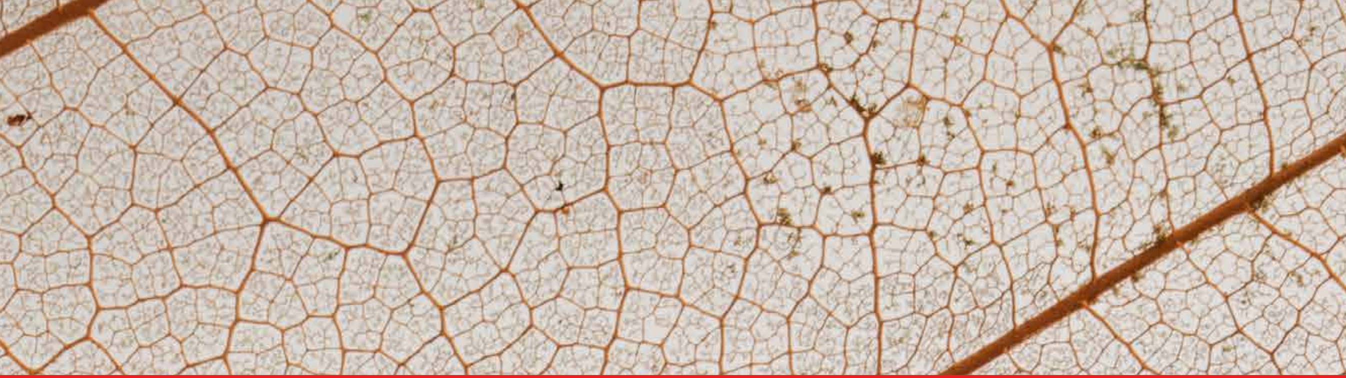

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# Pesticides

## Agronomic Application and Environmental Impact

*Edited by Kassio Ferreira Mendes*

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# Meet the editor

Kassio Ferreira Mendes is a Professor of Biology and Integrated Management of Weeds and a Professor of Biology and Integrated Management of Weeds at the Department of Agronomy, Federal University of Viçosa, Brazil. He graduated from the State University of Mato Grosso, Brazil, in 2011 and received a Master's in Agronomy (Crop Science) from the Federal University of Viçosa in 2013. He obtained a doctorate and post-doctorate degrees in Sciences - Nuclear Energy in Agriculture (Chemistry in Agriculture and Environment) from the Center of Nuclear Energy in Agriculture, Luiz de Queiroz Campus, University of São Paulo, Brazil, in 2017 and 2019, respectively. He completed research fellowships at the Department of Soil, Water, and Climate, College of Food and Agricultural Sciences, University of Minnesota, USA, and the United States Department of Agriculture - Agricultural Research Service (USDA-ARS). Dr. Mendes is a member of the Brazilian Society of Weed Science.

# Contents

# Preface

In this era of rapid agricultural advancement and heightened environmental consciousness, *Pesticides – Agronomic Application and Environmental Impact* emerges as a crucial text for understanding the complex interplay between modern farming practices and ecological wellbeing.

This book aims to bridge the gap between the necessity of pesticide use in modern agriculture and the pressing need to mitigate its environmental consequences. It delves into the scientific intricacies of pesticide application in agriculture, examining how these substances, essential for crop protection, can be managed to minimize their ecological footprint.

As the editor of this volume, I have had the privilege of collaborating with a diverse group of experts, each contributing their profound knowledge and insights into the multifaceted world of pesticides. The chapters within this book are carefully curated to provide a comprehensive understanding, starting from the basic chemistry of pesticides to the advanced techniques in their application and the strategies for mitigating their environmental impact.

This preface serves as a gateway into the rich and informative content that lies ahead. My goal is to present a balanced view, aiding readers in comprehending the critical role of pesticides in modern agriculture while being acutely aware of the responsibility to protect our environment.

It is my hope that this book will not only serve as a valuable resource for professionals in the field but also stimulate further discussion and research among scholars, practitioners, and policymakers. The journey through these pages is an invitation to explore, understand, and contribute to a field that stands at the crossroads of human sustenance and environmental stewardship.

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Chapter 1

# Understanding the Environmental Behavior of Herbicides: A Systematic Review of Practical Insights

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## Abstract

Herbicides play a crucial role in weed control in various agricultural and non-agricultural settings. However, their behavior in the environment is complex and influenced by multiple factors. Understanding their fate and retention, transport, and transformation is essential for effective herbicide management and minimizing their impact on ecosystems. This chapter begins by emphasizing the importance of studying herbicide behavior in real-world conditions, considering physical, chemical, and biological amendments in soil. It highlights how these amendments can directly affect weed control efficacy when residual herbicides are applied in pre-emergence. Detailed knowledge of herbicide behavior in the environment enables the adjustment of application rates based on soil type and climatic conditions, which is a key aspect of precision agriculture. The study of herbicide interactions in the environment has experienced significant growth across various subfields, particularly in the last three decades. It can be considered a multidisciplinary subject that encompasses areas such as agricultural, environmental, and biological sciences, as well as technology, physics, chemistry, and biomedicine. Overall, there are over 35,000 papers on herbicide behavior in the environment, and the trend indicates that the number of publications will continue to grow in the coming years.

**Keywords:** retention, transport, transformation, physical-chemical properties, soil

## 1. Introduction

The behavior of herbicides in the environment, particularly in the soil, depends on the interaction of various processes that determine their ultimate fate [1]. The processes of transport, retention, and transformation of herbicides are often studied separately, but many of them occur simultaneously at different intensities, depending on the characteristics of the application environment and the physicochemical properties of the products. Therefore, understanding soil properties, the involved climatic factors, and the mechanisms of herbicide interaction with the environment are essential for achieving more effective weed control using herbicides in a technically and economically viable manner, and/or for better understanding the ultimate fate (reduced impact) of these products in the environment [1].

Currently, there are a significant number of scientific publications both internationally and in Brazil that addresses the behavior of herbicides in the soil for weed management. However, almost all of these studies focus on a more scientific and theoretical approach, making it difficult for readers such as students, farmers, and professionals in the field to understand and apply the findings in practical situations.

Thus, considering the substantial volume of material available, there is an opportunity to convert this content into a chapter that aims to enhance and contribute to the practical technological knowledge of the reader, while still utilizing a solid theoretical foundation with concepts, examples, and illustrations. Therefore, the purpose of this chapter is to provide a holistic, up-to-date, and practical approach to understanding the behavior of herbicides in the environment, whether in agricultural settings or in interactions with fauna, flora, and humans.

In the following sections, we will discuss the physicochemical properties of herbicides and the processes that govern their behavior and fate in agriculture, including retention, transport, and transformation. In addition to these initial considerations, the interactions between soil-climate factors and herbicides, as well as their effects on the environment, will be discussed in a clear and objective manner.

## 2. Physical- Chemical properties of herbicides

Herbicides are compounds with diverse chemical structures and physical-chemical properties, and they can be grouped into different chemical families. Herbicides within the same chemical family have close similarities in their chemical structures and, therefore, similar physical-chemical properties. The physical-chemical properties of herbicides are one of the main factors that affect their initial distribution and behavior in the soil. Therefore, herbicides belonging to the same chemical class will exhibit similar behavior in the environment.

The main physical-chemical properties and equilibrium parameters that control the initial tendency of herbicides in the soil are the acid-base dissociation constant ($pK_a/pK_b$), water solubility ($S_w$), octanol-water partition coefficient ($K_{ow}$), vapor pressure (VP) or Henry's law constant ($K_H$), sorption coefficient ($K_d$ and $K_{oc}$), degradation half-life time (in the laboratory) and dissipation (in the field) ($t_{1/2}$ or $DT_{50}$), and residual lifetime in plant ($RL_{50}$). In a hypothetical scenario where environmental factors and climatic conditions are fixed, the distribution of herbicides among compartments (air, water, and sediment/soil) will depend on their physical-chemical properties [2, 3].

### 2.1 Acid-base dissociation constant ($pK_a/pK_b$)

Herbicides can be classified as ionizable and non-ionizable (neutral) compounds, having different reactivities and interactions with the soil. Ionization is the process by which an atom or molecule acquires a positive or negative charge, resulting in an atom or molecule with known electrical charge called an ion (anion or cation). Weak acid or base herbicides can be partially (but not completely) ionized in an aqueous solution, depending on the soil/solution pH. Due to partial ionization, there will be variable concentrations of neutral and ionized species in the solution.

The relative strength (degree of ionization) of the weak acid or basic compounds is measured by the ionization equilibrium constant, $pK_a$ or $pK_b$, which is dependent on the soil solution pH. It calculates the relative amounts of each species present in the soil solution. When the soil solution $pH = pK_a/pK_b$, the ionizable compound in question (whether acid or base) will be half (50%) protonated (non-ionized or molecular) and half (50%) deprotonated (ionized).

Thus, there will be equal amounts of ionized and non-ionized forms in the solution. In the soil, ionic herbicides behave differently from non-ionic herbicides. Therefore, it is crucial to know which groups of herbicides are classified as ionizable to have an understanding of their potential behavior once applied to the soil [4]. For example, there are non-ionizable (neutral) herbicides such as diuron, carfentrazone, flumioxazin, S-metolachlor, acetochlor, pyroxasulfone, and clomazone; basic herbicides such as atrazine and hexazinone; and acid herbicides such as metribuzin, 2,4-D, alachlor, ametryn, indaziflam, clethodim, chlorimuron-ethyl, glyphosate, dicamba, diclosulam, imazethapyr, nicosulfuron, sulfentrazone, and glufosinate-ammonium. Diquat is a cation (ion +).

In agronomic soils ($pH > pK_a$), weak acid herbicides are primarily found in an anionic form (negatively charged), while weak base herbicides are mainly found in a neutral form (without charge). Anionic herbicides will be repelled by soil colloids because soils are predominantly negatively charged [4, 5], which increases their leaching potential due to low sorption, consequently reducing weed control efficacy. In contrast, protonated species of basic herbicides will be more sorbed in highly acidic soils ($pH < pK_b$) and will have lower leaching in the soil profile. Therefore, under field conditions, knowing the herbicide ionization (especially acid herbicides applied directly to the soil in pre-emergence) is crucial for agronomic effectiveness in weed control, as liming practices to raise the pH for agricultural cultivation directly interfere with the herbicide's bioavailability in the soil solution [3].

### 2.2 Water solubility ($S_w$)

$S_w$ is a measure of the concentration of an herbicide that can dissolve in water at a specific temperature [3]. $S_w$ is usually measured in mg/L. According to Ney [6], $S_w$ is considered low when the value is less than 10 mg/L, moderate when the value ranges from 10 to 1000 mg/L, and high when the value is greater than 1000 mg/L. $S_w$ is strongly affected by polarity. Polarity refers to the uneven distribution of charge in a molecule. Generally, the affinity of a chemical compound with water increases with increasing polarity. The more hydrophilic (more polar) groups have a higher affinity with water (higher $S_w$) [7].

$S_w$ is one of the most important properties that affect the bioavailability for weed control and the environmental fate of herbicides, mainly through leaching transport. The higher the $S_w$ of the herbicide, the higher its bioavailability in the soil solution, meaning lower sorption to soil colloids. On the other hand, under this condition, the herbicide can be more easily leached and contaminate groundwater. Therefore, it is important to mention that leaching is necessary only at the soil surface (0–20 cm), where the herbicide is absorbed by the weed seed bank. Hexazinone and imazethapyr are herbicides applied directly to the soil and have high $S_w$; however, pendimethalin is highly sorbed to the soil due to its low $S_w$.

According to Carbonari et al. [8], the $S_w$ of a herbicide in water plays an important role in increasing or reducing its ability to reach the soil when applied on mulch cover. Silva and Monquero [9] also highlighted the importance of $S_w$ and the octanol-water partition coefficient ($K_{ow}$) as the most important characteristics to define the behavior of a herbicide applied on mulch cover, where high $K_{ow}$ values and low $S_w$ values represent less herbicide transport to the soil, affecting the efficacy of herbicides in weed control in sugarcane crops. Knowledge of $S_w$ is fundamental in recommending weed management in sugarcane (which has many registered herbicides), especially during dry and wet periods in ratoon and plant sugarcane.

### 2.3 Octanol-water partition coefficient ($K_{ow}$)

$K_{ow}$ is a dimensionless value defined as the ratio between the concentration of a herbicide in the saturated n-octanol phase and its concentration in water at equilibrium at a temperature of 25°C [10]. This coefficient is typically expressed in logarithmic form, as log $K_{ow}$. This property is applied evaluative to predict the distribution between environmental compartments in equations for estimating bioaccumulation in animals and plants and predicting the toxic effects of a substance [11, 12]. Log $K_{ow}$ represents a measure of the tendency of a chemical to shift from the aqueous phase to lipids, for example: (1) Positive values of log $K_{ow}$ indicate the hydrophobic property of compounds; (2) higher values indicate greater hydrophobicity of compounds; and (3) when the log $K_{ow}$ value is greater than 3, it indicates that the chemical is considered highly hydrophobic [13, 14]. The environmental significance of this parameter is that it can be used to predict the accumulation, mobility, and persistence of herbicides in the soil. Herbicides with high $K_{ow}$ values prefer organic (nonpolar) environments over aqueous environments (biota, soil, sediments, etc.).

The log $K_{ow}$ values of pendimethalin and glyphosate are 5.4 and – 3.02, respectively, indicating that pendimethalin may exhibit a strong tendency for sorption in the dead cover and bioaccumulation in the environment, while glyphosate is highly hydrophilic and does not bioaccumulate [3]. Herbicides with log $K_{ow}$ values below 2.7 (e.g., paraquat, mesotrione, and imazapyr), between 2.7 and 3 (e.g., atrazine), and above 3 (e.g., alachlor) have low, moderate, and high bioaccumulation, respectively.

Regarding the behavior of herbicides in plants, the interaction between $pK_a$/$pK_b$ and log $K_{ow}$ governs the distribution of products applied in post-emergence. For example, when a herbicide has intermediate membrane permeability, it will have some mobility in the phloem. Membrane permeability is estimated by log $K_{ow}$ values. Herbicides with log $K_{ow}$ values between −1 and 1 are expected to have phloem mobility after foliar applications. However, there are other acids, such as aryloxyphenoxypropionates (FOPs) (inhibitors of acetyl-coenzyme-A carboxylase—ACCase), that have log $K_{ow}$ values between 3 and 4.5, which are more lipophilic and therefore have limited mobility in the phloem. Generally, compounds with high polarity (log $K_{ow} < 0$) and strong ionization ($pK_a < 2$), such as glyphosate, are mobile through the phloem, although significant amounts move through the xylem. Translocation solely *via* the xylem occurs for herbicides that inhibit carotenoids and Photosystem II (PSII). When herbicides have high log $K_{ow}$ values, they are considered contact (non-systemic) herbicides, such as diquat (inhibitor of Photosystem I—PSI) and protoporphyrinogen oxidase (PPO) enzyme inhibitors [15].

### 2.4 Vapor pressure (VP)

The VP of a herbicide is a measure of its tendency to transform into vapor (gaseous state) and evaporate from its solid or liquid state. It indicates the volatility of the chemicals and their affinity with the air compartment [16]. Typically, the VP of the pure chemical is given in millimeters of mercury (mmHg) at 25°C. To convert to millipascal (mPa), the given value must be divided by $7.52\times10^{-6}$. VP is the primary parameter governing the behavior of herbicide vapor and its potential volatility, without considering the influence of environmental conditions. The herbicide active ingredients, formulation type, ambient temperature, and humidity can influence volatility [17].

The VP of different herbicide families, and even within compounds of the same family, can differ by orders of magnitude [18]. Herbicides can be divided into three categories of potential volatility based on VP values (mPa at 25°C): low volatility with VP below 5.0, moderately volatile with VP from 5.0 to 10, and highly volatile with VP above 10 [19].

Auxin herbicides mimic (such as 2,4-D and dicamba) and carotenoid inhibitors (such as clomazone) are commonly volatilized in the field as they have high VP [3]. Techniques such as nanoparticle encapsulation, formulation types, and soil incorporation of herbicides contribute to minimizing losses through volatilization. Therefore, it is important to mention that herbicide volatilization can also be measured by the Henry's law constant ($K_H$).

### 2.5 Sorption coefficient ($K_d$)

$K_d$ represents the ratio between the concentration of sorbed herbicide ($C_s$) in the soil and its concentration in the equilibrium solution ($C_e$) [20]. This concept, according to Weber et al. [21], involves measuring the amount of herbicide sorbed from a specific concentration per unit mass of soil. The higher the $K_d$ of a herbicide, the greater its sorption capacity in the soil. In light of the above, it is important to highlight that $K_d$ values are usually determined at herbicide concentrations that would occur when compounds are applied at recommended field rates followed by sufficient precipitation to bring the soil to field capacity [22]. As a result, herbicide leaching through the soil profile is inversely correlated with $K_d$ [3]. For example, the $K_d$ values of pendimethalin, atrazine, and metribuzin are 228 (non-mobile), 3.2 (moderately mobile), and 0.874 L $Kg^{-1}$ (mobile) [19]. These $K_d$ values are used in mathematical models (e.g., Linear, Freundlich, and Langmuir) to predict the mobility of herbicides in soils. Typically, sorption coefficients are normalized by the organic carbon content in the soil ($K_{oc}$). In practical terms, it is important to understand the percentage of herbicide sorbed, which, by subtracting the initially applied amount, determines the bioavailable quantity of the product in the soil solution, affecting weed control.

### 2.6 Degradation/dissipation half-life time ($DT_{50}$)

Overall, $DT_{50}$ (Dissipation or Degradation Time) or $t_{1/2}$ can be understood as the time required for the concentration of the product to decrease to half of its initial value [20, 23], and it can be considered a physicochemical property but is directly influenced by biological factors in the soil. With the same meaning but under controlled laboratory conditions, $DT_{50} = \ln(2)/k$ (the constant rate per day, k) indicates the time required to reduce the concentration by 50% from any concentration point during the incubation period [23]. Consequently, $DT_{90} = \ln(10)/k$ indicates the time required to reduce the initial concentration by 90%, nearly complete degradation of the herbicide. Thus, it is important to express the rate of decline as a first-order degradation ($C_t = C_0{*}e^{-kt}$), where $C_t$, $C_0$, and $t$ represent the total concentration, initial concentration, and time, respectively. The degradation process mainly occurs through microorganisms, although chemical degradation and photodegradation also influence the process. Furthermore, the dissipation half-life time ($DT_{50}$, described in the same way as degradation) can be measured under field conditions, evaluating not only degradation but also off-target transport [3]. The $DT_{50}$ of sulfentrazone is 541 days, which is considered highly persistent, the $DT_{50}$ of diclosulam is 49 days, considered moderately persistent, and the DT50 of glyphosate is 15 days (non-persistent) [19].

The values of herbicide DT50 are analyzed using analytical techniques with the use of solvents for extraction, which extract bound residues and the sorbed portion (non-bioavailable in the soil solution for plant absorption). Therefore, $DT_{50}$ sometimes does not directly reflect the residual effect of herbicides in the soil. For example, diquat has a $DT_{50}$ of 5500 days in the field, classified as highly persistent [19], yet there are no reports of carryover in crops sown a few days after the application of this herbicide. On the other hand, tembotrione has a $DT_{50}$ ranging from 4.2 to 87.2 days, classified as non-persistent [19]; however, there are reports of carryover in potato crops planted 5 months after application in Rio Paranaíba, MG, Brazil [24]. The observed symptoms were tuber cracking at harvest time, indicating that the quantity required to cause negative effects on succeeding crops is extremely low.

