sector

This ban includes the manufacturing, distribution, sale, and use of these pesticides. The ban was implemented due to the toxicity of the chemical to humans and the environment and its harmful effects on wildlife and non-target organisms. The presence of carbofuran residues in vegetables and fruits, exceeding maximum residue levels, highlighted the need to ensure the quality and safety of agricultural produce in the country.

1.5 Problem Statement

Carbofuran, or 2, 3-dihydro-2, 2-dimethylbenzofuran-7-yl-methylcarbamate, also known as Furadan (commercial name), is a carbamate insecticide, miticide, and nematicide that is effective against a wide range of crop pests. Besides carbofuran, it is critical to study its active metabolites and breakdown products. The metabolite products of carbofuran should be of greater concern because they can be found in the environment in higher amounts than the parent compound and can be as lethal as or more lethal than the parent compound (Feng et al., 2021; Richardson & Ternes, 2014). In soil, carbofuran will metabolise into 3- hydroxycarbofuran and 3-ketocarbofuran groups. These groups are probably just as hazardous as carbofuran itself.

The local climatic conditions, which vary between tropical and temperate regions, have an impact on the environmental fate and persistence of carbofuran and its transformation products. High temperatures and UV intensity can cause photodegradation to occur more rapidly. Chemical reactions in water and soil are regulated by variables such as pH, temperature, clay ratio, organic matter, and moisture content, as well as the activity of microbes (Malhotra et al., 2021; Tomašević et al., 2019).

Although there has been much research conducted on the fate and persistence of carbofuran in the environment, limited attention has been given to its by-products in tropical climates, particularly in Malaysia. The importance of understanding the comprehensive behaviour of carbofuran together with its transformation product is vital to establish pollution baseline levels for future reference. Other than that, pesticide persistence can be predicted by knowing its behaviour in water and soil. Pesticide fate and degradation processes in water-soil systems necessitate more research studies for risk evaluation, legislation, and safety and health purposes.

Pesticide fate modelling has been employed to predict pesticide behaviour in different parts of the environment for both new (unregistered) pesticides and pesticides that are already in use (registered). Predictions made by models did not always match up with measured data (Hand et al., 2021; Latino et al., 2017). Pesticide fate in the environment is complex, varying from pesticide to pesticide and field to field. As a result, pesticide half-lives obtained from the pesticide directory or the publications do not portray all aspects of the environment.

1.6 Research Objectives

The primary aim of this study is to evaluate the pathways of carbofuran and its transformation products within the water-soil column of a tropical paddy field ecosystem. The present study seeks to achieve the following objectives:

1.6.1 Objective 1

To determine carbofuran residue concentrations in selected paddy field ecosystems.

1.6.2 Objective 2

To estimate carbofuran degradation and its metabolites concentrations in paddy field water and soil samples.

1.6.3 Objective 3

To evaluate the adsorption capacities and the leaching potential of carbofuran in paddy field soil.

1.6.4 Objective 4

To predict the fate, changes in concentration, degradation, and dissipation of carbofuran in a water-soil column study by using PADDY model.

1.7 Scope of Study

This study focuses on the environmental behaviour, degradation, and persistence of the banned pesticide carbofuran and its metabolites carbofuran-phenol and 3-ketocarbofuran in tropical paddy field ecosystems in Malaysia. The research includes field investigations at paddy fields and irrigation channels in Mukim 5 Penaga, North Seberang Perai, Penang, where water and soil samples were collected and analysed to assess surface water quality and the distribution of pesticide residues over time. Laboratory experiments were conducted to understand the degradation of carbofuran under various environmental conditions, such as sunlight and darkness, to simulate real-world scenarios.

The study employed solid-phase extraction (SPE) and gas chromatography to quantify the presence of carbofuran and its metabolites in environmental matrices. Additionally, adsorption and leaching experiments were carried out to examine the interaction between carbofuran and different soil types, including paddy clay soil and sandy clay from irrigation channels. These tests aimed to assess the compound's sorption capacities, degradation kinetics, and mobility, providing insight into how soil composition and environmental variables influence pesticide fate.

Furthermore, the study incorporated the application and validation of the PADDY mathematical model to simulate and predict carbofuran concentrations in paddy water and soil. The model's predictions were compared with empirical data to evaluate its accuracy. The model was particularly effective in predicting water concentrations but less reliable for soil, likely due to environmental variability. Overall, this study provides an integrated approach to understanding the dynamics of carbofuran in tropical paddy ecosystems, using both empirical and model-based methods.

1.8 Significant of Study

This research is significant as it addresses a major gap in pesticide residue monitoring, particularly for carbofuran metabolites, in tropical agricultural environments. While carbofuran has been widely studied, its transformation products—many of which remain toxic—have received limited attention, especially in Malaysia. By focusing on these metabolites, this study enhances the understanding of "emerging pollutants" and their environmental persistence, providing critical data that can support the revision of agricultural and environmental policies.

The findings offer practical insights into how soil types and environmental factors like light exposure, organic matter, and microbial activity affect pesticide degradation and mobility. The observed differences in carbofuran behaviour between paddy and irrigation soils highlight the importance of site-specific assessments when considering pesticide application and regulation. Such information is crucial for farmers, environmental agencies, and policymakers seeking to implement safer, more sustainable agricultural practices in tropical climates.

Additionally, the study contributes to scientific advancement by validating the PADDY model, a valuable tool for simulating pesticide behaviour in rice cultivation systems. Its ability to accurately predict water concentrations makes it an effective model for future risk assessments and environmental impact evaluations. The study reinforces the importance of continued monitoring and modelling of pesticide residues to ensure food safety, water quality, and environmental health in regions where rice farming is a key economic activity.

1.9 Thesis Outline

Chapter 1 provides an overview of the research study, focusing on the introduction of the research's background and aims, the issue statement, problems, and gaps, as well as the significance of the study.

Chapter 2 provides an overview of the existing literature on pesticide use in the agricultural sector and paddy plantations of Malaysia. It explores the historical context of pesticide use and provides a thorough analysis of the classification of pesticides in the agricultural industry. Notably, this chapter focuses on the pesticides carbofuran, carbofuran phenol, and 3-ketocarbofuran, elaborating on their properties and significance in the field. Further elucidation was provided about the breakdown of pesticides via hydrolysis, photolysis, and biodegradation, with a particular focus on their environmental fate, toxicological implications, degradation pathways, solid-phase extraction methodologies, and gas chromatographic analyses.

Chapter 3 describes the materials and equipment used in the investigation as well as the process parameters required to conduct laboratory analyses. The study includes a comprehensive description of the investigated area, the collection of field data, the separation of specific analytes through the solid phase extraction (SPE) technique, the quantification of residual carbofuran substances in water samples, the analysis of the collected data, and the application of statistical methods for the purpose of this study. The study intends to provide a scholarly justification for the methodologies employed in carbofuran photodegradation, adsorption, column leaching, mathematical model application, and testing.

Chapter 4 discusses and presents research findings regarding physical environmental parameters and pesticide residue concentrations in water and soil samples. This study also aims to provide a detailed explanation of the photodegradation process, with a focus on how metabolites like carbofuran-phenol, 3-ketocarbofuran are made from the parent compounds. In addition, equilibrium and kinetic studies will be conducted to determine how these compounds behave. The study will also investigate the potential mobility of these substances in different types of soil and conclude with the development and validation of a mathematical model to predict the behaviour of carbofuran in paddy fields.

Chapter 5 presents the final discussions and puts forth recommendations for future research.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction of Pesticide Application in the Environment

Pesticides are substances or a mixture of substances that are used to destroy, repel, or mitigate pests (Mokkapati et al., 2022). Currently, there are various forms of pesticides, including chemical-based substances, biological agents such as bacteria or viruses), antimicrobial, disinfectant, or other devices. Pesticides are used against a wide range of pests, such as insects, plant pathogens, weeds, microbes, nematodes (roundworms), molluscs, mammals, birds, and fish that cause massive losses in plantations and properties, spreading infectious diseases, or act as a vector for diseases (Pathak et al., 2022). Moreover, the application of pesticides against pests and air-borne diseases improves the economic output from the agricultural sector and boosts the quality of crop yields (de Souza et al., 2020; Idayu et al., 2014). Despite having significant benefits, there are serious concerns regarding the effect of pesticides, such as the potential toxicity towards humans and other animals (Daliya et al., 2020).