### 2.7 Residual lifetime ($RL_{50}$)

The bioavailability of the herbicide in the soil is determined by the residual lifetime of the herbicide, which is defined as $RL_{50}$. $RL_{50}$ is defined as the residue level at which the active substance of the herbicide disappears in the plant [25]. $RL_{50}$ is estimated through bioassays, where injuries caused by the herbicide are observed in sensitive plants, indicating the herbicide's activity. Therefore, $RL_{50}$ of herbicides is different from $DT_{50}$ (often confused by researchers), and in most cases, $RL_{50} < DT_{50}$. $RL_{50}$ is used to indicate that 50% of the molecule has dissipated while the other half still has an effect on the plant. $RL_{50}$ depends on environmental factors, cropping system, herbicide properties, and the sensitivity of the species used as a bioindicator plant [25]. For example, $RL_{50}$ values for oxyfluorfen ranged from 51 to 59 days, and for linuron from 75 to 149 days in three tropical soils, using sorghum and cucumber as bioindicator species, respectively [26].

## 3. Herbicide behavior in the environment

The use of herbicides is essential for the current agricultural model, and without the use of this practice, ensuring food security in worldwide would likely be unfeasible. However, these products can have various environmental and social impacts, making it crucial that they are adequately used to preserve the natural resources that sustain the production.

Studies on herbicide behavior in the environment provide a better understanding of their dynamics and fate, primarily concerning retention processes (sorption, desorption, and precipitation; formation of bound residue and remobilization), transport processes (plant absorption, translocation, and metabolism; drift, volatilization, runoff, runin, and leaching), and transformation processes (chemical degradation, biodegradation, photodegradation, and mineralization), which typically interact with each other.

The fate and behavior of a herbicide in the environment are mainly related to the physical-chemical properties of the molecule, the matrix, and the environmental conditions. It is also important to note that when a pre-emergence applied herbicide remains active in the soil solution for weed control, it exhibits a positive residual effect. However, when it affects the crop in rotation/succession, it is known as carryover, a negative residual effect, as previously described.

### 3.1 Retention process

Typically, herbicides used in crops end up in the soil as their fate. Therefore, retention can be understood as a general process of sorption of herbicides in the soil, preventing the molecules from moving both inward and outward from the soil matrix. In practice, retention is one of the key factors that determine the efficacy of herbicides when applied for weed control, as it allows the prediction of the movement and degradation rate of the molecules applied to the soil.

Thus, it can be said that when a molecule is not retained in the soil colloids, it is exposed to other processes. Retention studies may be associated with the search for new methods of herbicide use, aiming for cost-effectiveness and reduced environmental risk. One possibility is the use of differentiated herbicide doses based on soil properties, similar to the usual practice of precision agriculture with fertilizer quantities.

Retention is the phenomenon by which a molecule is captured on the surfaces of mineral and organic colloids in soils. The term "sorption" is widely used because this capture occurs through adsorption, absorption, precipitation, or hydrophobic partitioning, and often the mechanism is not recognized [27]. A portion of the sorbed solute can return to the soil solution, a process known as desorption [28].

The main soil attributes that influence the sorption and desorption processes of herbicides are soil clay and organic matter (OM) content, cation exchange capacity (CEC), and pH. The physicochemical properties of the molecule (molecular structure, size, shape, solubility, speciation—presence of anionic form at normal pH, hydrophobicity, among others), as well as edaphoclimatic and management characteristics of the area, control this process [28].

One way to observe the sorptive behavior of herbicides is through the construction of sorption-desorption isotherms and the study of the kinetics of these processes in the soil. An isotherm is a curve that describes the retention of a solute in a sorbent at increasing concentrations [29]. In other words, it is the relationship between the concentration of the solute retained on $C_s$ and the concentration of the solute in the $C_e$. To construct an isotherm, the system must be in thermodynamic equilibrium, so the kinetics of the reactions should always be quantified, and all physicochemical parameters (e.g., temperature) must be constant and specified. The estimation of herbicide sorption is represented by the partition or sorption coefficient ($K_d$), which can be estimated by the following relationship: $K_d = C_s/C_e$. Therefore, it is important to highlight that the value of $K_d$ is appropriate to describe the sorption of a herbicide when linearity exists between $C_s$ and $C_e$ in an isotherm. Currently, the mobility potential of a herbicide is given by the logarithm of the sorption coefficient normalized to the organic carbon (OC) content of the soil ($K_{oc} = K_d/OC*100$). When $K_{oc}$ is: $<$ 1.0 (highly mobile), between 1 and 2 (mobile); 2 and 3 (moderately mobile); 3 and 4 (slightly mobile); 4 and 5 (poorly mobile); and $>$ 5.0 L $Kg^{-1}$ (immobile) [30].

**Figure 1A** illustrates the number of publications on herbicide retention in the soil from 1950 to 2023, with a current total of approximately 9341 published papers in this field. A consistent upward trend is observed from 1950 until the present day. However, up until 1990, the overall number of publications remained relatively low, with only 380 papers published. Subsequently, starting in 1995, there was a substantial increase in the quantity of publications, with rates surpassing 1000 papers every 5 years between 2005 and 2015. Furthermore, from 2016 to 2020, this rate further increased to 2146 publications. In the most recent three-year period (2021 to 2023), a total of 1676 papers were published, indicating an even more pronounced growth trend in the field of herbicide retention.

**Figure 1B** illustrates the distribution of herbicide retention papers published until 2023 across different subject areas. The top 10 areas with the highest number of publications were pre-filtered and analyzed. It was observed that broader subject areas such as Science & Technology and Life Sciences & Biomedicine had the highest number of indexed studies on herbicide retention, with 7909 and 5838 publications, respectively. Agricultural sciences also played a significant role, with Herbicides accounting for 4636 publications and Agriculture with 1976. The fields of chemistry and physics were represented by Physical Sciences (3487), Adsorption (3382), and Chemistry (3031). Environmental sciences were also prominent, as evidenced by Environmental Sciences (2965) and Environmental Sciences & Ecology (2910). It is important to note that the subject area of Pollution had over 1000 publications, indicating alternative approaches to retention studies, although not depicted in **Figure 1B**.

In herbicide retention studies, the term “adsorption” was the most commonly mentioned, appearing 6146-fold in abstracts and keywords. Adsorption is a term frequently used to describe the dynamics of both sorption and desorption processes of herbicides, although it is sometimes incorrectly used to solely refer to the sorption process. The terms “sorption” and “desorption” were mentioned 3577- and 2266-fold, respectively. The term “sorption-desorption,” which typically encompasses studies evaluating both behaviors, was less frequently used. The broader term “retention,” which encompasses these studies more comprehensively, appeared less frequently, with 2171 occurrences.

Some practical studies on herbicide retention in the soil are described below. Using information on $C_e$ and bioavailability (%) after desorption, Lima et al. [32] generated dose maps for indaziflam and metribuzin for the entire study area (17.51 ha) focused on precision agriculture. Indaziflam doses ranged from 4.17 to 6.97 g a.i. $ha^{-1}$ for *Amaranthus hybridus*, corresponding to a variation of 67.14% between the lowest and highest applied doses. *Eleusine indica* required indaziflam doses ranging from 4.24 to 7.08 g a.i. $ha^{-1}$, representing a variation of

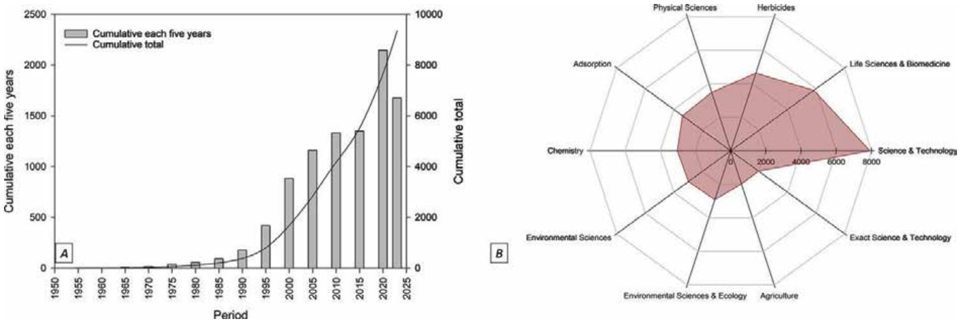

**Figure 1.**

*Papers on herbicide retention in the soil published each 5 years (gray columns) and total accumulated (black line) between 1950 and 2023 (A) and indexed in different subject areas (B). Source: Data were obtained from CAPES [31].*

66.98% between the lowest and highest applied doses. The authors also found that metribuzin doses ranging from 57.1 to 66.6 g a.i. $ha^{-1}$ were sufficient for the control of *A. hybridus*, corresponding to a variation of 16.63% between the lowest and highest applied doses. The species *E. indica* required metribuzin doses ranging from 94.3 to 110.1 g a.i. $ha^{-1}$, representing a variation of 16.75% between the lowest and highest applied doses.

The recommendations of different indaziflam doses for control *A. hybridus and E. indica* resulted in reductions of 17.56 and 15.70%, respectively, in the total amount of herbicide that would be applied compared to the highest recommended [32]. The reduction in metribuzin doses was equivalent to 9.8 and 9.9% for *A. hybridus* and *E. indica*, respectively. The greater variation in indaziflam doses compared to metribuzin is due to the higher sorption capacity exhibited by indaziflam compared to metribuzin. Thus, the spatial distribution of the soil's physical-chemical properties had a greater influence on the bioavailability after desorption of indaziflam and, consequently, on the recommended doses for weed control.

In a study on the spatial distribution of sorption-desorption of hexazinone and tebuthiuron, Mendes et al. [33] developed maps of herbicide bioavailability in the soil solution. However, there are no weed control efficiency tests conducted. Despite this, the authors emphasized that the application recommendation of pre-emergence herbicides, such as tebuthiuron and hexazinone, considering the soil physical-chemical properties, is an alternative to increase weed control efficiency and reduce the risk of environmental contamination.

Similarly, in a study that considered the soil sorption capacity for recommending cyanazine doses for weed control, Mohammadzamani et al. [34] found that the same control efficiency was achieved with a 13% reduction in the total applied dose. However, the authors did not differentiate the weed community by species. Thus, the aspects discussed here regarding the bioavailability after herbicide desorption and weed control efficiency studies provide a broader understanding of the variables involved in accurate dose recommendations in precision weed management [32].

On the other hand, any addition of organic compounds to the soil can directly affect the behavior of residual herbicides and consequently the weed control efficacy [35, 36]. For instance, the application of biochar to the soil is carried out for carbon sequestration, waste management, increased CEC, soil pH elevation, water retention, and nutrient source, which typically benefits agricultural production [37]. However, soil amended with biochar has a high sorption capacity for herbicides, meaning it decreases the bioavailability of the product in the soil solution [38]. The negative effects of biochars on weed control are more noticeable when it comes to pre-emergence herbicides [35].

In a study conducted by Mielke et al. [39], application rates <1% (w/w) of sugarcane straw biochar sorbed ~23% and desorbed ~15% of metribuzin, similar to unamended soil, for all pyrolysis temperatures. However, soil amended with 10% pyrolyzed biochar at temperatures of 350, 550, and 750°C sorbed 63.8, 75.5, and 89.4%, and desorbed 8.3, 5.8, and 3.7% of metribuzin, respectively. Thus, the authors reported that high pyrolysis temperatures and biochar application rates showed the capacity to immobilize metribuzin and improve soil fertility, which can influence weed control efficacy.

In American soils, Mendes et al. [40] found that amendment with biochar from soybean stover, sugarcane bagasse, and wood chips increased alachlor sorption between 4- and 33-fold compared to unamended soil. Biochar from soybean stover, sugarcane bagasse, and woodchips increased indaziflam sorption in the soil by 7, 55, and 69%, respectively [41]. Based on these results, it is expected that biochar additions will affect the bioavailability of herbicides for transport and degradation in the soil.

When evaluating the addition of bone char in a tropical soil, Mendes et al. [42] found that only 1.4 t $ha^{-1}$ of the bone char decreased the control of eight weed species by 50%. Wood chips biochar applied at 0.5 kg $m^{-2}$ decreased weed control by 75 and 60% with atrazine and pendimethalin, respectively [43]. The addition of wheat straw biochar decreased the control of *Lolium rigidum* with trifluralin and atrazine, requiring an increase in herbicide doses by 3–4-fold [44]. A similar phenomenon was observed for the control of *Echinochloa crus-galli* with diuron, requiring twice the dose to be applied [45].

The application of diuron in agricultural areas with anthropogenic soils in the Amazon region (*Terra Preta de Índio*) may result in inefficient weed control, as these soils can decrease the bioavailability of the herbicide in the soil solution due to high levels of OC, which confer high sorption and low desorption of the herbicide, as well as faster degradation compared to sandy soil [46].

### 3.2 Transport process

The transport of herbicides in the soil has a significant influence on their performance in the field and their potential for contaminating water resources. Therefore, in addition to agronomic efficiency aspects, field studies aiming to understand the movement of herbicides in the soil are essential to predict the contamination potential of these molecules. Upon reaching the soil, the main pathways for herbicide transport are runoff/runin, volatilization, and leaching.

Papers on the transport of herbicides in the environment have seen a significant amount of research, with approximately 10,200 publications identified between 1950 and 2023 (**Figure 2A**). Prior to 1995, the frequency of publications was relatively low. However, in the 2000, there was a notable increase, surpassing 1000 publications every 5 years. By 2010, this rate had already increased to 1500 publications, and by 2020, it approached 2000 publications. From 2021 to 2023, an additional 1223 publications were recorded, demonstrating the sustained interest of researchers in investigating the transport of herbicides in the environment.

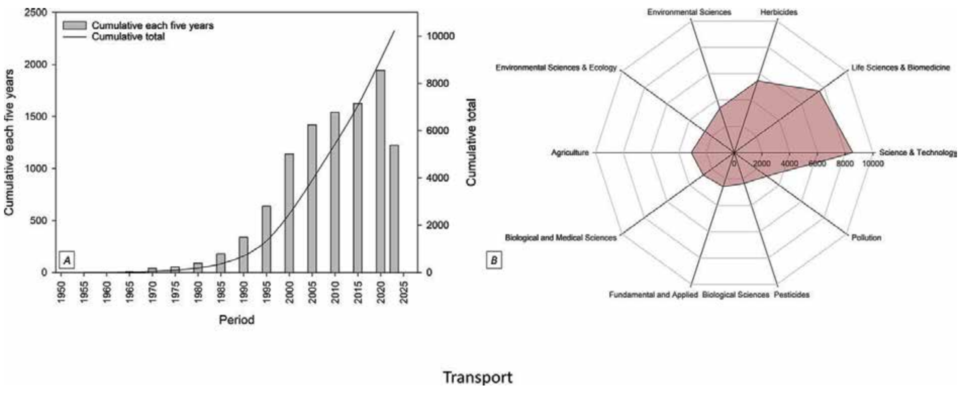

**Figure 2.**
*Papers on the transport of herbicides in environment published each 5 years (gray columns) and total accumulated (black line) between 1950 and 2023 (A) and indexed in different subject areas (B). Source: Data were obtained from CAPES [31].*

Studies on the transport of herbicides in the environment encompass a wide range of subject areas, including technology, agricultural, and environmental sciences, as well as environmental, biological, and pollutants sciences (**Figure 2B**). The diverse approaches taken by researchers contribute to the distribution across these disciplines. For instance, investigations focusing on the movement of herbicides within the 10–20 cm soil layers for weed control purposes would likely fall under the domain of agricultural sciences. Conversely, studies assessing the risk of leaching and groundwater contamination by the same herbicide would be categorized under environmental sciences or pollutants.

Similar to studies on herbicide retention, the subject areas of Science & Technology and Life Sciences & Biomedicine show the highest number of publications, with 8587 and 7586, respectively (**Figure 2B**). Including these broader subject areas likely serves as a strategy to broaden the readership and impact of the publications. The subject areas of Herbicides, Agriculture, and Pesticides are also prevalent, with 5456, 3094, and 2335 papers, respectively. Furthermore, Environmental Sciences and Environmental Sciences & Ecology are represented with 3384 and 3371 papers, respectively.

When examining the distribution of studies on herbicide transport in the environment, it is evident that the term “environmental transport” is the most frequently encountered in abstracts and keywords, appearing 5708-fold. This is understandable as it is a broad term that enhances the visibility of the paper, although it does not precisely indicate the specific evaluation conducted in the study. Other terms such as “leaching” and “runoff” are also common, occurring 2385- and 1724-fold, respectively, while “drift” and “volatilization” are mentioned 1209- and 553-fold, respectively. This indicates that studies focusing on herbicide interactions with the soil are more prevalent than those examining interactions with the atmosphere. This difference can be attributed to the complexity and multitude of factors involved in quantifying drift and volatilization compared to leaching and runoff assessments.

### *3.2.1 Runoff/Runin*

The movement of herbicides on the soil surface, from treated areas to untreated areas, after heavy rainfall is referred to as runoff or runin when it occurs subsurface (more challenging to measure). The removed herbicide can be present in the soil solution or sorbed to soil particles. Herbicide runoff is governed by a complex interaction between herbicide properties, soil properties, climatic factors, and specific environmental conditions at the site. The main soil and site properties that affect herbicide concentration in water runoff are as follows: slope, soil texture, soil structural stability, soil moisture content, surface vegetation cover, irrigation, precipitation characteristics, topography, hydrology, and geological characteristics. Therefore, soil management practices, as well as the amount of crop residues, also influence water, soil, and herbicide loss.

An important aspect in reducing herbicide losses *via* runoff is the conservation of soil and water resources, which allows for better soil structure and increased permeability. Among the key management practices is the adoption of no-till farming, maintenance of vegetative cover, irrigation control, and the use of buffer zones. For example, Vaz et al. [47] reported that sugarcane straw on the soil surface reduced water runoff, sediment, and diuron losses but had little effect on hexazinone losses. Crop residues cannot prevent the runoff of highly soluble molecules such as hexazinone. The authors stated that maintaining 7 t $ha^{-1}$ of straw on the soil surface was sufficient to mitigate water runoff, sediment, and diuron losses.

Regarding herbicide properties, the type of molecule, sorption capacity, persistence, and water solubility are the most important properties that affect surface runoff. Highly soluble herbicides have a tendency to dissolve in water and are more prone to be carried by runoff. Herbicides with high $K_d$ values, such as glyphosate and its metabolite aminomethylphosphonic acid (AMPA), are transported in runoff by sorption to soil particles [48]. Surface runoff of the herbicide will increase when rainfall or irrigation brings water to the surface more rapidly than it can infiltrate into the soil [49]. However, it is important to check weather conditions before applying herbicides to reduce surface water pollution.

### *3.2.2 Volatilization and drift*

Volatilization is the process by which herbicide molecules transition from a liquid state to vapor form, potentially leading to their loss to the atmosphere. In the atmosphere, herbicides can be transported over long distances, reaching undesired locations. This process can decrease the effective time of the herbicide in the applied area. The main factors that affect volatilization are the properties of the herbicide, soil, and environment. In herbicides belonging to the chemical group of thiocarbamates (such as molinate and thiobencarb) and trifluralin, this process can be so intense that slight incorporation after application reduces vapor losses and increases their efficiency.