Malaysia is an agriculture-based country with vast areas reserved for plantation and farming. Oil palm and rubber are the two main plantation crops that occupy over 3.8 million ha of land or equivalent to 70% of the total agricultural land area. In addition, rice is a crucial agricultural crop that contributes nearly 60% of the country's annual rice consumption (Hassan et al., 2018). Given the huge demand for plantation produce in recent years, pesticides have been extensively used. As rice is the main staple food in the country, around 70% of the pesticides are used in paddy fields to ensure that the demand for rice is met (Bhattacharjee et al., 2012).

As a result, it was reported that ground and surface water pollution from the use of pesticides had introduced many undesirable effects and problems in tropical countries, including Malaysia, which has heavy rainfall, high humidity, and high temperature (Farahani et al., 2007; Tayeb et al., 2019). The pesticides fate in the environment is analysed in terms of the transport, transfer, and transformation processes that determine their persistence and mobility. Previously, the herbicides fate in paddy fields and vegetable plantations in Cameron Highlands, Pahang and Kluang, Johor as well as cultivated tobacco areas have been studied (Ismail et al., 2015; Sapari & Ismail, 2012). It was also reported that surface and ground-water pollution due to pesticides has become a growing concern in tropical countries, including Malaysia (Tan & Beh, 2015; Maznah et al., 2022)

Furthermore, the reaction pathways and breakdown of pesticides are crucial to determine the process involved, especially the characteristics of the intermediates and by-products. In this way, proper management and control of the discharge of pesticides into the environment can be implemented (Koe et al., 2020). 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 river is channelled into plots, retained for a certain period before being drained out 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.

2.2 Malaysia Paddy Plantation

Paddy rice cultivation (*Oryza sativa*) across every continent except Antarctica has made paddy cultivation cover approximately 1% of the earth's surface. Over half the world's population uses rice as 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 and planted in the eight major rice production areas in Peninsular Malaysia and Sabah in Borneo as shown in Figure 2.1 (Sabere et al., 2013; Rahman, 2019). Malaysian rice was grown yearly due to the seasonal rainfall as well as hot and humid climate. Rice is planted and harvested in a roughly similar cycle. The main season is called the wet season, as paddy planting starts between August 1st and February 28/29th. Meanwhile, the off-season is the dry season when paddy planting starts between March 1st and July 31st (Department of Agriculture, 2014).

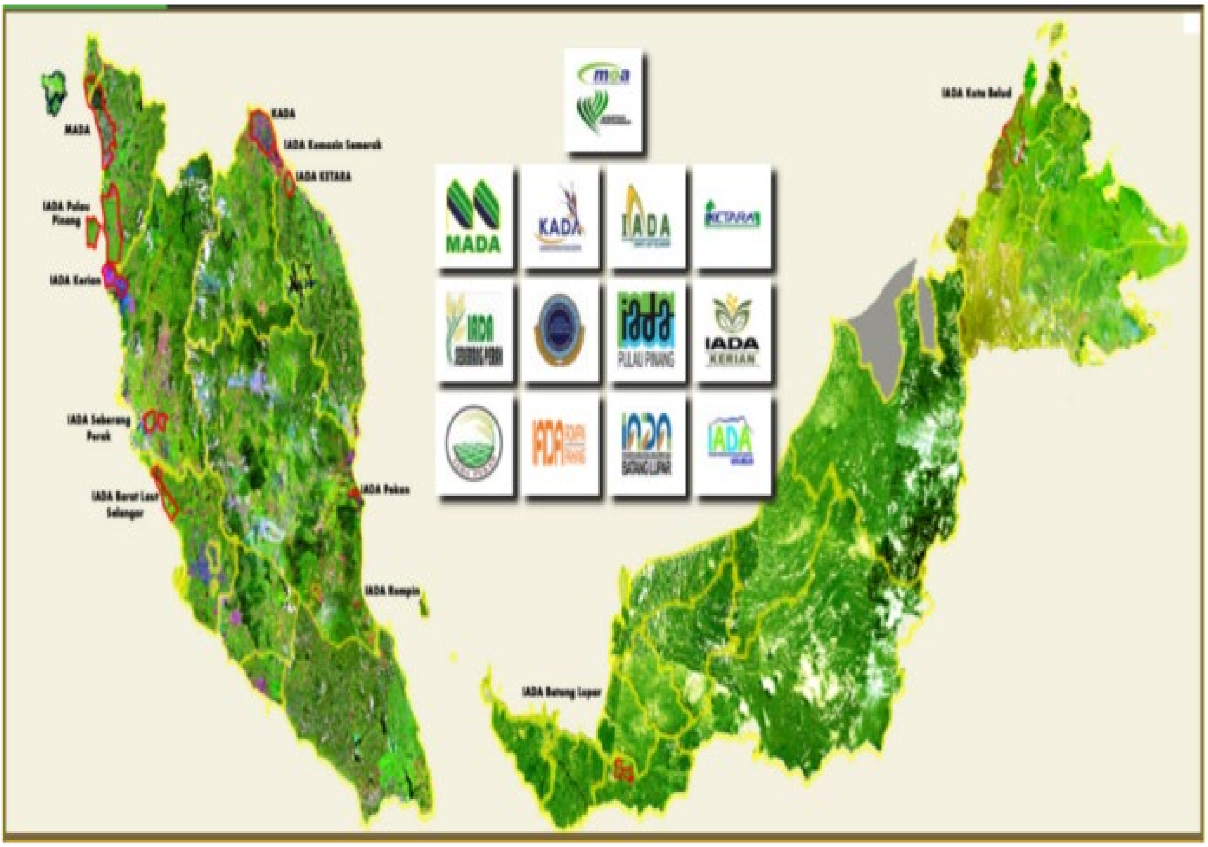

Figure 2.1 Map of paddy field areas in Malaysia (Department of Agriculture, 2019)

The rice paddy harvested during the main paddy season in Malaysia is shown in Table 2.1. Rice production has generally increased over time, with the highest production recorded at 1,825,000 tons in both 2018/2019 and 2019/2020. Afterward, there was a small decline in 2021/2022 (to 1,677,000 tons), but production picked up again in 2022/2023 at 1,700,000 tons. The reduction in yield suggests factors such as possible environmental impacts, variations in farming practices, or resource limitations that may have affected the crop yield. The largest granary in Malaysia is in Muda, Kedah, covering an area of 98,860 hectares. Following Muda, Kemubu in Kelantan spans over 32,400 hectares, while Kerian in Perak covers 24,010 hectares. Other notable granaries include, Seberang Perak and Sungai Manik in Perak, and Seberang Perai in Penang (Rahman, 2019).

Table 2.1 Average area, production and yield of rice paddy in Malaysia from 2011 to 2023 (USDA, 2023)

Market (Year)	**Area (1000 Ha)**	**Production (1000 Tons)**	**Yield (T/Ha)**
2011/2012	675	1,690	3.9
2012/2013	688	1,694	3.8
2013/2014	690	1,755	3.9
2014/2015	688	1,800	4.0
2015/2016	690	1,800	4.0
2016/2017	695	1,820	4.0
2017/2018	695	1,820	4.0
2018/2019	700	1,825	4.0
2019/2020	700	1,825	4.0
2020/2021	680	1,800	4.1
2021/2022	650	1,677	4.0
2022/2023	655	1,700	4.0
5-year Average 2017/18 - 2021/22	**685**	**1,789**	**4.0**

2.3 Pesticide Use in Malaysia's Agriculture

Major pesticide use in Malaysia is primarily attributed to the country's progressive agriculture sector, which uses pesticides in farming various vegetables, fruits, paddy, rubber, and palm oil plantations (Kamaruzaman et al., 2020). Pesticides are extensively employed to reduce pest-related yield losses as it also can increase yield and save labour and money while indirectly boost production and income (Popp et al., 2013).

The Malaysian Crop Care and Public Health Association (MCPA) stated that the total expenditure on agricultural chemicals in Malaysia during the financial years 1995 and 2010 were approximately RM 289 million and RM 364 million, respectively (Seng & Sahid, 2010; Dilipkumar et al., 2020). Figure 2.2 shows wide disparities of pesticides use per cropland area within regions: for example, Japan, China and the Republic of Korea have application rates exceeding 10 kg/ha, whereas the most of other Asian nations are below 1 kg/ha.