However, Carbonari et al. [50] found that the combination of dicamba diglycolamine (DGA) salt with potassium salt of glyphosate and a volatility reducer was the mixture with the lowest volatility and the most suitable combination to recommend to farmers. The volatility reducer was effective in reducing dicamba volatilization alone and DGA in combination with all glyphosate salts (potassium, ammonium, and diammonium salt).

Herbicide drift through sprays can be defined as the movement of the molecule from the target area to non-target areas where the application was not intended. This transport occurs through the movement of spray droplets or vapors, which can cause injury or residue levels in neighboring susceptible plants, reducing productivity and affecting the morphology of these crops [51, 52].

Drift of herbicides, especially synthetic auxins, has gained prominence due to the release of genetically modified maize, soybean, and cotton cultivars resistant to 2,4-D and dicamba, resulting in an increased use of these products. Drift of 2,4-D and dicamba can result in quantitative and qualitative losses in the production of sensitive crops planted in areas adjacent to transgenic events that utilize these herbicides. For example, Brochado et al. [53] reported that “ponkan” tangerine seedlings exhibited injury symptoms after exposure to simulated drift (1/16 of the recommended dose) of dicamba and 2,4-D.

There are two types of drift, namely endodrift and exodrift. Endodrift occurs when there are losses of the product within the cultivation area itself, such as herbicide runoff from leaves to the soil, mainly due to the use of excessively large droplets or excessive spray volume. Exodrift is the displacement of the herbicide molecule outside the treated crop area, either in particle or in vapor form. Vapor drift refers to the movement of the herbicide after it has converted into a gaseous form, while particle drift involves the movement of droplets outside the application area [54, 55].

### *3.2.3 Leaching*

Leaching is described as the downward movement of herbicides within the soil matrix or with soil water, and its intensity is determined by their physicochemical properties as well as soil and climate properties.

In practical terms, the movement of herbicides in the soil has a significant influence on their performance in the field. Limited leaching is desirable as it can make the herbicide more efficient by moving it from the soil surface to where weed seeds are concentrated. However, excessive leaching can contribute to the herbicide being carried into the groundwater, leading to undesirable contamination.

According to Oliveira and Regitano [56], the two most important properties related to the leaching process are $K_d$ and $DT_{50}$. Sorption determines the bioavailability of a herbicide in the soil solution, while the $DT_{50}$ reflects persistence in the soil, and both regulate the leaching potential. In this regard, several models have been developed to classify the leaching potential of herbicides. Regional-scale leaching indices are useful in decision-making processes or remediation of contaminated environments, as mathematical models based on numerical simulations typically require a wide range of parameters that can be challenging to obtain [57].

The Groundwater Ubiquity Score (GUS), proposed by Gustafson [58], is an empirical index that classifies compounds based on their leaching tendency: $GUS = \log DT_{50} (4 - \log K_{oc})$, where GUS represents a dimensionless index, $DT_{50}$ represents the degradation half-life time of herbicide in the soil (days), and $K_{oc}$ represents the sorption coefficient normalized for organic carbon content (L $Kg^{-1}$). Herbicides with $GUS < 1.8$ are considered non-leachable, while values above 2.8 indicate leachability. Those with values between 1.8 and 2.8 are considered intermediate.

The criteria adopted by the California Department of Food and Agriculture (CDFA), proposed by Widerson and Kim [59], establish that herbicides with $K_{oc}$ values less than 512 L $Kg^{-1}$ and $DT_{50}$ greater than 11 days are classified as leachable products. On the other hand, Cohen et al. [60] established that herbicides with $K_{oc}$ values below 300 L $kg^{-1}$ and $DT_{50}$ values above 21 days are considered leachable, whereas those with $K_{oc}$ values above 500 L $Kg^{-1}$ and $DT_{50}$ values below 14 days are classified as non-leachable products.

The criteria of the Environmental Protection Agency (EPA) involve the following values: $S_w$ at 25°C > 30 mg $L^{-1}$; $K_{oc} < 300–500$ L $Kg^{-1}$; $K_H$ constant $<10^{-2}$ Pa $m^3$ $mol^{-1}$; speciation (the presence of anionic form at normal pH, between 5.0 and 8.0); $DT_{50}$ in soil >21 days and in water >175 days; field conditions favoring soil percolation, such as annual rainfall index >250 mm; unconfined aquifer and porous soil. Herbicides that meet these characteristics are considered potentially groundwater polluting agents.

In the calculation of three theoretical criteria (GUS, CDFA, and Cohen) based on the physicochemical properties of herbicides, Inoue et al. [61] assessed the potential leaching risk of herbicides in the state of Paraná, Brazil. The authors found that the classification regarding leaching potential demonstrated that acifluorfen-sodium, alachlor, atrazine, chlorimuron-ethyl, fomesafen, hexazinone, imazamox, imazapyr, imazaquin, imazethapyr, metolachlor, metribuzin, metsulfuron-methyl, nicosulfuron, picloram, sulfentrazone, and tebuthiuron are potentially leachable.

Computational simulation models are valuable tools for evaluating the behavior of herbicides. However, it should be considered that these models simplify the product's behavior in the environment or in specific environmental compartments, and thus, the results should be interpreted considering the simplifications of the model [57].

When selecting a simulation model, several criteria should be considered, according to Cohen et al. [62]. These criteria include validation and calibration with experimental data, suitability of the model for the specific study, availability of the model and user support, availability of input data, and ease of use.

The quantification of leached herbicides in the soil profile is highlighted by analytical techniques such as chromatography and the use of radiolabeled molecules [57]. In terms of qualitative methodologies, there is the bioassay technique, which allows studying the movement of the herbicide through the soil profile using plants sensitive to the tested products [63]. For example, Pereira et al. [64] studied the leaching of clomazone in soil samples collected from different regions of Brazil and used sorghum for herbicide detection. Greater leaching occurred in soils with lower pH and lower OM content. Other studies using clomazone in different soils also reported an increase in herbicide sorption with soil organic matter, reducing leaching [65]. Regarding herbicide mixtures, Refatti et al. [66] determined the leaching potential of herbicides used in the Clearfield® system for irrigated rice and concluded that mixtures of imazethapyr + imazapic, imazapyr + imazapic, and imazethapyr leached into the soil, reaching depths of up to 25 cm in floodplain soil. However, in a study conducted by Mendes et al. [67], the application of mesotrione, alone or in a mixture with S-metolachlor and terbuthylazine, did not influence the leaching of this herbicide.

On the other hand, adjuvants such as mineral oils are widely used in herbicide application to reduce drift and droplet evaporation, as well as to enhance herbicide absorption by the plant. Thus, the addition of mineral oil (1 and 2% v/v) at the time of pre-emergence atrazine application did not interfere with the transport of this herbicide in the arable soil profile *via* leaching; therefore, the adjuvant may have a positive effect only on the herbicide-plant relationship [68].

The presence of mulch on the soil brings about significant changes in weed occurrence and also affects the behavior of herbicides applied in these production systems [8]. The mulch acts as a barrier to the herbicide's arrival in the soil, as it is intercepted and can be sorbed or degraded within the mulch itself. Even after the herbicide reaches the soil, the mulch influences its dynamics by altering water dynamics in the soil, OM content, and microbial activity.

In a study conducted by Araldi et al. [69], two different transposition behaviors of herbicides in sugarcane straw were observed. One behavior was related to metribuzin and hexazinone, which quickly passed through the mulch layer (with ~20 mm of rainfall), while another behavior was observed with atrazine, clomazone, and diuron, which required approximately 60 mm of rainfall to be transported from the plant residue, based on the maximum amount of herbicides removed from the straw.

With the addition of vinasse, Takeshita et al. [70] found that 71% of aminocyclopyrachlor reached the leachate (>30 cm depth), while <50% reached the leachate in the other treatments (filter cake and sugarcane straw). The bioavailability of aminocyclopyrachlor was not reduced with the addition of organic material to the soil, which may favor weed control. However, the presence of vinasse increases the risk of herbicide leaching to deeper soil layers than the weed seed bank.

In the presence of sugarcane straw, Silva et al. [71] reported that aminocyclopyrachlor was distributed in the soil profile, mainly from 0 to 25 cm depth, and that 40% more herbicide was retained in the straw with 20 t $ha^{-1}$. Thus, the authors concluded that the presence of high amounts of straw retains aminocyclopyrachlor but does not prevent it from reaching the soil; the high $S_w$ of the herbicide and intense precipitation (200 mm) over a short period of time (48 h) are factors that contribute to the herbicide passing through this barrier.

The addition of carbonaceous materials to the soil can also affect herbicide leaching. For example, Mendes et al. [72] showed that soils amended with animal bone char, regardless of particle size (0.3–0.6 and 0.15–0.3 mm), increased the sorption of aminocyclopyrachlor and mesotrione, decreased desorption, and consequently decreased the leaching of both herbicides in the soil. For remediation purposes, this is a great strategy to immobilize herbicides in the upper soil layer, but in agronomic terms, it can directly affect the effectiveness of weed seed bank control.

### 3.3 Transformation process

The transformation of herbicides can begin with their dilution in water in the application tank and refers to changes in the chemical nature of the molecule through physical processes (photodegradation), chemical processes (oxidation, reduction, hydrolysis, formation of water-insoluble salts, and chemical complexes), or biological processes (biological degradation or biodegradation). In general, transformation is considered complete (mineralization) when it results in the formation of $CO_2$, $H_2O$, and minerals, and incomplete (metabolism) when it generates metabolites.

The herbicide must be in the soil solution or weakly sorbed to undergo chemical or biological degradation. However, it becomes unavailable for degradation by soil microorganisms or various chemical reactions when strongly sorbed by soil colloids.

The ideal herbicide is one that remains active in the environment for a sufficiently long time to control weeds in the crop where it was used but not so long that it causes injury to susceptible crops in rotation/succession. Therefore, understanding herbicide degradation in the soil is important, especially for herbicides that exhibit greater persistence in the soil and may result in a process called carryover, affecting sensitive crops grown in rotation.

Overall, lower temperatures, lower precipitation, and shorter crop cycles, especially in the case of soybeans with early-maturing cultivars to advance second-crop planting, are factors that increase the possibility of carryover. In the recent study by Inoue et al. [73], the carryover of various herbicides in the soil is addressed, considering various agricultural crops grown in rotation and succession. The main crops sensitive to herbicides include sunflower, soybean, common bean, coffee, sorghum, corn, millet, cotton, canola, among others.

Among the various types of herbicide behavior, transformation has received the most attention in the scientific literature from 1950 to 2023, with over 16,500 publications (**Figure 3A**). Initially, there were only a few studies until the 1970. However, exponential growth has been observed since the 1990, with over 1500 papers every 5 years between 2000 and 2015. The highest peak was reached in 2016–2020, with 3522 publications, and an additional 2515 publications between 2021 and 2023. If this trend continues, the publication rate could surpass 4000 every 5 years by 2025.

Just like studies on retention and transport, the subject areas with the highest number of publications on herbicide transformation in the environment are Science & Technology and Life Science & Biomedicine (**Figure 3B**). Science & Technology has 13,764 papers, while Life Science & Biomedicine has 11,391 publications. Similar patterns can be observed in other subject areas such as Herbicides (7517) and Agriculture (3469), as well as Environmental Sciences (5284) and Environmental Sciences & Ecology (5248), in addition to Physical Sciences (4163) and Chemistry (3556). This wide range of subject areas highlights the various approaches that can be taken in studying herbicide transformation. For instance, examining the residual effects of a specific herbicide falls under agricultural sciences, while selecting

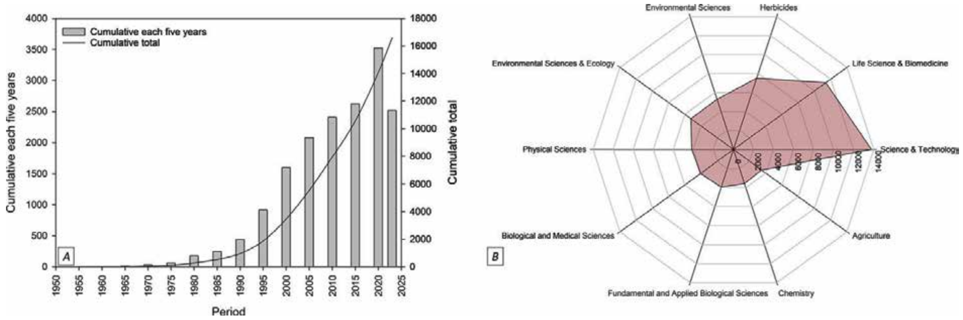

**Figure 3.**
*Papers on the transformation of herbicides in environment published each 5 years (gray bars) and total accumulated (black line) between 1950 and 2023 (A) and indexed in different subject areas (B). Source: Data were obtained from CAPES [31].*

phytoremediation plant species for herbicide-contaminated soils can be categorized under environmental or biological sciences.

Among the main approaches in studies on herbicide transformation in the environment, the term “degradation” is the most commonly mentioned in abstracts and keywords, with 12,685-fold, while “dissipation” is mentioned 2041-fold. Both terms are broad, but “degradation” is more suitable for evaluations conducted under controlled conditions (such as laboratory or greenhouse), while “dissipation” is more appropriate for less controlled conditions (such as field studies). However, it is worth noting that the term “degradation” is used in the majority of studies, including those conducted in field settings. The term “mineralization,” which is more specific in its scope, appears 2395-fold. Regarding specific types of transformations, “chemical transformation” is mentioned 7124-fold, “biodegradation” 4381-fold, and “photodegradation” 1225-fold.

### *3.3.1 Photodegradation*

Photodegradation is the degradation of a molecule by solar radiation, especially ultraviolet (UV) light [74]. This occurs due to the absorption of UV light, which is the most destructive to the herbicide and causes the excitation of its electrons, breaking certain bonds in the molecules. The extent of photodegradation by sunlight is highly dependent on the UV sorption profiles of the herbicide, the environment, and the emission spectrum of sunlight [1], as the energy required to break the chemical bonds in herbicide molecules typically ranges from 250 to 400 nm [74]. Photolysis can be a direct process, in which a substance is transformed through the absorption of light energy, or an indirect process in which other substances absorb energy, transform, and then alter the primary substance [1]. On one hand, photodegradation can be beneficial by reducing excessive persistence of residues in the soil, but it can also be undesirable in terms of potentially reducing weed control efficacy when it occurs shortly after herbicide application. However, fast-acting herbicides that undergo photodegradation in the top 3-mm layer should be incorporated into the soil at the time of application, as photodegradation can diminish weed control effectiveness [52]. For example, trifluralin, atrazine, bentazon, clethodim, and diquat are herbicides that can rapidly undergo photodegradation, while phenylureas may only photodegrade when exposed to long periods of light. Gozzi et al. [75] demonstrated that ethoxysulfuron and chlorimuron-ethyl are also subject to photodegradation. Therefore, surface-applied herbicides are often degraded (lost), particularly if an extended period of drought follows their application.

### *3.3.2 Chemical degradation*

The chemical degradation of herbicides in the soil occurs through chemical reactions and is common for various molecules. Oxidation, reduction, mineralization, hydrolysis, ester formation, photolysis, polymerization, and dehalogenation reactions are common in abiotic degradation. For example, the preferred degradation pathway of 2,4-D occurs through oxidative dealkylation and aromatic ring cleavage [76]. High temperatures and good moisture facilitate these chemical reactions. Additionally, extreme pH values can increase the hydrolysis of certain herbicides [77].

In this regard, the main transformation pathway of herbicides in the application tank is chemical degradation, especially through the process of hydrolysis. This process also initiates a series of degradative activities that occur in the soil and becomes indispensable in transformation processes. Hydrolysis is an important degradation pathway for sulfonylureas and chloroacetamides through acid-catalyzed cleavage and base-catalyzed contraction/rearrangement [78, 79], but not for imidazolinones [80]. A qualitative kinetic assessment was conducted by Lovell et al. [81] to characterize the sorption of isoxaflutole during its rapid hydrolysis into its bioactive metabolite, diketonitrile (DKN). The authors found that the desorption of isoxaflutole coupled with hydrolysis promotes the reactivation of the herbicide's function after rainfall and contributes to the compound's efficacy by replenishing the soil solution with its bioactive metabolite. This herbicide exhibits an unusual behavior compared to others, as it is functionally reactivated by rainfall events, providing weed control. Supporting this statement, Oliveira Jr. et al. [82] found that isoxaflutole exhibited high stability in clayey soil even after three simulated rains of 20 mm, spaced 30 days apart and followed by 120 days of dryness after its application.

### *3.3.3 Biological degradation*

Biological degradation occurs through the action of microorganisms and is considered the main mechanism of herbicide disappearance in the soil. Herbicide degradation in the soil can be accelerated using processes that increase microbial activity, such as adding OM and fertilizers, managing soil moisture content, pH, and temperature, deep plowing, and utilizing adapted microorganisms (bioremediation). In this regard, understanding the influence of OM on various processes related to herbicide behavior in the soil allows for the adoption of more appropriate management practices regarding weed control and remediation of contaminated areas [83].

For example, the application of biochar in the soil is strongly correlated with herbicide degradation processes [84]. The authors stated that if the goal is to apply the herbicide in pre-emergence after adding biochar to the soil, caution should be taken as biochar can either decrease or increase the persistence of the chemical, affecting weed control efficacy over time. On the other hand, if the objective is herbicide remediation in contaminated soils, the interference of biochar in the herbicide's bioavailability in the soil solution can increase the microbial diversity in the soil, which are the agents responsible for herbicide degradation.

When herbicides are bioavailable, they are subject to degradation by microbial or enzymatic action. For degradation in the soil, herbicides involve algae and actinomycetes, but bacteria and fungi are the most important. Biodegradation involves the use of herbicides as a source of N, C, and S. Herbicide degradation by biotic reactions is generally followed by oxidative processes such as beta-oxidation, C cleavage, C hydroxylation, N oxidation, N demethylation, C cleavage, C reduction, N reduction, hydrolysis, and mineralization. Herbicides, in most cases, lose their herbicidal activity after degradation. Only a few metabolites retain herbicidal activity (e.g., isoxaflutole).

Subsequent applications of the same herbicide, coupled with favorable environmental conditions for microbial development, can result in rapid degradation, leading to reduced product efficacy. For example, the dissipation of diuron was favored in orchard areas where this herbicide was applied repeatedly [85]. This fact was confirmed by the herbicide dissipation in areas with a history of application (12 years), and the authors found a $DT_{50}$ of 37 days. However, when comparing the results with those obtained from an area where the herbicide was applied for the first time, they observed a $DT_{50}$ of 81 days. The authors attributed this lower $DT_{50}$ of diuron to soil microorganism adaptation, thus favoring its biodegradation and consequently reducing the residual effect on weed control.

Soil microbiota can utilize herbicides in two ways: as a food (substrate) for their growth and, on the other hand, herbicides can also influence the microorganisms responsible for degradation [86]. Microorganisms exhibit five different strategies for herbicide metabolism, which are catabolism, cometabolism, polymerization or conjugation, accumulation, and side effects of microbial activity, as described below [86].

#### *3.3.3.1 Catabolism*

In catabolism, the herbicide serves as a source of energy and nutrients for the growth and development of degrading microorganisms. This process generally leads to complete degradation of the molecule (mineralization). For example, an increase in soil microbial activity with the application of glyphosate has been reported in the literature. It is known that many microorganisms use glyphosate as a source of P in its absence in the environment [87, 88]. However, in soils with oxidic mineralogy, Prata et al. [89] observed increased sorption with decreasing doses of P added to the soil. P competes with glyphosate for sorption sites, and therefore, nutrient deficiency enhances the sorption of the herbicide and consequently increases its degradation.