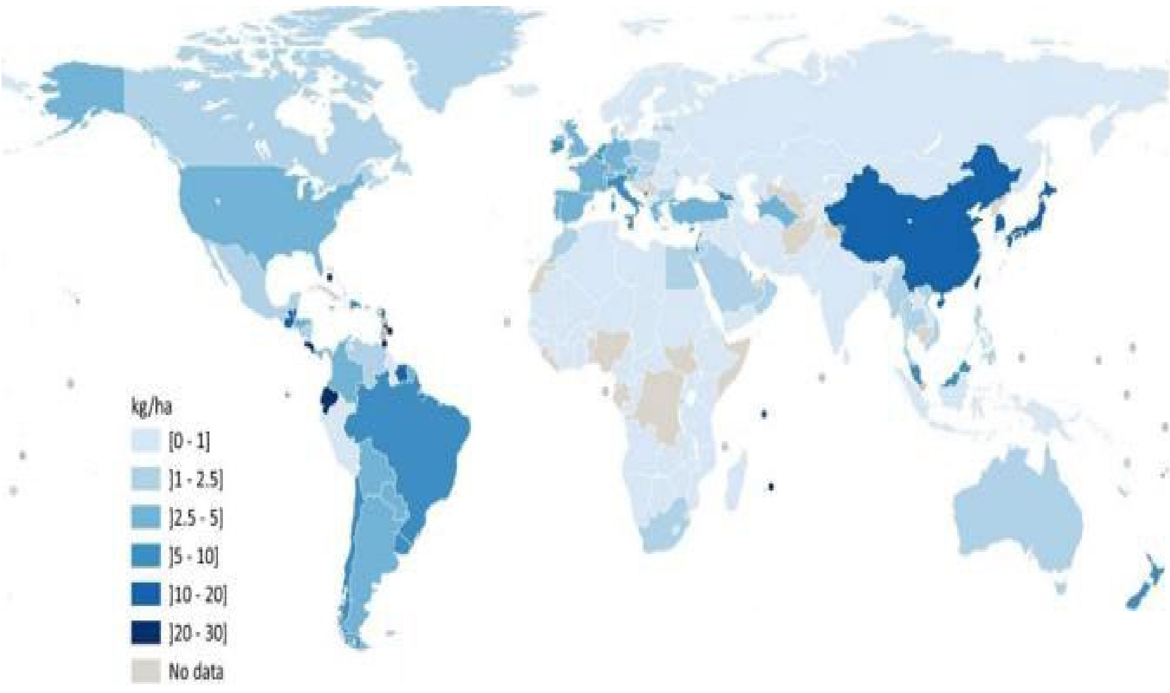

Figure 2.2 Pesticides use per cropland area, 2020 (FAO, 2020)

This represents an average annual growth rate of 1.6% in the net value of agricultural pesticides used during the past 15 years. Recently, approximately two million tonnes of pesticides are used annually which are herbicides (50%), insecticides (30%), fungicides (18%), as well as rodenticides and nematicides (Sharma et al., 2019).

2.4 Pesticide Use in the Paddy Plantation

Agriculture is one of the world's most growing industries and a major contributor to food. Only 25% of agricultural land is organic; the rest uses pesticides. 15% of all pesticides used in agriculture are used in paddy cultivation (Kaleka et al., 2022). Farmers in Malaysia use pesticides to control pests, especially in paddy plantation. It has become customary to use pesticides to prevent Brown Planthopper, *Nilaparvata lugens*, a pest that damages paddy fields. Therefore, modern paddies, pesticides, irrigation, and new technology have been utilised intensively to solve the issues and boost production, changing the ecological structure and increasing pests (Rahaman et al., 2018).

Rice is Malaysia's most important food crop for two reasons. First, rice is the main basic food. Most adults in Malaysia ate 2.5 plates of rice per day. Second, rice is the main source of income and livelihood for rice farmers, especially small-scale and landless farmers (Kasim et al., 2018). Paddy production accounts for 40% of farmers' total income. Therefore, Malaysia's paddy and rice policies aim to enhance farmers' incomes, sustain stable prices, and secure purchasers' food supply.

The exploitation of pesticides in paddy fields is subjected to indiscriminate and intense use. The herbicides 2, 4-D and paraquat are the most common pesticides used in large parts of the paddy plantation in Malaysia (Hamsan et al., 2017). The pesticides are used in paddy fields to control the post-emergence of annual and perennial broad-leaved aquatic weeds, as well as to eliminate various types of grassy and broad-leaved weeds (Tudi et al., 2021). In addition, carbofuran is also used to control rodents in rice fields and rhinoceros beetles in oil palm plantations (Jonip et al., 2019).

Table 2.2 shows pest issue in paddy plantation and its pesticides recommendation. The main finding is that effective pest and disease management in Malaysian paddy plantations relies on targeted pesticide applications for insect pests, diseases, and weeds, with specific recommendations for each issue to maintain rice crop health and productivity (Department of Agriculture, 2018). According to Fahad et al. (2019), 10-15% of Asia's rice production was greatly impacted by crop diseases. *Magnaporthe oryzae*-caused rice blast and *Rhizoctonia solani*-caused sheath blight are the two major rice pathogens that significantly reduce 5% of rice crops production (Gianessi, 2014; Sathe et al., 2021).

Depending on the type of planting, the time of year, the location, the predominant weed flora, the number of weeds, the management practices used, and the length of the infestation., weeds can reduce rice yields by 5-85% in Malaysia. Generally, *Oryza sativa L., Echinochloa* spp*., Paspalum* spp*. and Cynodon dactylon* (L.) Pers. were the most common types of grassy weeds found in rice grown from direct seeding (Dilipkumar et al., 2017).

Table 2.2 Type of pest issue in paddy plantation (Department of Agriculture, 2018)

Pest	**Pesticides recommendations**
Insects pest	
1. Brown planthopper (*Nilaparvata lugens*)	Dimethoate, etofenprox, and malathion
2. Whitebacked planthopper (*Sogatella furcifera*)	Phenobucarb, etofenprox, and buprofezin
3. Stem borer and soil insects	Carbofuran

Rice disease	**Pesticides recommendations**
3. Rice blast (caused by *Pyricularia oryzae*)	Treat seeds with benomyl fungicide (4 gm / kg of seeds) or captan (2 gm / kg of seeds).
4. Sheath blight (*Rhizoctonia solani*)	Fungicides such as edifenphos (0.1% b.a) or isoprothiolane (2 kg b.a./ha)
Weed	**Pesticides recommendations**
5. Weedy rice (*Oryza sativa* L.)	The application of glyphosate before land preparation or seeding reported being effective
6. Jungle rice (*Echinochloa colona* (L.) Link)	Preemergence application of oxadiazon or pendimethalin or postemergence application of cyhalofop, butachlor, and fenoxaprop can be effective.

2.5 Classification of Pesticides

Pesticides are classified according to their target organism, chemical composition, and physical form. Additionally, pesticides may be inorganic, synthetic, or biopesticide (MC & Ioana, 2020; Shokrzadeh & Saravi, 2011). Table 2.3 presents classification of agricultural pesticides depends on their target pests. The main finding from the table is that pesticides are classified based on the target pest they control, with each type of pesticide designed to manage specific organisms such as algae, insects, fungi, plants, and rodents.

Table 2.3 Classification of pesticides according to target pesticides (US EPA, 2018)

Pesticide	Target pest	Action
algicide	algae	To control the algae that feed on plants and animals
avicide	birds	Repel pests including insects (mosquitoes) and birds.
bactericide	bacteria	Kill bacteria that on plants and animals.
fungicide	fungi	Kill fungi including molds and rusts
herbicide	plants	Kills plants and weed that do not wanted in the plantation
insecticide	insects	Kill insects and others
miticide	mites	Kill mites that feed on plants and animals.
molluscicide	snails, slugs	Kill mites that feed on plants and animals.
nematicide	nematodes	Kill worm that feed on plants and animals.
piscicide	fish	Kill fish that do not want
rodenticide	rodents	To control the rodents that feed on plants and animals.

2.5.1 Insecticide

Insecticides used to kill insects. Most of agriculture, medicine, industry, and households use insecticides. The use of insecticides is attributed with boosting 20th-century agricultural productivity by reducing crop losses caused by pests, which in turn has led to higher yields and improved food security (Botitsi et al., 2017). For example, studies have shown that the widespread use of insecticides in rice and maize farming has helped mitigate damage from pests such as the rice stem borer and maize weevil, directly boosting crop yields (Oerke, 2006). Most insecticides may even alter ecosystems because most of them are toxic to humans and others accumulating in the food industry. Contact insecticides kill insects they contact (Ahmad et al., 2024). Plants produce natural insecticides like nicotine, pyrethrum, and neem. Nicotine-based insecticides are banned in the U.S. to prevent food contamination. Inorganic insecticides are made with metals, while organic insecticides are synthetic chemicals that make up most pesticides today (Das, 2012; Parimala & Nuzhat, 2022).