In a study conducted by Souza et al. [88] on the biodegradation of imazapyr in two soils with different textures and subjected to different herbicide doses, increased microbial respiration was observed in the presence of the herbicide, and they stated that the microbiota was able to utilize imazapyr as a source of C for its growth.

Atrazine can be used as a source of N by soil microbiota, and therefore, its degradation may be favored under nutrient-restricted conditions [90]. The same authors observed a reduction in atrazine degradation when mineral N was added to the soil.

#### *3.3.3.2 Cometabolism*

Cometabolism occurs when the herbicide is transformed through metabolic reactions but does not serve as a source of energy for the microorganism. Usually, complete transformation of the molecule does not occur, thus requiring a secondary biodegradable substrate as a source of C and energy [91]. The addition of OM to the soil can demonstrate the cometabolic transformation of herbicides in the soil. The fact that this addition increases microbial activity or biomass suggests that the transformation of many herbicides, such as diuron [92] and ametryn [93], occurred through cometabolic processes.

### *3.3.3.3 Polymerization or conjugation*

Polymerization or conjugation is the process in which the original herbicide molecule or its metabolites combine with natural soil compounds, such as amino acids or carbohydrates, or with another herbicide molecule. The formation of the conjugate typically makes the molecule more polar and thus more hydrolysable. The formation of the metabolite dichloroaniline, characteristic of many urea-derived herbicides such as diuron, isoproturon, monuron, among others, can be considered a result of the polymerization of simpler metabolites; that is, two diuron molecules must be transformed to form a dichloroaniline molecule [94, 95].

### *3.3.3.4 Accumulation*

Accumulation occurs when a herbicide molecule is incorporated into the microorganism without being transformed. This accumulation can occur through active or passive processes and raises significant concerns, as this microbial interference only represents the temporary removal of the molecule [95]. Percich and Lockwood [96] reported the accumulation of atrazine in actinomycetes.

### *3.3.3.5 Side effects*

The side effects of microbial activity occur when the herbicide is transformed as a result of changes in pH, redox potential, among others, promoted by microbial activity. pH elevation, for example, can contribute to the hydroxylation of many molecules, making them more polar and thus susceptible to degradation [92].

In summary, according to Lavorenti et al. [95], biodegradation occurs due to the production of enzymes by herbicide-degrading microorganisms, which, when in contact with these molecules, inside or outside the microorganism cells, participate in a series of reactions such as oxidation, reduction, hydrolysis, dealkylation, decarboxylation, hydroxylation, methylation, dealkoxylation, among others.

Nakagawa and Andréa [97] observed that the mineralization of atrazine (about 15% was mineralized) only occurred under natural conditions (non-sterile soil), indicating that the action of microorganisms was crucial in breaking down the triazine ring of the molecule. In practice, the preferred degradation pathway of the herbicide is important because it indicates how agricultural practices will affect its degradation and persistence in the environment. When degradation occurs through catabolism, the deficiency of the element that the herbicide serves as a source can favor this process.

Lastly, it is important to highlight that bound residues of herbicides in the soil can return to the soil solution (remobilization) and become bioavailable again for plants and be mineralized by microorganisms, which can negatively affect subsequent crops or non-target organisms. Supporting this statement, Viti et al. [98] found that diuron, hexazinone, and metribuzin were remobilized from the soil with the addition of vinasse, filter cake, or sugarcane straw, due to the reactivation of soil microbial activity.

The degradation of herbicides is an important mechanism that tends to control the persistence, activity, and transport of the herbicide in the soil profile [86]. The rate of herbicide degradation in the soil occurs through a combination of processes (photolysis, chemical, and biological) and is dependent on the molecule's structure, influenced by soil and climate factors, which vary from location to location and from year to year. Therefore, degradation is dependent on various environmental factors that can affect both the population density of microorganisms and their degradation potential.

## 4. Conclusions

The study of herbicide interactions in the environment has experienced significant growth across various subfields, particularly in the last three decades. It can be considered a multidisciplinary subject that encompasses areas such as agricultural, environmental, and biological sciences, as well as technology, physics, chemistry, and biomedicine. Overall, there are over 35,000 papers on herbicide behavior in the environment, and the trend indicates that the number of publications will continue to grow in the coming years.

Under field conditions, any amendment (physical, chemical, and/or biological) in the soil can directly affect weed control with the use of residual herbicides (applied pre-emergence). Therefore, detailed knowledge regarding the herbicide's behavior in the environment allows for adjusting the product doses according to soil type and climatic conditions, which is an important aspect of precision agriculture. Additionally, it enables understanding the risks of carryover and drift caused by herbicides in crops, adjusting soil management to mitigate herbicide transport through runoff/runin, implementing remediation techniques for contaminated soils and the use of environmental indicators, employing simulation models to predict herbicide behavior and fate, and conducting ecological and environmental risk analysis for regulatory purposes.

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### Chapter 2

# Chromatic Validation of Herbicides Used in Vegetable Production

*Timothy L. Grey and Kayla M. Eason*

## Abstract

Herbicides are necessary for successful vegetable production in the Southeastern United States. Along with bare-ground production, low density polyethylene (LDPE) mulches are often utilized to produce multiple crops (2–4) by rotation over the course of a 12-to-24-month period. These include fresh market tomato, pepper, cucurbits, eggplant, and cabbage. For LDPE mulch vegetable production, between each crop growers must apply contact and residual herbicides to mitigate weeds. However, these herbicides can remain on the mulch and injury transplants. Herbicides are often soil applied for bare soil production as well as under the LDPE mulch. Herbicide carry-over in soil using these vegetable production methods can also result in management issues. Proper quantification analyzing the dissipation is critical in the decision-making process for growers to prevent unnecessary crop losses. A series of experiments have been conducted to quantify the dissipation of the herbicides flumioxazin, fomesafen, ammonium-glufosinate, glyphosate, halosulfuron-methyl, paraquat, S-metolachlor, and sulfentrazone over time using UPLC/MS and bioassay methods. These methods are presented.

**Keywords:** herbicide, chromatography, mass spectrometry, vegetable, polyethylene mulch, dissipation, adsorption, soil

## 1. Introduction

Weed control in fresh market production of vegetable crops has significantly changed over the past 25 years due to the elimination of the preplant soil fumigant methyl bromide (MBr). Purple (*Cyperus rotundus*) and yellow nutsedge (*C. esculentus*) are the some of the most common and troublesome weeds in fresh market vegetable production throughout the southeastern US (**Table 1**) [1, 2]. The sharp tips of the emerging nutsedge shoots readily pierce low-density polyethylene (LDPE) mulch (**Figure 1**) and lead to intensive nutsedge infestations [3].

Along with nutsedges, many other winter and summer weed species proliferate rapidly as vegetables are supplemented with water and nutrients via drip irrigation from tubes inserted at the time a polymer mulch is laid (**Figure 2**). The use of black polyethylene mulch may alter the environmental characteristics of the cropping system to the benefit of many weed species [4]. As MBr is no longer a weed control option for soil sterilization in plasticulture systems, herbicides are now used to maintain successful fresh market vegetable production over the course of multiple

| Rank | Vegetables – Cucurbits | | Vegetables – Other | |
|---|---|---|---|---|
| | **Most common** | **Most troublesome** | **Most common** | **Most troublesome** |
| 1 | *Amaranthus* spp. | *Amaranthus* spp. | *Amaranthus* spp. | *Amaranthus* spp. |
| 2 | common lambsquarter | *Cyperus* spp. | common lambsquarter | *Cyperus* spp. |
| 3 | *Cyperus* spp. | common lambsquarter | common purslane | common lambsquarter |
| 4 | *Ambrosia* spp. | *Ipomea* spp. | yellow nutsedge | common purslane |

*Common weeds are defined as weeds most frequently seen while troublesome weeds are those that are the most difficult to control.*

**Table 1.**
*Most common and troublesome weeds in vegetables.*

**Figure 1.**
*Cyperus spp. that has pierced through LDPE mulch (photo by Kayla Eason).*

**Figure 2.**
*Bare soil and low-density polyethylene (LDPE) mulch type beds used for vegetable production (left) (photo by Timothy Grey) and spraying LDPE mulch and weed infestations (right) (photo by Sidney Cromer).*

crops [5]. This includes the use of herbicides applied to the soil surface as mulch is laid, or between crops as part of the rotation (**Figure 2**) [6]. Most LDPE mulch laid for spring vegetable production is followed by a second crop in the autumn and potentially a third crop the following spring [7]. These succeeding vegetable crops can be transplanted directly into the existing mulch covered beds. This allows for multiple crop production using the same beds. This is done in order to minimize expenses associated with mulch and drip tape irrigation by distributing costs over multiple crops. However, the use of herbicides can result in injury and crop losses when sensitive vegetable species are exposed to previous applications [6]. The quantification of herbicide residues from field applied experiments is critical to maintain plant safety, and consistent vegetable production. This is accomplished by using analytical methods that utilize laboratory chromatic validation of herbicides in soil and from the surface of polyethylene mulches used in plasticulture systems.

## 2. Importance

Rotation of vegetable production using the same bare soil or LDPE mulch systems reduces cost and promotes environmental stability as there is less soil tillage and LDPE mulch waste produced that must be placed into a landfill [7]. Spring vegetables grown after LDPE mulch fumigation include watermelon [*Citrullus lanatus* (Thunb.) Matsum and Nak.], pepper (*Capsicum annuum* L.), tomato (*Lycopersicon esculentum* Mill.), squash (*Cucurbita pepo* L.), and eggplant (*Solanum melongena* L.). A second autumn crop often includes cabbage (*Brassica oleracea* L.), eggplant, cucumber (*Cucumis sativus* L.), or squash [3–6]. There was no injury issue with respect to rotation of vegetables when using MBr as a fumigant. However, using soil applied herbicides initially and between crops as a burndown of the existing crop or weeds, creates a unique concern for potential injury from residues remaining in the soil or on the LDPE mulch, especially to transplants. The adsorption, desorption, mobility, biological degradation, and soil/LDPE mulch properties are important factors that determines the persistence of herbicides used in fresh market vegetable production. Applying residual herbicides to the soil surface at the time LDPE mulch is laid helps to improve weed control, while also maintaining and extending productive use of the LDPE mulch for subsequent crops. Applying herbicides between crops as part of the rotational process improves crop establishment success, and also mitigates weeds that could harbor other insect and disease pests. Therefore, understanding herbicide chemistry will be an integral part of continued successful fresh market vegetable production.

## 3. Herbicide use in vegetable production

The loss of MBr for weed control led to herbicide alternatives for vegetable production. Since the early 2000s, there have been several herbicide registrations in vegetable crops put in place for bare soil, row middle, soil applied prior to mulch laying, and over-the-top of mulch. These include fomesafen (5-[2-chloro-4-(trifluoromethyl)phenoxy]-N-(methylsulfonyl)-2- nitrobenzamide) [8], flumioxazin (2-[7-fluoro-3,4-dihydro-3-oxo-4-(2-propynyl)-2H-1,4-benzoxazin-6-yl]- 4,5,6,7-tetrahydro-1H-isoindole-1,3(2H)-dione) [9], sulfentrazone (N-2,4-dichloro-5-[4-difluoromethyl)-4,5-dihydro-3-methyl-5-

oxo-1H-1,2,4-triazo-1-yl]phenyl]methanesulfonamide) [10], halosulfuron-methyl (methyl 3-chloro-5-[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino] sulfonyl]-1-methyl-1H-pyrazole-4-carboxylate) [11], S-metolachlor (2-chloro-N-(2-ethyl-6-methylphenyl)-N-[(1S)-2-methoxy-1-methylethyl]acetamide) [12], glyphosate (N-phosphonomethyl)glycine) [13], paraquat (1,1′-dimethyl-4,4′-bipyridnium dichloride) [14], and ammonium-glufosinate (2-amino-4- (hydroxy-methylphosphinyl)butanoic acid) [15]. These herbicides encompass many different mechanisms of action (MoA) and control a wide variety of monocot and dicot weed species [16]. **Table 2** describes several physiochemical properties of the aforementioned herbicides. This variety of herbicides assists growers with ensuring adequate weed control while maintaining crop safety, however proper planning is required to prevent injury to seeded or transplanted crops.

Since plastic mulch systems are often used for multiple vegetable crops over several years, weed control is crucial to maintain the integrity of the mulch. Selecting a herbicide that controls weeds while eliminating subsequent crop injury is imperative. The main determining factors when selecting herbicides, with respect to use, are if

| **Herbicide** | **Molecular weight** | $K_d$[b] | $K_{oc}$[c] | **Acid Dissociation Constant** | **Water Solubility** | $K_{ow}$[d] |
|---|---|---|---|---|---|---|
| | **g/mol** | **(mL/g)** | | **pKa** | **mg/L** | **log $K_{ow}$** |
| Fomesafen | 438.76 (acid)<br>460.74 (Na Salt) | — | 60 | 2.7 | 50 (acid)<br>600,000 (Na salt) | 2.89 (pH 1) |
| Flumioxazin | 354.34 | — | 500 to 13,000 | Non-ionizable | 1.79 | 2.55 |
| Sulfentrazone | 387.19 | < 1.0 | 43 | 6.56 | 780 | 0.99 (pH 7) |
| Halosulfuron-methyl | 434.81 | 0.36 to 1.6 | 124 | 3.5 | 1650 | 1.7 (pH 5)<br>−0.02 (pH 7) |
| *S*-Metolachlor | 283.80 | 2.16 | 200 | Non-ionizable | 488 | 2.89 |
| Glyphosate | 169.07 (acid)<br>207.16 (K salt) | 324 to 600 | 24,000 | 2.6 *(acid)* | 15,700 *(acid)* | 0.0006 to 0.0017 |
| Ammonium-glufosinate | 181.13 (acid)<br>198.16 ($NH_4$ salt) | — | 100 | <2, 2.9, 9.8 | 12,000 (*acid*) | 0.53 (pH 7) |
| Paraquat | 186.26 | — | 1,000,000 | Non-ionizable | 620,000 (*salt*) | −4.5 |

[a] *Shaner DL. Herbicide Handbook. 10th ed. Lawrence (KS): Weed Science Society of America; 2014.*
[b] *$K_d$, Soil sorption coefficient: the ratio of sorbed pesticide to dissolved pesticide at equilibrium in a water/soil mixture.*
[c] *$K_{oc}$, Soil organic carbon sorption coefficient: calculated as $K_d$ divided by the weight fraction of organic carbon present in soil.*
[d] *$K_{ow}$, Distribution coefficient between octanol and water.*

**Table 2.**
*Physiochemical properties[a] of various residual (fomesafen, flumioxazin, sulfentrazone, halosulfuron-methyl, and S-metolachlor) and contact (glyphosate, ammonium-glufosinate, and paraquat) herbicides applied in vegetable production for weed control.*

the MoA has residual or contact efficacy to the target crops and weeds. With vegetable production systems utilizing various types of herbicides, analytical extraction can quantify residue information and determine herbicide behavior in soil and on mulch.

### 3.1 Residual-type herbicides

Helling [17] describes residual herbicides as those chemicals which provide season-long weed control due to persistence in soil but can have carryover that may injure susceptible rotational crops. This has proven critical in the grower decision making process in terms of vegetable rotations [18, 19]. In the herbicides listed above, fomesafen, flumioxazin, sulfentrazone, halosulfuron-methyl, and *S*-metolachlor all are residual herbicides used in southeastern US vegetable production.

Fomesafen is a member of the diphenyl ether herbicide family and registered for control of dicot species in agronomic crops, and yellow nutsedge in vegetables [16]. It has soil residual activity [20–22] with a half-life ranging from 6 to 12 months under aerobic conditions [23]. Fomesafen field half-life ($DT_{50}$) varied as soil under LDPE mulch was 47 days verses 12 days for bare soil [24], indicating reduced dissipation for this method of use. The behavior of fomesafen in soil is environment dependent [16]. With a typical production soil pH, fomesafen would exist in anionic form, becoming more available as soil pH drops [21]. Multiple studies evaluated preemergence soil residual activity in vegetables, with testing in tomato for control of American black nightshade (*Solanum americanum* Miller) [25], cucurbits for *Amaranthus* spp. and other weeds [26], crop tolerance in cantaloupe [27], and pepper [28, 29]. When used in combination with other herbicides in tomato production, fomesafen provided improved purple nutsedge control compared to fomesafen alone [30]. Through multiple public and private research efforts, fomesafen now has state specific vegetable crop registrations as noted via the IR-4 project for cantaloupe, eggplant, pepper, squash, strawberry, tomato, and watermelon [31].

Flumioxazin is a preemergence N-phenylpththalimide herbicide used to control a broad spectrum of weeds in a variety of cropping systems, such as peanut (*Arachis hypogaea* L.), orchard crops, and plasticulture strawberries [32–34]. Flumioxazin has negligible photodecomposition but does have variable soil half-lives, which are soil pH dependent [16]. Research on flumioxazin dissipation from LDPE mulch indicated wash-off with water as the main dissipation mechanism, as compared to the same method looking at dry conditions [35]. The $DT_{50}$ for the wash off experiment was 6 hours, with flumioxazin levels undetectable by 24 hours after treatment. The $DT_{50}$ of 57 hours for the dry experiment indicated that flumioxazin was persistent and could lead to critical efficacy and injury issues if a grower transplants vegetables onto flumioxazin treated LDPE mulch. This has led to many caveats associated with flumioxazin registrations. For strawberry there is a 30-day PRE-transplant interval when soil applied, and many precautionary requirements for row middle applications, due to potential contact with LDPE mulch [9, 31].

Sulfentrazone is a soil applied, non-phloem translocated, moderately persistent in soil, aryl triazolinone herbicide [16]. In agronomic crops it has been used to assist with herbicide resistant weed management issues around the world [36]. Given its soil residual activity, the primary uptake mechanism is via plant root absorption followed by xylem translocation [16]. Sulfentrazone $DT_{50}$ varies as noted with soil under LDPE mulch was 12 to 13 days verses 11 to 20 days for bare soil [24]. Sulfentrazone is a weak acid (pKa of 6.56) and availability increases as soil conditions become more alkaline [37]. Sulfentrazone provides control of both purple and yellow nutsedge. However, growers must consider rotational restrictions to ensure proper use requirements to prevent potential crop injury from carryover [8].

Halosulfuron-methyl is a primidinylsulfonylurea herbicide [16] with preplant incorporated, preemergence, and postemergence *Cyperus* spp. activity [38, 39], lending to its effective use in numerous vegetable crops [5, 40]. It has multiple vegetable registrations for soil application prior to laying LDPE mulch, and over the top of the mulch between crops [13]. This group of herbicides is typically applied at low use rates, however they still show residual soil activity. Halosulfuron-methyl soil $DT_{50}$ ranges from 6 to 98 days, depending on soil texture, moisture and temperature regimes [41, 42]. Postemergence halosulfuron-methyl applications over the top of LDPE mulch allows growers to control nutsedge between vegetable crop transplanting [5]. However, persistence on the LDPE mulch can be dependent on multiple abiotic processes including thermal energy from the sun, as noted with a $DT_{50}$ of 55 MJ $m^{-2}$ for halosulfuron-methyl [43]. Halosulfuron-methyl is an important tool for nutsedge control in vegetable production, and dissipation research is critical.