2.5.2 Herbicide

Herbicide, also called as weed killer, is a chemical used to effectively eliminate unwanted plants. Specific herbicides kill specific targets while causing minimal damage to the desired crop. Some of these work by disrupting with weed growth and plant hormones. All plant material they come into contact with is destroyed by non-selective herbicides that clear waste ground, industrial sites, and railway embankments (Zainudin, 2013).

In the tropical regions, chlorophenoxy herbicides 2, 4-D and MCPA control sedges and broadleaf weeds in transplanted wetland rice. Usually, sodium and potassium salts are used, which can be found as a water-soluble powder or liquid.

Propanil was first used as a contact herbicide to kill grassy weeds after they had grown (Shekhawat et al., 2020). After that, over the past 30 years, a lot of research has shown that herbicides like bensulfuron-methyl, pyrazosulfuron-ethyl, bentazon, butachlor, 2, 4-D, MCPA, piperophos + 2, 4-D, propanil, thiobencarb, quinclorac, and fenoxaprop- ethyl can be used on transplanted rice (Paiman et al., 2020).

2.5.3 Fungicide

Fungicides kill or inhibit fungi or fungal spores. Fungi can harm crops, reducing yield, quality, and profit. Contact fungicides are not absorbed into plant tissue and only protect the sprayed area (Caffi & Rossi, 2018). Fungicides keep rice from getting diseases that can damage the crop in terms of quality and quantity. Thind (2017) says that 8.4% of the fungicides market is for rice. Several steps are needed to make and describe a new molecule that can be used as a fungicide. First, the new lead molecule is tested in-vitro to see how well it works against the target pathogen. Then, it is tested in the field to see how well it works against the target disease and to find the best dose/rate for controlling the target disease. Triazole and strobilurin fungicides controlled dirty buds and rice blast in the field (Kumar et al., 2013).

2.5.4 Rodenticide

Rodenticides are used to destroy rodents. Rodents are rats and mice, as well as squirrels, woodchucks, chipmunks, porcupines, nutria, and beavers. They can harm harvests, damage home codes, transmit ailments, and cause environmental destructions. Rodents, humans, dogs, and cats are all warm-blooded animals, meaning our bodies function in similar ways (Isackson & Irizarry, 2020). Rodenticides have the same impact when consumed by any warm-blooded creature like humans, cats and rodents. This is because our bodies work in fundamentally the same ways as mammals (warm blooded creatures). Rodenticides are generally formulated as baits, which are intended to draw in animals, flavoured by fish oil, molasses or peanut spread. Baits are utilized as a part of horticultures that contain ground meat, vegetables, grains, or natural products (Nakayama et al., 2019).

2.6 History of Carbofuran Pesticides

Carbamates are carbamic acid's derivatives (esters), and the pesticide carbofuran is one of those carbamate pesticides. The xylem transports a number of carbamates throughout the body. Pests on shoots and roots can be controlled, even if they are difficult to reach otherwise (Becker et al., 2015). Therefore, soil insecticides and nematicides are common applications for aldicarb, carbofuran, oxamyl etc (Sánchez-Bayo et al., 2013).

2.6.1 General background

Carbofuran (2,3-dihydro-2,2-dimethyl benzofuran-7-yl-N-methylcarbamate) is a broad-spectrum pesticide that functions as a systemic insecticide, acaricide, and nematicide. Its chemical structure is shown in Figure 2.3.

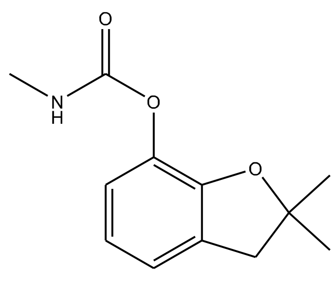

Figure 2.3 Carbofuran chemical structure (USEPA, 2006).

Carbofuran is categorised under the general group of carbamate derivative and pesticides that contain carbofuran known as Furadan, Curaterr, Carbodan, Carbosip, and Chinufur (Figure 2.4) .