*S*-metolachlor is a chloroacetamide herbicide that inhibits very long chain fatty acid biosynthesis, that controls yellow nutsedge, annual grasses, several small-seeded broadleaf weeds, and has been agronomically available since the 1970s [16]. It is an important herbicide option for transplant tomato production in the Southeastern US in that it can be preplant incorporated, preemergence, and postemergence applied [3, 30]. *S*-metolachlor is water soluble at 480 mg $L^{-1}$ [16], allowing for analytical and bioassay analysis of its dissipation in soil [44, 45] and LDPE mulch production systems [35]. A beneficial aspect of using *S*-metholachlor in vegetable production is its relatively short $DT_{50}$ in soil systems allowing for multiple plant back options. There are 60-day rotational restrictions in terms of 2nd and 3rd crop rotations in LDPE mulch systems for many cucurbits, vegetable fruiting, and *Brassica* groups [11].

### 3.2 Contact-type herbicides

Contact-type herbicides refer to those which are applied for specific control options to mitigate weeds that could interfere with the succeeding crops. They can also be used to destroy the pervious crop when rotating in plasticulture systems. Registered herbicides for these types of weed control options include glyphosate [14] and paraquat [12] with ammonium-glufosinate having several pending uses in vegetables [10].

Glyphosate inhibits the synthase of the enzyme 5-enolpyruvylshikimate-3-phosphate (EPSP), which disrupts the shikimic acid pathway, therefore leading to a reduction in aromatic amino acids and eventual plant death [46], and utilized around the world in multiple cropping systems. Glyphosate is relied on as an over-the-top herbicide application for several vegetable crops grown on LDPE mulch, with a required 1.25 cm of water applied prior to transplanting, due to its negligible photodegradation losses and high-water solubility (**Table 2**) allowing for movement off of the plastic mulch [5, 35]. Gray et al. [35] reported glyphosate was still available in efficacious amounts on LDPE mulch out to 120 hours after treatment when no water was applied to wash it off. While glyphosate may be a viable option for control, growers still have to be conscious of potential crop injury [5]. Given its broad-spectrum of weed control for grass, broadleaf, and perennial species, is relatively inexpensive, and available in multiple generic forms, glyphosate will continue to be utilized by vegetable growers using LDPE and bare soil vegetable production.

Ammonium-glufosinate is a glutamine synthetase inhibitor, causing a buildup of ammonium in tissues and subsequently inhibiting photosynthesis and photorespiration, which leads to plant death [47]. Ammonium-glufosinate is water soluble (**Table 2**) and has pending registrations for use in LDPE mulch systems in the southeastern US [10]. As with glyphosate, the proper amount of irrigation or rainfall before vegetable transplant after ammonium-glufosinate application will be important to prevent injury [48].

Paraquat is a bipyridylium that inhibits photosystem I, which creates reactive and toxic radicals within the plant [49]. The actual cause of tissue damage in a plant is from a mixture of the rapid cycling between the paraquat ion and paraquat radical and the large number of electrons flowing through photosystem I. Symptoms progress to necrosis within 1 or 2 days from application. Paraquat is currently registered for bare soil and LDPE mulch production for its control of annual grass and broadleaf weeds [12] but must be properly managed to prevent crop injury [5]. Gray et al. [35] reported paraquat was still available in efficacious amounts on LDPE mulch out to 120 hours after treatment when no water was applied to wash it off, but photodegradation is a major dissipation mechanism. The rapid efficacy and excellent control of many weed species, along with multiple dissipation mechanisms from LDPE mulch with rainfall and sunlight, allows growers an alternative to glyphosate and ammonium-glufosinate for contact herbicide selections.

## 4. Research

The use of soil applied and over-the-top of mulch herbicides in vegetable plasticulture systems presents a unique opportunity in understanding the dynamics of herbicide dissipation and persistence when evaluated using a variety of field, bioassay, and laboratory techniques. Quantification of herbicides can be achieved using various instrumentation, with high performance liquid chromatography (HPLC) coupled with mass spectrometry (MS) being one of the most common and powerful tools available, given its ability to separate, identify, and quantitate various compounds present in a wide range of sample types. Studies conducted to quantify vegetable herbicide soil dissipation or movement from the mulch surface had similar objectives and sample preparation methods, while chromatographic and mass spectrometer instrument parameters were adapted to best fit individual compounds.

### 4.1 Field experimental procedures

Both residual and contact herbicide field studies were conducted on Tifton loamy sand, utilized raised beds (1.8 m x 6.1 m) that were left bare or covered with LDPE mulch or totally impermeable film (TIF), and all herbicides applied at their respective field rates. Soil applied herbicides under mulch were sampled by cutting an ‘L’ shape in the mulch using a box cutting knife and pushing an aluminum cylinder (7.62×7.62 cm) into the soil until flush with the surface (**Figure 3**). Soil cores were wrapped in aluminum foil and stored individually at −10°C until analysis. Sampling of contact herbicides applied over-the-top of mulch was done by cutting a square (0.1 $m^2$) out of the mulch using an open-faced frame and box cutting knife (**Figure 3**). Mulch samples were placed and stored individually in plastic bags at −10°C until analysis.

### 4.2 Herbicide extraction

Solid phase extraction methods are dependent on the sample type, physiochemical properties of the target herbicide, and equipment available. Residual herbicides can be extracted from soil by combining a sub-sample of the soil core with an organic solvent mixture, shaking on a reciprocating shaker for several hours, and then transferring the supernatant into another vial for analysis or further cleanup if needed. While methods following that outline are widely used, specialized equipment can expedite the extraction process. One such example is microwave-assisted extraction (MAE), which can greatly reduce the volume of solvent and soil consumed while also reducing extraction time [50–52]. Contact herbicide extraction from the surface of mulch is accomplished by placing mulch samples into flasks filled with solution, shaking the flasks for several hours on a reciprocating shaker, and once complete transferring a sub-sample to a smaller vial for analysis or further cleanup.

### 4.3 Herbicide quantification

Once herbicide extraction is completed, vials (typically 2 mL in size) are placed into designated slots within the specialized chromatographic system. The analytical analysis methods vary by herbicide due to differing solubility, structure, and other physiochemical properties. Specific methods for the validation of residual and contact herbicides used in vegetable production is described in the subsequent subsections (4.3.1–4.3.7). For the purpose of this chapter, all herbicides were analyzed by a Waters™ Acquity HPLC system coupled with a Waters™ 2998 PDA UV detector and Waters™ QDa MS detector (**Figure 4**). Unless otherwise noted, LC separation was performed on a Symmetry C18 reverse-phase column (4.6×75 mm, 3.5 μm; Waters Corporation) for fomesafen, flumioxazin, *S*-metolachlor, and sulfentrazone, a Cortecs® C18 reverse-phase column (4.6×50 mm, 2.7 μm; Waters Corporation) for halosulfuron-methyl and paraquat, and an Anionic Polar Pesticide column (2.1×100 mm, 5 μm; Waters Corporation) for glyphosate and ammonium-glufosinate. The various herbicide amounts were quantified by correlating peak

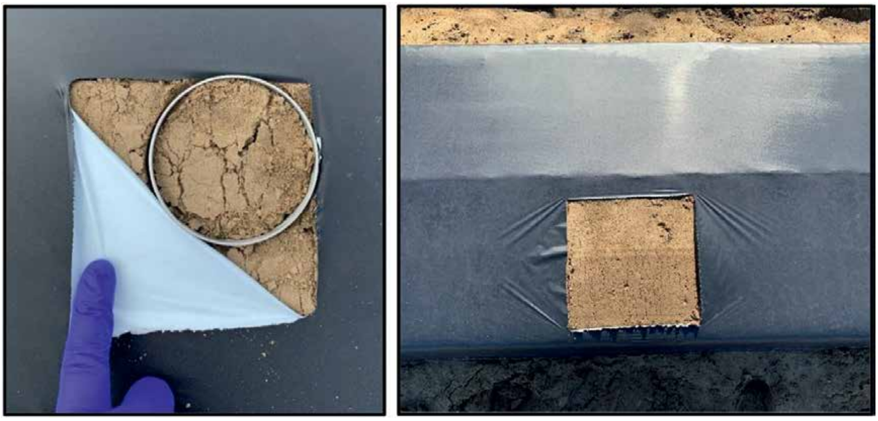

**Figure 3.**
*Procedure for sampling soil under mulch using an aluminum soil core (left) and an example of mulch sampling (right), which depicts a 0.1 m$^2$ square sample taken from LDPE mulch (photos by Kayla Eason).*

area detected to those of analytical grade standard solutions of various known concentrations. Selectivity was tested by using blank samples with no interfering peaks detected.

#### *4.3.1 Fomesafen*

Chromatographic conditions consisted of a gradient mobile phase, water ($H2O$) + 0.1% formic acid (A) and acetonitrile (ACN) + 0.1% formic acid (B), that started at 90% A, decreased to 10% A at 4.0 min, held isocratic for 2.0 min, then ramped up to 90% A at 6.1 min. The flow rate was 0.6 mL/min with a run time of 8 min. The MS was run in electron spray ionization (ESI) negative mode utilizing both multiple reaction monitoring (MRM) from 50 to 600 Da and single ion recording (SIR) at 437 Da (**Figure 5**).

#### *4.3.2 Flumioxazin*

LC separation was performed at an ambient column temperature for each sample. The mobile phase consisted of ACN + 0.1% formic acid (A) and $H2O$+ 0.1% formic acid (B) and held isocratic at 70% A for 2.7 min per injection. Flow rate was set to 0.75 mL/min and the injection volume was 10 μL. The MS was run in ESI positive mode using MRM from 5 to 600 Da and SIR at 355 Da (**Figure 6**). Methods were adapted from previous literature [52, 53].

#### *4.3.3 Sulfentrazone*

The LC mobile phase consisted of ACN + 0.1% formic acid (A) and $H2O$ + 0.1% formic acid (B) and held isocratic at 60:40 (%A:%B) for 2.5 min. The injection volume was 2.5 μL with a flow rate of 1.0 mL/min. The MS was run in ESI negative mode using MRM from 5 to 600 Da and SIR at 385 Da (**Figure 6**).

**Figure 4.**
*Waters™ Acquity high performance liquid chromatography system (top and bottom left) equipped with a column heater (middle) and coupled with a Waters™ 2998 PDA ultraviolet detector (top right) and Waters™ QDa mass spectrometer detector (bottom right).*

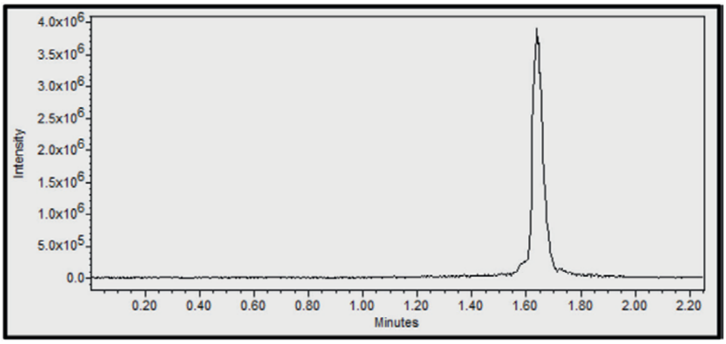

**Figure 5.**
*Chromatogram depicting fomesafen.*

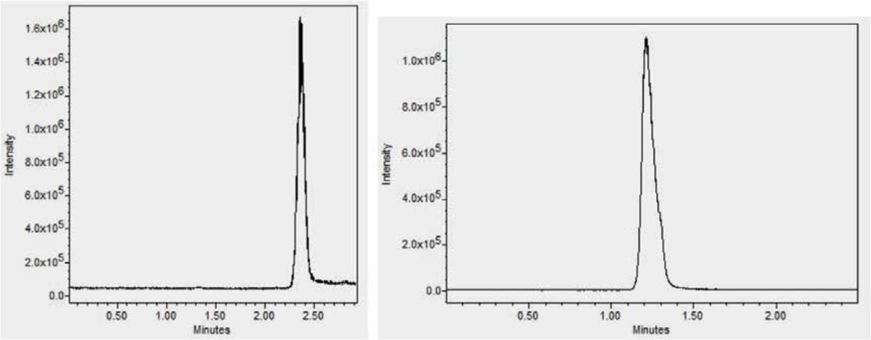

**Figure 6.**
*Chromatogram depicting flumioxazin (left) and sulfentrazone (right).*

### *4.3.4 Halosulfuron-methyl*

The mobile phase, H2O+ 0.1% formic acid (A) and ACN + 0.1% formic acid (B), followed a gradient at 70% A for the initiation, at 0.8 min was 10% A, held at 10% A for 1.2 min, increased to 70% A at 2.3 min, and then held at 70% A for 1.0 min. Flow rate was 1.0 mL/min with an injection volume of 8.0 μL. The MS was run in ESI positive mode using MRM from 50 to 600 Da and SIR at 435 Da (**Figure** 7). The column was maintained at ambient temperature for each injection.

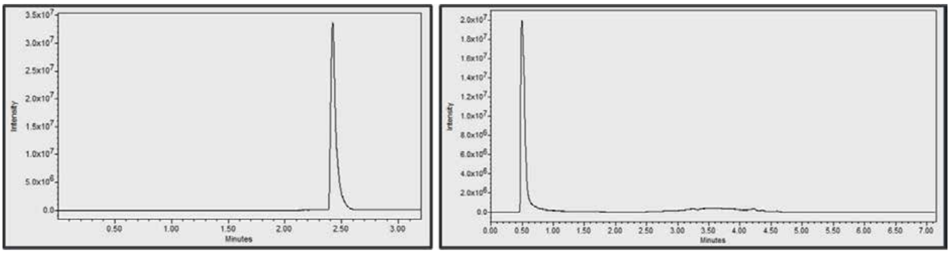

**Figure 7.**
*Chromatogram depicting halosulfuron-methyl (left) and S-metolachlor (right).*

### *4.3.5 S-metolachlor*

LC conditions consisted of a mobile phase, H2O + 0.1% formic acid (A) and ACN + 0.1% formic acid (B), which followed a gradient of 90% A at initiation, 10% A at 2.1 min, held isocratic for 3.0 min, ramping up to 90% A at 5.1 min, and then held isocratic for 2.0 min. The flow rate was 1.37 mL/min with a run time of 7.0 min and an injection volume of 200 μL. The column was heated and maintained at 25°C for each injection. The MS operated in ESI positive mode using MRM from 50 to 600 Da and SIR at 284 Da (**Figure 7**).

### *4.3.6 Glyphosate and ammonium-glufosinate*

Mobile phase was H2O + 0.9% formic acid (A) and ACN + 0.9% formic acid (B), with the gradient starting at 10% A, ramping to 60% A at 2.0 min, and increasing to 90% A at 4.0 min. The flow rate was maintained at 0.75 mL/min for 3.5 min. The injection volume was 7.5 μL and column temperature set to 40°C for the entire run. There was a strong (10:90 ACN:H2O) and weak seal wash utilized (90:10 ACN:H2O). Two injections were run per sample at a run time of 4.0 and 2.0 min per injection for glyphosate and ammonium-glufosinate, respectively. The MS operated in ESI negative mode using MRM from 50 to 600 Da and simultaneously running SIR at 168 and 180 Da for glyphosate and ammonium-glufosinate, respectively. **Figure 8** shows a chromatogram of glyphosate at 168 Da and ammonium-glufosinate at 180 Da using these chromatographic and MS conditions. This method was developed specifically for the novel anionic, polar pesticide column [54].

### *4.3.7 Paraquat*

LC conditions consisted of a 200 mM ammonium formate buffer (pH 3.7) (A) and ACN (B) mobile phase, which was held isocratic at 50:50 (%A:%B) for 3.0 min at a flow rate of 0.5 mL/min. The injection volume was 20 μL and column temperature set to 30°C for the entire run. A H2O:ACN seal and needle wash solvent (50:50 v/v) was used. The MS operated in ESI positive mode using MRM from 50 to 600 Da and simultaneously running SIR at 186 Da.

## 5. Data analysis

Chromatographic data requires further analysis before validation. Most herbicide dissipation data are subjected to either a linear or non-linear regression method [55].

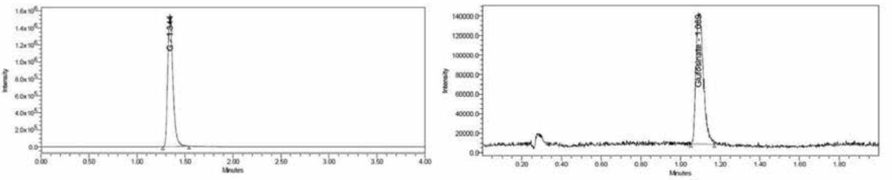

**Figure 8.**
*Chromatogram depicting glyphosate (left) and ammonium-glufosinate (right).*

The kinetic model used should best describe individual data since herbicide dissipation can vary greatly between compounds. Most residual herbicide dissipation data can be described using a single first-order kinetic model, specifically the exponential decay equation:

$$\mathrm{y} = B_0 e^{-k(t)} \tag{1}$$

where $y$ is the measured herbicide concentration, $B_0$ is the initial herbicide concentration when time ($t$) is 0, $k$ is the first-order dissipation constant, and $t$ is the amount of time elapsed after herbicide application. The amount of time taken for 50% of a herbicide to dissipate (half-life) can be determined when following single first-order kinetics:

$$DT_{50} = \ln(2)/k \tag{2}$$

where $DT_{50}$ is the half-life and $k$ is the dissipation rate determined when herbicide concentration is regressed against time. These equations (Eqs. (1) and (2)) can be used to describe herbicide dissipation in soil and from the surface of mulch.

Temperature, moisture, sunlight, and microbial populations can all influence the rate of herbicide dissipation, with factors being intertwined and influential on each other. Given the complexity of herbicide behavior, dissipation cannot always be described using the exponential decay equation (Eq. (1)). When herbicide concentrations follow both a slow and fast decay pattern, a bi-phasic kinetic model (Eq. (3)) can be used to describe dissipation:

$$y = \left((B_0)(\%Fast)(0.01)\right)e^{-k_{fast}(t)} + \left((B_0)(100-\%Fast)(0.01)\right)e^{-k_{slow}(t)} \tag{3}$$

where y is the measured herbicide concentration, $B_0$ is the initial herbicide concentration when time ($t$) is 0, %Fast is the fraction of the model accounted for by the faster of the two phases, $k_{\text{fast}}$ is the first-order dissipation rate constant for the fast phase of the model, $k_{\text{slow}}$ is the first-order dissipation rate constant for the slow phase of the model, and $t$ is the amount of time elapsed after herbicide application. The $k_{\text{fast}}$ and $k_{\text{slow}}$ rate constants can be applied to the half-life equation (Eq. (2)) to determine the half-life for both phases of herbicide dissipation.

## 5.1 Validation of herbicide concentrations over time

When quantified using chromatography, herbicide dissipation over time coupled with edaphic and environmental information creates a complete picture of how the specific compound will behave. This information directly impacts decision making when selecting the appropriate herbicide to use. The following results are interpretations of quantified herbicide concentrations over time using the methods previously discussed.

When comparing fomesafen dissipation under LDPE mulch and in bare soil, application under mulch greatly extended the half-life (**Figure 9**). In bare soil beds fomesafen dissipation was rapid when compared to dissipation under LDPE mulch

(**Figure 6**), with a half-life of 2 days for bare soil and 58 days under mulch. **Figure 9** also highlights the difference between a single first-order kinetic model and bi-phasic kinetic model, with samples under LDPE mulch best fitted to the exponential decay equation (Eq. (1)) and the bare soil samples fitted to a double exponential decay equation (Eq. (3)). The half-life of flumioxazin (30 days) is shorter than fomesafen and sulfentrazone (71 days).

Glyphosate and ammonium-glufosinate dissipation from the surface of LDPE mulch can be described by the exponential decay equation (**Figure 10**). $DT_{50}$ was determined to be 3.3 and 1.4 days for glyphosate and ammonium-glufosinate, respectively. Both herbicides were below the respective limit of detection by 18 days after application. Using similar sampling, processing, and analytical methods Hand et al. [56] reported glyphosate to have a half-life of 2.2 days when applied to the surface of plastic mulch. These findings correlate to the amount of rainfall received, which given the water solubility of both glyphosate and ammonium-glufosinate was the most influential factor in dissipation (**Figure 11**).

Further investigation on the removal of herbicides from the surface of plastic mulch found that after at least 0.63-cm of irrigation glyphosate and ammonium-glufosinate both had less than 0.1% (of the applied concentration) remaining on the mulch. S-metolachlor wash-off from the surface of LDPE mulch required at least 1.27-cm of irrigation to have less than 5% remaining. Halosulfuron-methyl concentrations on the surface of mulch after 1.27-cm of irrigation were less than 2%.

## 6. Conclusion

Many vegetables are produced using a plasticulture system, which generally consists of raised beds of soil covered with plastic mulch. Herbicides are applied to

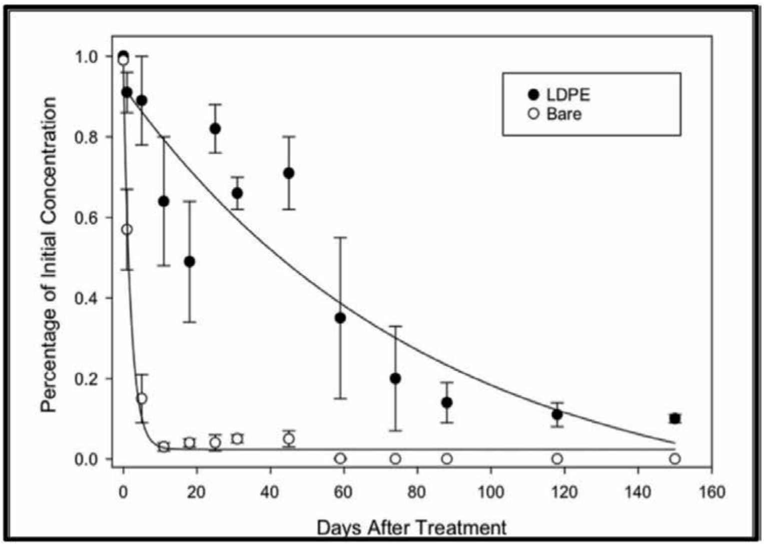

**Figure 9.**
*Fomesafen dissipation in soil left bare or under LDPE mulch. Each line represents the first-order change in herbicide concentration as a percentage of the applied amount. Data points indicate the means of replications with error bars representing the standard error of each mean.*

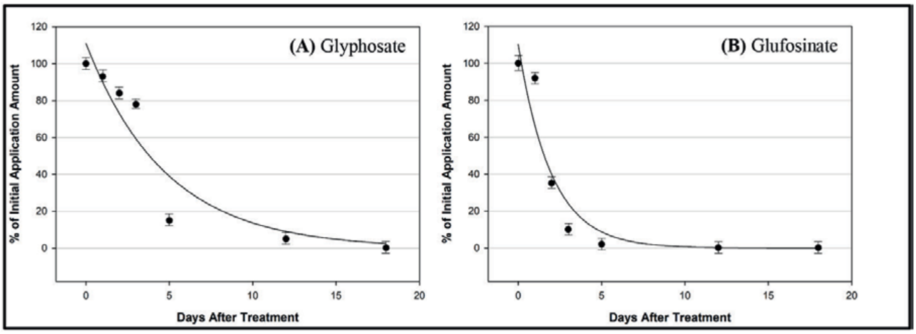

**Figure 10.**
*Herbicide dissipation from the surface of LDPE mulch over time using the exponential decay equation (Eq. (1)) with nonlinear regression applied, for glyphosate (A) and ammonium-glufosinate (B). Each line represents the first-order change in herbicide concentration as a percentage of the applied amount. Data points indicate the means of replications with error bars representing the standard error of each mean. Parameter estimates for glyphosate (A): $y = 110.922e^{(-0.2092x)}$, $R^2$ of 0.8996, and a k-value of 0.2092; ammonium-glufosinate (B): $y = 110.077e^{(-0.5069x)}$, $R^2$ of 0.9114, and a k-value of 0.5069.*

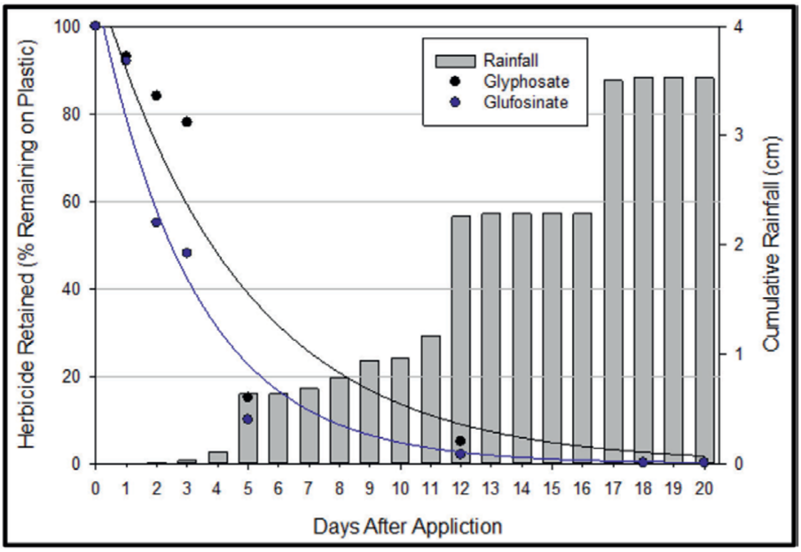

**Figure 11.**
*Glyphosate and ammonium-glufosinate dissipation from the surface of LDPE mulch over time as influenced by rainfall. Each line represents the first-order change in herbicide concentration as a percentage of the applied amount. Data points indicate the means of replications with error bars representing the standard error of each mean. Parameter estimates for glyphosate (A): $y = 110.922e^{(-0.2092x)}$, $R^2$ of 0.8996, and a k-value of 0.2092; ammonium-glufosinate (B): $y = 110.077e^{(-0.5069x)}$, $R^2$ of 0.9114, and a k-value of 0.5069. Bars represent cumulative rainfall over time.*

the soil once beds are made but before they are covered with mulch. These herbicides need to provide the longest residual weed control possible while still maintaining crop safety. Producers often utilize the same plastic mulch for two to five crop production cycles over the course of multiple growing seasons, allowing growers to spread the cost of production over multiple crops and mitigating the cost of reapplying mulches for each crop. The time between the termination of one crop and the planting of another allows for the germination, emergence, and establishment of troublesome weeds in old plant holes. Often, one of the greatest challenges in plastic mulch vegetable systems is eliminating the first crop and any weeds growing under and through holes in the mulch prior to planting the subsequent crop. Herbicides that can be applied over-the-top of plastic mulch prior to transplanting a crop without damage are crucial for maintaining vegetable weed management systems. Herbicide use in vegetable production can raise concerns if information is not known about carryover effects or how the individual herbicide will behave in soil or on the surface of the mulch bed. This can be mitigated by quantifying herbicide dissipation in various vegetable production scenarios by utilizing field and analytical techniques, such as chromatographic systems.

Chromatography is a multi-faceted analytical tool that can separate, identify, and quantitate various compounds present in a wide range of sample types. These analytical systems can be used to quantitate the persistence of various herbicides on soil and plastic mulch. Coupling chromatographic outputs with environmental data, such as rainfall and cumulative solar radiation, we can predict half-life information and dissipation rates for individual herbicides. Growers can directly use this information when making crucial weed management decisions.

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## Chapter 3

# Use and Management of Herbicides in Agricultural Crops in the Central Area of the Gulf of Mexico

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## Abstract

Herbicides, like in many other regions, are a critical aspect of modern agriculture. They are essential tools for weed control, which is very important for crop health and yield optimization. However, their use must be carefully managed to minimize environmental impact and ensure the safety of both farmers and consumers. The primary aim of this study was to assess the utilization of herbicides in the agricultural regions of the central Gulf of Mexico. The research employed a survey-based methodology, utilizing a structured questionnaire as the primary tool for gathering insights into the application and management of herbicides within the region. The surveyed producers displayed an average age of 61 years, and their educational background averaged 4.4 years of schooling. The research uncovered the utilization of 14 different active ingredients spanning 18 commercial brands, all readily available in the municipalities within the study area. One prominent observation emerging from this analysis is the notable absence of technical training among the producers in herbicide use and management. Their approach to pesticide application, particularly herbicides, relies heavily on empirical knowledge. This analysis highlights the need for improved technical training and the promotion of best practices in herbicide management within this agricultural community.

**Keywords:** herbicides, paraquat, carcinogen, ethics, training for agrochemical use

## 1. Introduction

The extensive use of pesticides in agriculture has raised concerns due to the presence of residual levels in food products, posing inherent risks to both public health and the environment [1–3]. While pesticide research has predominantly focused on the detection and dispersion of residues, particularly organochlorine compounds like dichloro diphenyl trichloroethane (DDT) and its metabolites stemming from historical health campaigns [4, 5] relatively limited attention has been given to a broader range of compounds. This includes organophosphates, fungicides, and herbicides, which are widely employed in the global agricultural sector, suggesting that these compounds may be readily accessible to the general population through various routes.

These findings align with international reports on pesticide residues, such as chlorpyrifos, diazinon, ethyl parathion, methamidophos, mancozeb, methomyl, and metribuzin, detected in freshly harvested strawberries (*Fragraria ananassa*) in the state of Mérida, Venezuela [2]. Additionally, research has indicated a higher concentration of pesticides in the peel of potatoes (*Solanum tuberosum*) compared to the internal part, with eight compounds detected at concentrations expressed in mg $kg^{-1}$: chlorpyrifos (7.3), diazinon (11.8), dimetoato (0.56), metamidofos (5.0), carbofuran (1.4), mancozeb (11.4), metomilo (0.030), and metribuzin (0.10) [6].

In the Latin American and the Caribbean region, data collected by the Food and Agriculture Organization (FAO) for the year 2010 reported a total pesticide usage of 222,367.59 tons. Among these, herbicides constituted the largest group, accounting for 11,788.14 tons, followed by insecticides with 46,994.62 tons, and finally fungicides and bactericides with 61,584.83 tons [7]. However, it is important to note that the statistical data from FAOSTAT incorporates data from various sources, including official and semi-official, estimated or calculated data [8, 9], introducing some uncertainty into the information. This uncertainty is reflected in the fact that according to Goméz-Arroyo et al. [7], approximately 46% of the region lacks comprehensive information on pesticide consumption, in contrast to organizations like FAO [6].

This situation underscores the potential for either underestimation or overestimation of pesticide usage patterns, complicating our understanding of their real impact on specific regions, as well as their long-term consequences for public health and the environment.

The available data on pesticide usage in Mexico are limited, rendering them inadequate for comprehensive analysis. Specific figures detailing the volume of usage for distinct pesticide groups such as insecticides, herbicides, and fungicides are notably absent. This paucity extends to information pertaining to the patterns of pesticide utilization, and application frequencies throughout crop cycles and annual cycles. In addition, data concerning contamination levels of these compounds in aquatic ecosystems are practically non-existent, despite the knowledge of the toxicological effects associated with many of these substances [5, 10–12]. Consequently, understanding the use of pesticides in Mexican agricultural practices remains constrained, with a dearth of detailed information regarding, which substances are employed across various sectors, seasons, and geographical regions [10, 13–15].

According to Silviera-Gramont et al. [16], the absence of updated figures relating to application quantities and frequencies, coupled with the lack of official statistical data specifying the usage of individual active ingredients for particular crops, recommended application practices, and dosages, can be attributed to the lack of robust regulatory oversight and monitoring in Mexico [15]. Albert [17] and Silviera-Gramont et al. [16] similarly underscore the dearth of information concerning the utilization and consumption of pesticides within the agricultural sector, save for data compiled during censuses or surveys, where quantities of agricultural fertilizers, insecticides, and pesticides are recorded.

The detection of pesticides from various chemical groups in water sources has been associated with their inappropriate and excessive usage. This not only imperils the quality of other agricultural activities conducted within the same regions but also jeopardizes the well-being of agricultural workers and the food security of consumers of these products [2, 6, 7, 10, 18–20]. A deeper understanding of the specific usage patterns of different chemical groups is imperative to address this issue effectively. Therefore, there is an urgent need to generate comprehensive information concerning the utilization, management, and impact of compounds like herbicides, backed by scientific rigor. In line with this objective, this research endeavors to elucidate the use and management practices employed by agricultural producers in the central Gulf of Mexico with regard to the herbicide paraquat, an area renowned for its pivotal role in the production of commercially significant crops.

## 2. Materials and methods

### 2.1 Study area

The study encompassed various locations within the municipalities of Medellín, Cotlaxtla, and Tlalixcoyan, situated in the central region of the state of Veracruz. These municipalities are characterized by the cultivation of key fruit crops, including pineapple, papaya, lemon, and sugar cane (see **Figure 1**). Notably, the study area is in

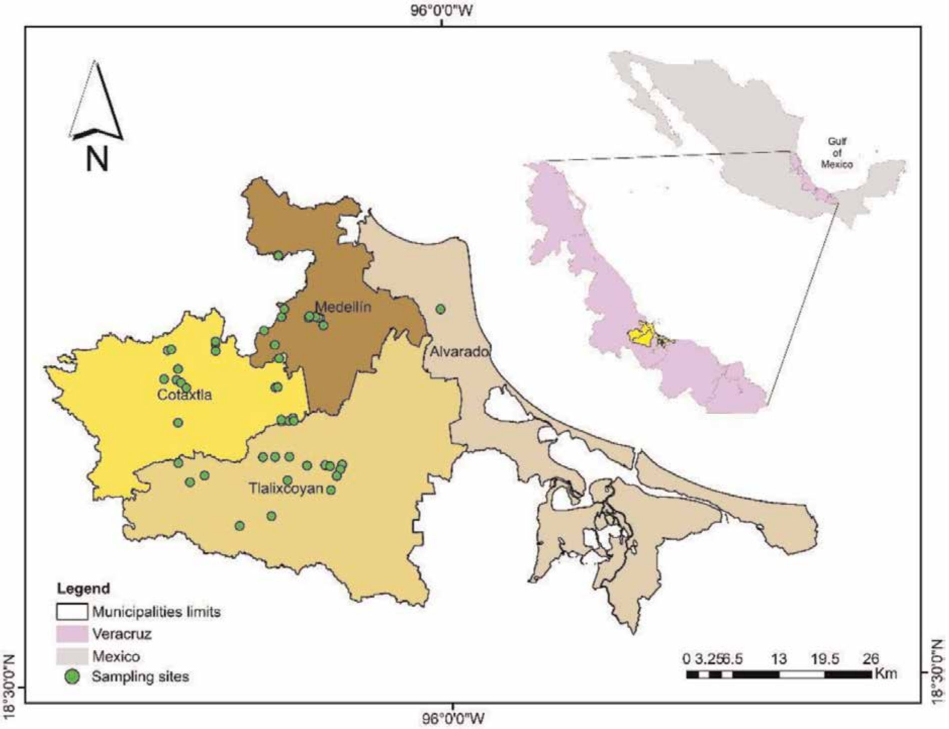

**Figure 1.**
*Study area of herbicide use in the central zone of Veracruz, Mexico.*

close proximity to significant bodies of water, adding to its ecological importance. These water bodies include the Cotaxtla river in the municipality of Cotaxtla, the Blanco river in Tlalixcoyan, and the Mandinga Lagoon in the municipality of Medellín de Bravo.

### 2.2 Study design for herbicide use diagnosis

A survey-based technique was used, utilizing a well-structured questionnaire for conducting interviews with agricultural producers. This questionnaire served as the primary tool for comprehensively assessing and characterizing the application, use, and management of herbicides [4, 14, 21, 22]. The questionnaire was thoughtfully designed in three sections:

The first section aimed to gather information about the producers, encompassing details such as age, education, gender, municipality, and locality.

The second section focused on elucidating the characteristics of the cultivated areas. This involved factors like the available land area per producer, the time of year, cultivated crop varieties, concentrations, planting density, application methods, and herbicide management practices.

The third section was developed to establish associations between the quantity of herbicides used per active ingredient, chemical group, and the associated toxicological risks inherent to their application and management. This section facilitated the calculation of the total pesticide usage, planting surfaces, dosages, and active ingredient concentrations [4, 14, 21]. All data from these interviews were consolidated into a database, enabling the evaluation of herbicide use and management patterns across the region.

### 2.3 Data analysis

To analyze the acquired data, the TIBCO Statistica 14.0.0.15 software (TIBCO Software Inc., Palo Alto, CA, USA) was employed. An exploratory analysis was conducted, including descriptive statistics such as means and frequencies, to discern insights into both the producers and the characteristics of the cultivation areas. To further identify techniques employed for herbicide use and management in the primary agricultural zones of the central Veracruz region, the principal component analysis (PCA) was used as a statistical tool.

A total of 12 variables were selected from the sociodemographic and herbicide use data obtained from the survey. The principal components that could explain the greatest possible variability were found, as well as the correlation between variables and components.

## 3. Results and discussion

### 3.1 Producer characteristics

The population of farmers who participated in the interviews had an average age of 61 years, with the oldest being 83 years old and the youngest being 37. The maximum age recorded aligns with the findings of Polanco-Rodríguez et al. [22] who reported a maximum age of 85 years among farmers in the Yucatán agricultural area, although the minimum age was 17 years. The highest level of education attained by the participants was 12 years, but the average education level was 4.4 years, representing

| Variable | Average | Minimum | Maximum |
|---|---|---|---|
| Age (years) | 61 | 37 | 83 |
| Gender (%) | 88% men<br>12% women | 2 | 6 |
| Schooling (years) | 4.4 | 1 | 12 |
| Time dedicated to agriculture (years) | 38 | 1 | 73 |

**Table 1.**
*Characteristics of the target population interview in agricultural areas of the central Gulf of Mexico.*

incomplete basic education. Furthermore, a percentage of the producers had no formal education, as illustrated in **Table 1**.

The duration of agricultural activity varied from a minimum of 1 year to a maximum of 73 years. It is worth noting that 40% of the population in their research had incomplete basic education, followed by a group with no formal education at 32%, while 10% had completed secondary education, and only 2% reported having attended preparatory education [22].

In contrast, Tabares and López [23] reported findings in the Marinilla municipality of the Antioquia district in Colombia, where farmers' ages ranged from 18 to 50 years, with the majority falling between 31 and 50 years old. This suggests a younger population without necessarily higher education levels. These findings are consistent with Tabares and López [23], where 83.4% of respondents had completed primary or incomplete studies, while only four people had acquired higher, technical, or university education.

Similar to findings by Polanco-Rodríguez et al. [22], who reported a predominantly male presence in agricultural activities, accounting for 92% of the population, this investigation also observed a notable proportion of males within the target population, comprising 83% of those interviewed [19]. However, it is important to recognize that the characterization of the target population specifically pesticide users, has often been overlooked in previous research. Studies such as those conducted by González-Arias et al. [21] and Hernández-Antonio and Hansen [4], have primarily focused on evaluating pesticide use in terms of crop types, dosages, and usage frequency. These studies tended to disregard the individuals who are the main users of these pesticides, individuals whose practices significantly influence the application of these compounds.

Within the context of Mexico, only a limited number of studies have delved into the issue of pesticide use and its correlation with population characteristics such as age, education, and the duration of engagement in agricultural activities. This scarcity of research makes it challenging to compare these results with existing literature. Notably, the state of Yucatán, for instance, has reported that individuals with low levels of education tend to have a reduced perception of health and environmental risks associated with pesticide usage [22]. The level of education, particularly when it is basic or incomplete, significantly impacts the ability to comprehend instructions for the proper use of pesticides. Difficulties in reading and understanding such instructions can potentially increase the risks associated with pesticide handling [23].

In this study, the maximum cultivated area reached 84 hectares, while the minimum was 1 hectare. This contrasts with the findings of Hernández-Antonio and Hansen [4] who reported a cultivated area of 108,865 in the Irrigation District (DR)

| Variable | Average | Minimum | Maximum |
|---|---|---|---|
| Cultivated area (ha) | 8.95 | 1 | 84 |
| Main crop (%) | — | 4.08% (Banana) | 44.86 (pineapple) |
| Secondary crop (%) | — | 2.04 (pumpkin, cassava, rice, watermelon, lemon) | 14.28 (corn) |
| Third crop (%) | — | 2.04 (chili, grass) | 12% (corn) |
| Water mirror depth well (m) | 3.08 | 1 | 30 |
| Total well depth (m) | 13.75 | 1 | 130 |

**Table 2.**
*Characteristics of agricultural areas in the central zone of the Gulf of Mexico.*

063 of Guasave Sinaloa, a cultivated area of 202,065 ha in a reference agricultural area (ZAR). The variation in cultivated areas between regions is closely related to agricultural activity management and the volumes of herbicides applied. Moreover, this investigation highlighted that the individuals interviewed in the study area predominantly consist of small-scale producers who rely on groundwater sources for irrigation. The availability and accessibility of water sources vary considerably, with an average water mirror of 3 m and a maximum of 30 m (**Table 2**). In contrast, Hernandez-Antonio and Hansen [4] reported significantly larger irrigation areas of 106,518 hectares in DR 063 and 400 hectares in ZAR in Sinaloa. This underscores the substantial differences in the scale and scope of agricultural practices between regions in Mexico.

### 3.2 Herbicide use

The characteristics of the different crops in the region generate the use of a wide variety of herbicides. The farmers interviewed with indicators used up to three different chemical groups of herbicides, which were used in different concentrations (**Figure 2**). It was identified that the third chemical group of herbicides was used in a lower concentration (**Figure 3**) compared to the main group but the herbicide concentration of the third group was higher than the second group (**Figure 4**). The results indicated the use of 14 active ingredients from 18 trademarks in the municipalities of the study area in this investigation. Farmers reported the use of active ingredients of glyphosate and paraquat Polanco-Rodríguez et al. [22] indicated the use of these herbicides classified in the toxicological category as highly toxic and probable causes of cancer in the population according to the International Agency for Research on Cancer (IARC) by Agency for Toxic Substances and Disease Registry (ATSDR) [18, 24]. Likewise, in the municipalities of Yucatán, a total of ten herbicides belonging to different chemical groups were reported, of which they indicated the use of at least two active ingredients such as glyphosate, paraquat, and paraquat dichloride classified as highly toxic [22].

The herbicides of group 1 (principal) The herbicides of the group with maximum application doses were picloram, propanil, and dichloropropioanilide with 20,000.00 (mg $L^{-1}$ ha), the second group of herbicide was 2,4-D with 15,625.00, glyphosate,

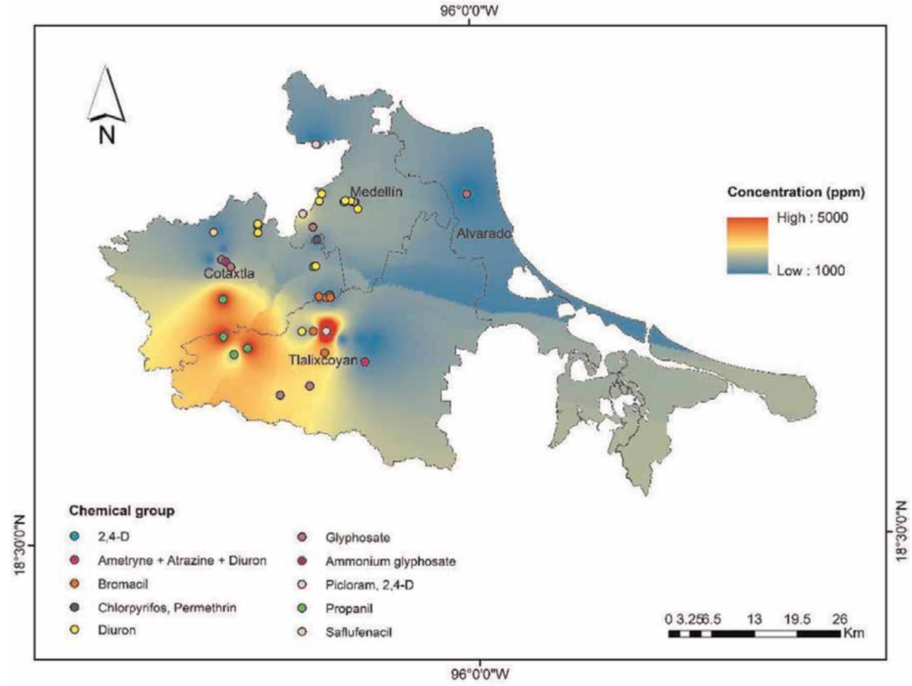

**Figure 2.**
*Main chemical groups of herbicides used in the central zone of Veracruz, Mexico.*

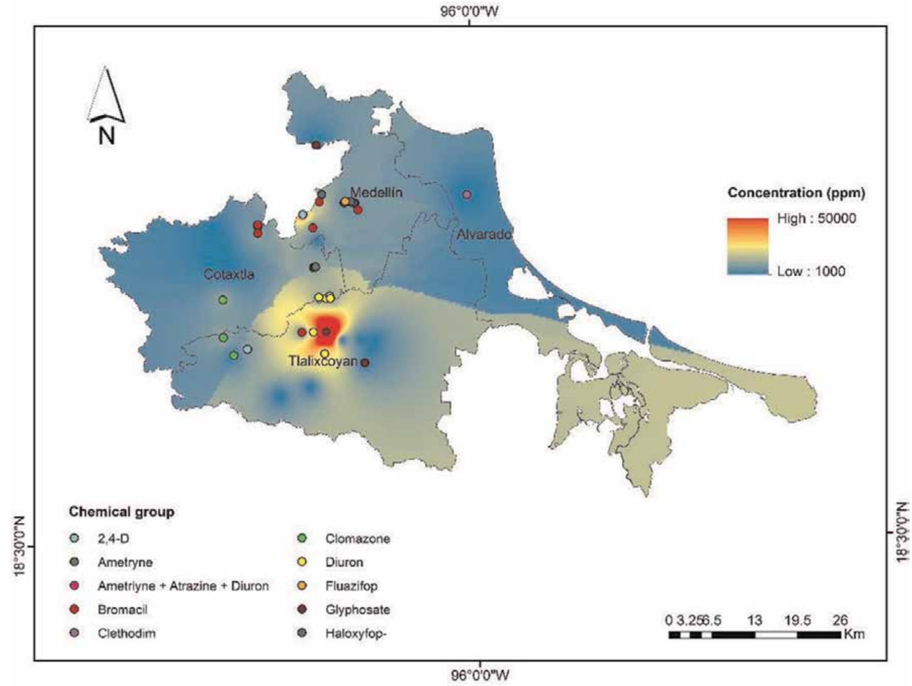

**Figure 3.**
*Second chemical group of herbicides used in the central zone of Veracruz, Mexico.*

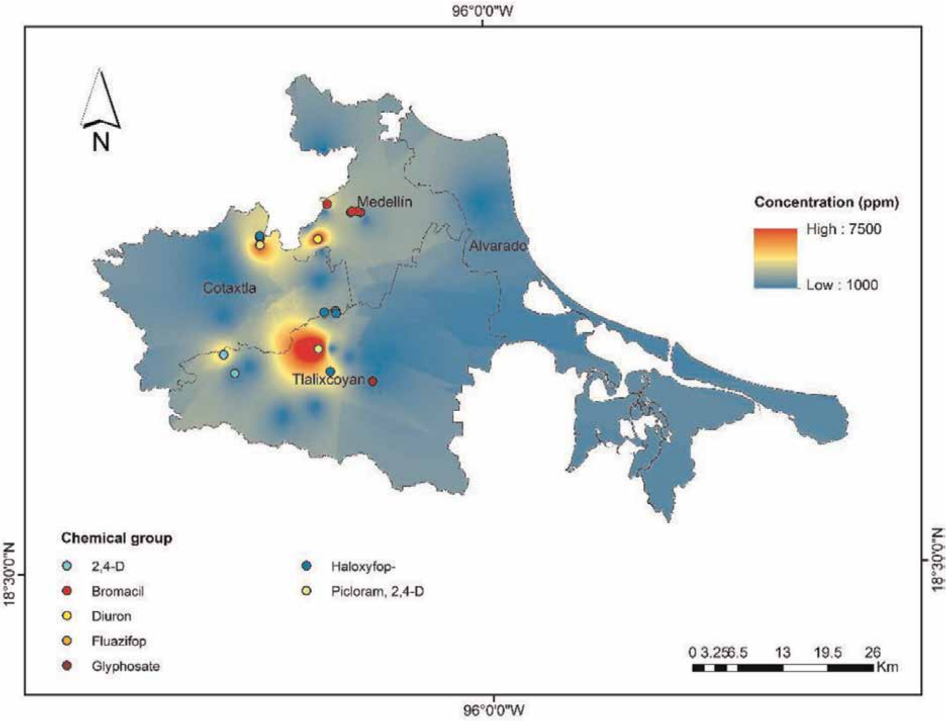

**Figure 4.**
*Third chemical group of herbicides used in the central zone of Veracruz, Mexico.*

ametrine clomazone with 10,000.00 (mg $L^{-1}$ ha) (**Table 3**). Finally, the third type of herbicide was picloram with 6250.000 and diuron with 5000.000 (mg $L^{-1}$ ha). Regarding paraquat, this was used by 26.53% of those interviewed with the commercial names of gramoxone, paraquat, and lumbrequat. The maximum concentration reported was 20,000.00 and the average concentration used of 2683.673 mg $L^{-1}$ ha.

| **Active ingredient (a.i.) herbicide 1** | **Dose of a.i. (mg $L^{-1}$ ha)** | **Active ingredient (a.i.) herbicide 2** | **Dose of a.i. (mg $L^{-1}$ ha)** | **Active ingredient (a.i.) herbicide 3** | **Dose of a.i. (mg $L^{-1}$ ha)** |
|---|---|---|---|---|---|
| Diuron | 3660.71 | Haloxifop | 1750.00 | Bromacil | 1500.000 |
| Picloram | 20,000.00 | Bromacil | 2023.71 | Fluazifop-butyl | 1250.000 |
| Glyphosate | 7500.00 | Fluazifop-butyl | 1250.00 | Haloxifop | 1350.000 |
| Bromacil | 1166.67 | Glyphosate | 10,000.00 | Picloram | 6250.000 |
| Ametrine/ Atrazine/D | 10,000.00 | 2,4-D | 15,625.00 | Diuron | 5000.000 |
| Propanil | 20,000.00 | Ametrine | 10,000.00 | Glyphosate | 101.000 |
| Dichloropropyanilide | 20,000.00 | Diuron | 2000.00 | 2,4-D | 2500.000 |
| Glyphosate 36 | 10,000 | Ametrine/Atrazine/Diuron | 3500.00 | Adherent | 5000.000 |
| Saflufenacil | 1500.00 | Clomazone | 10,000.00 | | |

| Active ingredient (a.i.) herbicide 1 | Dose of a.i. ($mg L^{-1}$ ha) | Active ingredient (a.i.) herbicide 2 | Dose of a.i. ($mg L^{-1}$ ha) | Active ingredient (a.i.) herbicide 3 | Dose of a.i. ($mg L^{-1}$ ha) |
|---|---|---|---|---|---|
| Glufosinate ammonium | 10,000 | Butyl Acid Ester/2,4-D | 2500.00 | | |
| | | [1-[3-chloroalkyloxyimino] propyl-5] (Clethodim) | 2000.00 | | |

**Table 3.**
*Use of active ingredient of the three main groups of herbicides in the agricultural areas of the center of the Gulf of Mexico.*

The evaluation of the use of herbicides through the survey technique allows identifying patterns of use of this compound in certain regions of Mexico. Coincides with the above, Silveira-Gramont et al. [16] and Pérez-Olvera et al. [18] indicated that in order to assess the danger posed to the health of the inhabitants of the passive compound exposure, reliable and up-to-date information is required on crops planted and pests, doses, volumes, forms of application of the pesticides used and particularly in the case of that represent a potential health risk. However, the information available in official statistics in Mexico on the use of agrochemicals is very general, without differentiation between annual and perennial crops, extensive and intensive crops, fruit trees, and other categories of agricultural production, because all the previous characteristics influence variations on the way these compounds are applied and therefore their potential effect on the environment [17].

### 3.3 Use herbicide paraquat

A total of 77% of the interviewees indicated knowing the herbicide name paraquat under the common names of paraquat, gramoxone, and lumbrequat, while the rest do not know these names. Of the total number of people interviewed who indicated that they knew about the paraquat herbicide, only 37% currently use it, of which 85% affirm that its use is efficient for weed control, 7% mention only using it in areas independent of their crops, and the remaining 7% do not know enough about its efficiency. Coinciding with the above, Ramírez-Mora et al. [25] reported through a survey that identified the use of different types of pesticides in the irrigation district of La Antigua in Veracruz; reporting that paraquat represented a lower percentage of minor use with 7.4% of the total number of pesticides used; the above was related to the type of cultivation carried out in the region and the potential damage that this herbicide can represent for it.

Differences in the use of paraquat have been reported according to the type of crop, the frequency of use, and the concentrations used. Likewise, Medina-Meléndez et al. [26] indicated that coffee producers in the state of Chiapas mentioned that paraquat was the most used product; however, they reported that it was used in lower average concentrations and frequency of use with 1 L/200 L tank (5000 $\mu L\ L^{-1}$) and an application frequency of only 1 time per year. The average concentration of paraquat used by the producers was 2.02 L of herbicide per 200 L tank of water, that is, a concentration of 10,100 μL of paraquat per liter of water. The range of concentrations reported by the producers presented a range of 1 L per 200 L tank (5000 μL/L) up to

| Concentration | Municipalities | | | |
|---|---|---|---|---|
| | Cotaxtla | Tlalixcoyan | Medellín | General |
| Average paraquat (μL/L) | 10,900 | 10,000 | 5000 | 10,100 |
| Range (μL/L) | 7500–10,000 | 10,000 | 5000 | 5000–20,000 |
| Average per hectare (μL/L ha$^{-1}$) | 18,639 | 24,200 | 20,000 | 22,200 |

**Table 4.**
*Paraquat herbicide concentrations used by the producers interviewed in the central zone of Veracruz, Mexico.*

4 L per 200 L tank (20,000 μL/L). Producers report using an average of 2.2 tanks for each hectare of crops, which means an average concentration of 22,220 μL/L of paraquat per hectare (**Table 4**). The highest concentration of paraquat used by farmers in the central area of Veracruz was reported in the municipality of Tlalixcoyan (**Figure 5**).

Among the main reasons indicated by the interviewees who claim to know about the herbicide paraquat, but report not using it, included that it damages their main crops (62.5%), there is little efficiency to control weeds (16.6%), they do not currently cultivate (12.5%), and they do not know its proper use (8.3%). Paraquat is freely marketed in Mexico under different commercial brands. However, the use of paraquat is restricted in some regions of the world [27] and it can only be purchased from marketers without the need to submit a written recommendation from an official or private technician [25].

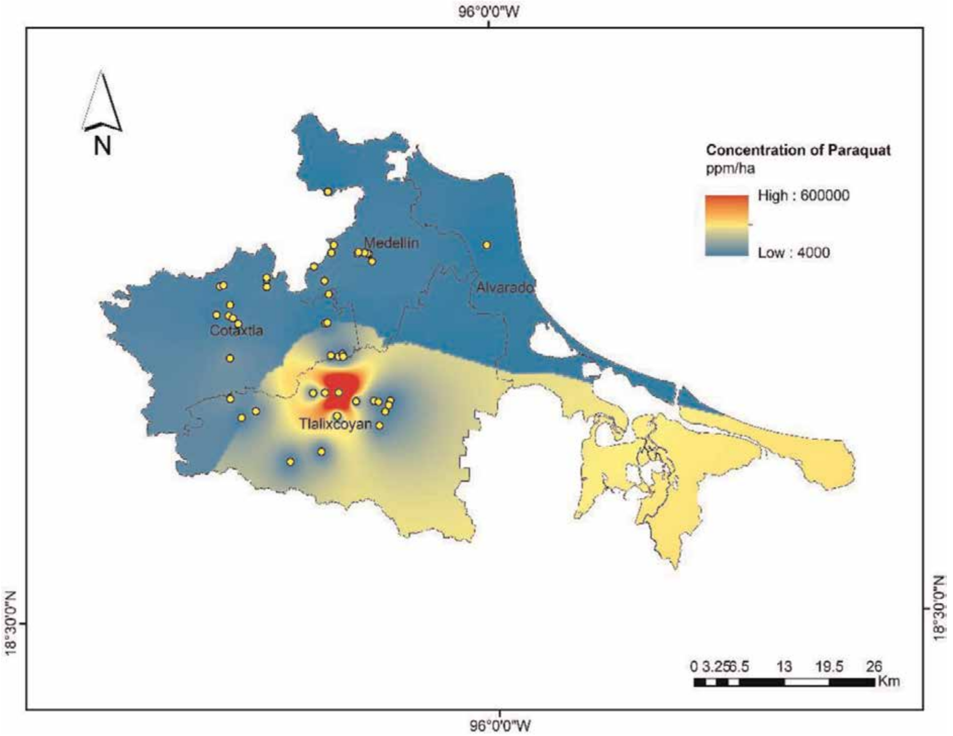

**Figure 5.**
*Paraquat concentration used in the central zone of Veracruz, Mexico.*

According to INECC [28], there is no exact information on the list of active ingredients registered in Mexico, since the information compiled in the Official Catalog of Pesticides from 1991 to 2004 does not include information on the compounds produced, but not those that were produced, imported, sold and applied, much less their amounts of use. Therefore, the lack of data on the types, doses of pesticides, and where they were used has been a consistent historical trend in Mexico [5, 18, 28]. This demonstrates the difficulty in comparing the use of herbicides such as paraquat in different types of crops and regions of Mexico. Due to the different methodologies used and the type of data collected in the various investigations, it is difficult for the average, maximum, and minimum values of the amounts used for each pesticide used in Mexico [28]. Likewise, the need to understand the problem of the intensive use of herbicides is highlighted, since the doses used exceed the recommended doses for this use and to establish the risk and impact of the use of this type of pesticide.

### 3.4 Toxicological risk due to its mode of application and management of herbicides

The use of six herbicidal types was identified in which active ingredient is within the highly toxic toxicity classification (II), such as paraquat and glyphosate (**Table 5**). In studies conducted in the municipalities of Yucatán, a total of ten herbicides belonging to different chemical groups and toxicity levels were reported, of which they expressed the use of at least two active ingredients such as glyphosate, paraquat, dichloride classified as highly toxic [22, 25].

The frequency of application of herbicides only in the study area was lower than reported by Polanco-Rodríguez et al. [22] reported a frequency in the use and application of all pesticides by men in a 41% semi-annual use, followed by 31% quarterly and 25% with a monthly use. While Sivó-Agulló et al. [29] indicated that 47.6% of agricultural workers in towns of Albacete Spain revealed to have a management or relationship with pesticides throughout the year, this reflects that they have a greater period of contact and risk for the use of pesticides.

In this study, 83.67% of the interviewed individuals testified that they had not received training in the use of herbicides, and the decision in their management was empirically carried out through the experience of the farmer (91.83%). A percentage

| Chemical denomination | w/w | Tradenames | Toxicity |
|---|---|---|---|
| Glyphosate: | 79,2% p/p (792 g/kg) | Faena | II |
| Diuron (3-(3,4-diclorofenil)-1,1-dimetilurea) | 800 g. of a.i/kg | Karmex, Diuron | III |
| Clomazone | 36% p/v, Sodium nitrate 5% | Command CS | III |
| Picloram<br>2,4-D | Equivalent 64, 1 g<br>240 g | Tordon 101 | IV |
| 2,4-D | 49.40% (equivalent in weight) | Hierbamina | III |
| Ametrine<br>Atrazine<br>Diuron | 194 g<br>194 g<br>194 g | Caña Z plus | III |
| Propanil | 360 g of a.i/L | Lanza 360 CE, Propanil 480 | II |

| Chemical denomination | w/w | Tradenames | Toxicity |
|---|---|---|---|
| Clethodim | 240 g/L | Azadon 240 EC | II |
| Haloxifop-r-metil éster: | 10.51%, equivalent to 108 g of a.i/L | Galant Ultra | II |
| (Fluazifop-butil): Butyl(R)-2-{4[[5-(trifluorometil)-2-piridinil] oxi] fenoxi} propanoato | Equivalent to 125 g de a.i/L | Fusilade | IV |
| Ametrine: N2-etil-N4-isopropil-6-metiltio-1,3,5-triazina-2,4-diamina | Equivalent 800 gr. a.i/Kg | Ametrex 80 WG | III |
| 2,4-D acid butyl ester<br>Glyphosate | Contains 49.64% of product (equivalent to 400 g of a.i/L)<br>30.34% | Herbipol | III |
| Glufosinate ammonium | 150 g of a.i. L, concentration 13.45% | Tarang 150 | II |
| Dicloruro paraquat | Concentration of 27,6% | Gramoxone, lumbrequat, paraquat | II |

**Table 5.**
*Toxicological classification and persistence of herbicides used in agricultural areas of the center of the Gulf of Mexico. Abbreviations: I: Extremely toxic; II: Highly toxic; III: Moderately toxic; IV: Slightly toxic.*

lower than 4.08% proved that the management of herbicides by the suggestion of the sellers of agrochemicals, and a similar percentage was obtained for the combination of experience and help from the seller. A total of 69.29% of the interviewees indicated that they apply the herbicides themselves and the remaining 36.75% hire personnel for their application. The main application method was with a backpack pump with 93.87%, while the remaining 6.12% used a tractor. According to Tabares and López et al. [23] they mention that 83% of the farmers have not received training regarding the safe handling of pesticides and approximately 80% of them do not use adequate protective equipment to carry out the work.

The principal component analysis identified different degrees of significant association ($p < 0.05$) between certain groups of variables; this was positively high between the variable x3 named as experience working in the field and the frequency of application of herbicide per year (variable x9); as well as the variable x6 that corresponded to the number of tanks per Hectare and the concentration of herbicides used per hectare (**Figure 6**). Meanwhile, a moderate positive correlation was obtained between the cultivated extension variable and the herbicide concentration per hectare. In contrast, a high negative correlation was obtained between the variables of pH regulator use and knowledge of damage caused to the environment.

The importance of sociodemographic variables such as age and schooling of the producers with productive variables such as cultivated area and use of herbicides was also identified (**Figure 6**). Therefore, by having a larger area for cultivation, larger producers choose to increase the concentrations of herbicides such as paraquat and the concentration per hectare. It was identified that the relationships between the variables and the axes that represent the components F1 and F2 together represent 46.13% of the initial information contained (**Figure 6**). The presence of three vector groups was identified: the green circle indicates the existing correlation between the variables x4, x6, x7, and x10; the yellow circle indicates the existing correlation between the

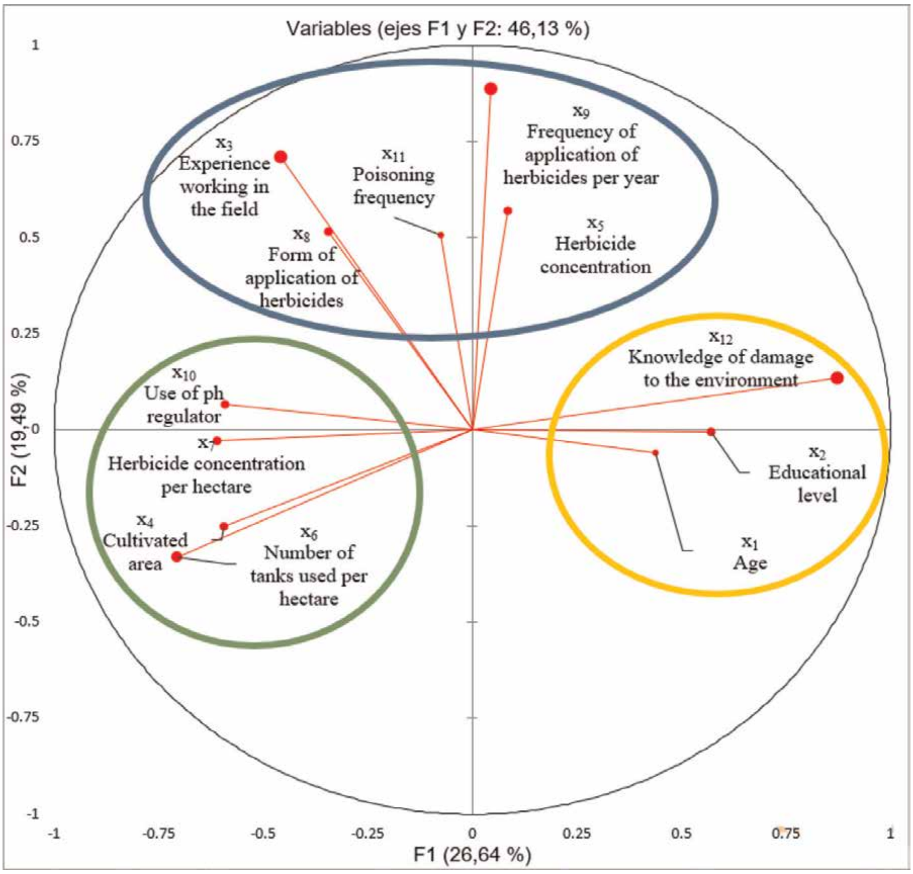

**Figure 6.**
*Correlation of sociodemographic variables with the use and management of herbicides in the municipalities of Veracruz, Mexico.*

variables x1, x2, and x12; Likewise, these groups of variables are closer to the axis of the principal component F1, which better explains the variables. The last group of vectors indicated in the blue circle is closer to the principal component F2 in its positive part.

The frequency of the use of protective equipment was related to the age of the people interviewed, where the group responded that they always wear protective equipment with higher frequencies in the younger intervals, while the respondents who used it were sometimes the oldest groups between the range of 65–74 years and over 75 years [29]. Likewise, the protective equipment for the application of agrochemicals consists mainly of the use of long-sleeved shirts with 51% and does not have protective suits for this activity, followed by the use of lenses with 10%, masks 6%, gloves 5%, and 12% do not use any protective equipment during the application of pesticides [22].

The results in this study area showed that 65.30% of the interviewed individuals did not use any protective equipment when applying herbicides, 14.28% wore a mask, 8.16% wore gloves, and 6.12% wore boots, it should be noted that the use of this protective equipment was used separately and therefore no one wore full protective equipment. Sivó-Agulló et al. [29] indicated the same trend when reporting in their investigation that only 12.6% of workers used all personal protective equipment to carry out pesticide application.

The source of information for many farmers can have two main origins. They indicated that 25.3% of the farmers interviewed in their research always rely on the explanation of the seller, so they depend on the information they provide for the use of the pesticide and consider it unnecessary to read the product label [29]. The previous approach contrasts with another response given by the same respondents since 85.7% of them said they always read the label of all products before using it. Training plays a central role in reducing the risk of exposure and inappropriate use of pesticides by farmers, indicated the questionable quality of the safety measures used by the workers, indicated that if 52.3% of the interviewees said they always ignore the product they are working with, it will be difficult for them to use the appropriate protective equipment to perform this work [22, 29].

The use and management of herbicides in the study area of this research indicated the lack of ethical-technical knowledge of farmers on the effect on their health by not using protection equipment or receiving training in the management of these substances. As well as their limited knowledge about the effect of these substances on the environment. Coinciding with the foregoing, farmers of corn and soybean in Missouri identified that industrialization of agricultural production generates pressure on farmers on decisions between doing what they believe is right and doing what they feel they must in order to survive [30]. Decision-making identified in this research allowed the localization as primary source of information in the implementation of herbicides to knowledge empirical transmitted between farmers of the region, the use of these compounds management through the trial and error in the doses herbicide.

Cardoso and James [31] identified through a survey applied to producers crops like corn, sorgo, and livestock, that the ethical framework of farmers affects their decision to participate in these practices. In the case of the corn and sorgo culture producers, identified an ethical framework combination, the characteristics of the farm and the farmers correlated with the decisions on the use of agrochemicals. Therefore, the level of education of farmers and training on the use of highly toxic compounds as some of the herbicides used could influence a lower negative effect by the use of these compounds. In Missouri, farmers identified that the ethical challenges of agriculture in the region focused on terms of farmers behavior on crop management [30].

The reduction of toxicological risk due to improper use of herbicides requires the integration of knowledge of how it is used, and the management and implementation of strategies to reduce its use. In accordance with Polanco-Rodríguez et al. [22] it is necessary to apply international regulations, as well as the implementation of educational programs fundamentals on agroecology on sustainable agriculture to avoid the application of pesticides with carcinogenic potential.

## 4. Conclusions

Applying a structured survey to herbicide users in this study area allowed us to assess the composition of their population, and to explain how they use and manage these compounds. An unfinished basic education academic level was identified in the highest percentage of the population. Frequent use of herbicides such as glyphosate and paraquat identified, which are classified as highly toxic, as well as the importance of making a selection of these compounds according to each crop, and knowing what is the necessary dose of application. The lack of a greater number of researches in

Mexico is highlighted, especially in the study area that includes the problem of herbicide use and its long-term effect on ecosystem health.

The ethical responsibility of farmers would be associated with the lack of access to training by government and scientific institutions that offer farmers training for the proper management of herbicides and monitoring the integral use of pesticides. It is necessary to implement continuous monitoring of the use of agrochemicals with high toxicological potential in the region, and it is essential to implement technical training programs by trained personnel where protection measures are explained for those responsible for the activity, to avoid health risks due to misuse and management of pesticides.

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## Conflicts of interest

"The authors declare that they have no conflict of interest."

## Appendices: questionnaire applied to producers

The objective of this questionnaire is to identify the techniques of use and management of herbicides carried out by farmers in the main agricultural areas of the central zone of the state of Veracruz. The information provided will be handled confidentially and will be used for the development of this research.

| | |
|---|---|
| **Date:** | |
| Location: | Geographic coordinates |
| Municipality | |
| Full name (Interviewed) | |

## A. Sociodemographic data

1 What is your age (years)?

2. Sex: () Female () Male.

3. What is your education (years)? () No studies () Primary () Secondary () High School () Higher Technical () Bachelor's Degree () Other.

4. What are the crops you grow? () Pineapple () Papaya () Lemon () Watermelon () Beans () Corn () Other.

5. What is the area of cultivated land (ha)?

6. How long have you worked in the field (years)?

7. What is the possession of cultivated land? () Own () Rented () Other.

8. What type of irrigation used? () Drip () Microaspersion () Well () Temporary () Other.

9. What is the frequency of watering? () Daily () Once a week () Every fortnight () Temporary.

() Other.

10.1 Do you have a well on your plot? () But because?

10.2 What is the depth of the well (meters)?

## B. Type of herbicide used

11. What are the herbicides used to control weeds (trade names)?

| **Herbicide #1** | **Herbicide #2** | **Herbicide #3** |
|---|---|---|
| **11.1 Concentration** | **11.1 Concentration** | **11.1 Concentration** |
| Applied area (ha) | Applied area (ha) | Applied area (ha) |
| Other: | | |

12. Do you know what the active ingredient paraquat is? ()Yes () No.

12.1. Do you currently apply the herbicide paraquat? () Yes () No 12.2 Why?

13. What is the concentration per area used of the herbicide paraquat on your crops (L/ha)?.

## B.1 Use of herbicides

14. Do you apply herbicides to your crops? () Yes () No () Other.

15. What is the way to apply herbicides? () Backpack pump () Scrubbers () Tractor () Other.

16. How many times do you apply it during the crop cycle? ()Daily () Weekly () Fortnightly () Monthly () 3 Months () Other.

17. What concentration of the most used herbicide do you use (L/ha)?

18. What is your knowledge about the application of herbicides based on? () Own experience () Suggestion from other farmers () Suggestion from the seller of agrochemicals () Label indication () Other.

## C. Training and occupational risk for the use of herbicides

19. Have you ever received training to apply herbicides? () Yes () NO.

20. Do you use any type of personal protective equipment when applying herbicides?

() None () Glasses () Mask/face shield () Apron () Gloves () Boots () Other.

21. Have you felt any discomfort after applying only herbicides? () None () Headache () Dizziness () Vomiting Fever () Allergy () Other.

21.1 Have you felt any discomfort after applying any other chemical?

| Insecticide | Fungicide | Fertilizers |
|---|---|---|
| Type of discomfort | Type of discomfort | Type of discomfort |
| Other: | | |

22 How many times have you felt discomfort? () Once () Every time you apply a product () Never () Other.

23. Are you aware of the environmental damage caused by the use of herbicides?
() Yes () No

Control data.

| | Interviewer Name | |
|---|---|---|
| **Application date** | | |
| Start time | | End time |

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### Chapter 4

# Potent Insecticide Plant

*José André Barroso*

## Abstract

In this chapter, we will address the effectiveness of these two powerful insecticidal plant species on the survival of eggs and larvae of *Bemisia* spp. (*Hemiptera*), *Sordidus* spp. (*Coleoptera*) and *Spodoptera* spp. (*Lepidoptera*). To obtain the essential oil, the cold pressing method described by Pinheiro and adapted by Barroso was used, where 900 g of seeds of the plant material was placed in the oven at a temperature of 45 ± 2°C for 48 h, then the seeds were crushed in a Britânia Diamante Black 4 blender at a speed of 900 W. It was pressed manually in an oil press machine. The resulting aqueous material was placed in a container and sealed with parafilm to prevent evaporation. It was left to rest in the dark at a temperature of 18 ± 2°C in an oven for 48 h. It was decanted to separate the essential oil and then filtered to remove suspended solid particles. For the Bioensio with eggs and larvae, four flasks covered with fine mesh were used, each containing 50 eggs of each species, at a temperature of 25 ± 2°C. For both cases, 2 ml of essential oil from the three prepared solutions was used. It was verified that: the essential oils of *Ricinus communis* are effective on the mortality of *Bemisia* spp., *Spodoptera* spp. and *Sordidus* spp. larvae, reaching 100% mortality in 7, 9 and 9 days of exposure, respectively; the essential oils of *Azadirachta indica* are effective on the mortality of *Bemisia*spp., *Spodoptera* spp. and *Sordidus* spp. larvae, reaching 100% mortality in 9, 7 and 6 days of exposure, respectively; the solution of *Azadirachta indica* and *Ricinus communis* was the most effective in achieving mortality on *Bemissia* spp., *Spodoptera* spp. and *Sordidus* spp. in 5, 4 and 5 days, respectively.

**Keywords:** plants, *Azadirachta indica*, *Ricinus communis*, mortality, insects

## 1. Introduction

Chemical warfare is a problem that has been going on for many decades. The effects of the use of chemical insecticides led Carson [1] to describe in his work Silent Spring the great environmental consequences resulting from the use of these substances.

For a long time, dichloro-diphenyl-trichloroethane (DDT) was used, but this compound has the ability to persist for a long time in the environment, accumulating in animal and vegetable organisms, thus its use was disapproved. However, the frequent use of insecticides (such as: organophosphates, carbamates and pyrethroids) can lead to the development of insect resistance to these compounds, compromising control and favoring the transmission of diseases [2]. In addition to the development of population resistance to insecticides, there may be a decrease in the population of natural enemies, health risks for humans and animals, contamination of groundwater and a decrease in biodiversity [3].

The environmental problems arising from the use of these chemicals, including public health, led researchers, scientists and others to direct the fight against vectors to another dimension, thinking about sustainability. As a result, background knowledge on phytopharmaceuticals used in some regions of the world for decades was used. For a long time, plants served as a medicinal base for human civilizations.

Therefore, the use of plants with insecticidal properties is not a recent practice. The first phytoinsecticides were pyrethrin extracted from chrysanthemum *Chrysanthemum cinerariaefolium*, nicotine (*Nicotiana tabacum* L.), rotenone (*Derris* sp.), ryanodine (*Rhyania speciosa*) and sabadina (*Schoenocaulon officinale*) [4].

In this chapter, we want to evaluate the insecticidal effect of two plant species with great potential, *Azadirachta indica* and *Ricinus communis*.

*Azadiractha indica*: Also known as neem belonging to the *Meliaceae* family, it originates from Southeast Asia and is cultivated in all African countries, Australia and Latin America. Originally from a tropical climate, the plant develops well at temperatures above 20°C in well-drained, nonacidic soils and altitudes below 700 m [5, 6].

Researchers have discovered that neem works both in the pesticide and medicinal areas. Its seeds and leaves have been found to combat more than 200 species of insects, cockroach pests, moths, aphids, among others. The tree is probably the only and best source of biopesticide in existence, a potential plant.

*Ricinus communis*: It is a tropical and subtropical evergreen shrub belonging to the *Euphorbiaceae* family. In official Portuguese-speaking countries, the plant is also known as castor bean or castor oil plant [7]. This shrub comes from northeast Africa and the Middle East. It is a fast-growing plant that is distributed throughout tropical and subtropical climates in places such as old fields, rocky slopes and along roadsides. Castor grows best in full exposure to sunlight and can reach up to 6 m in height, but measures an average of 2.5 m [7].

There are studies conducted by researchers on the effect of castor on insects, for example, Barroso [5, 6] evaluated the effect of this plant on *Aedes* spp., verifying high mortality rates, and repellency and other significant effects. The author places this plant almost on the same level as neem, but it must be handled with great caution because of its active ingredient.

Specifically, we will address the effectiveness of these two powerful insecticidal plant species on the survival of eggs and larvae of *Bemisia* spp. (Hemiptera), *Sordidus* spp. (Coleoptera) and *Spodoptera* spp. (Lepidoptera).

## 2. Methodology

### 2.1 Collection and identification of plant material

For the bioactivity tests on *Lepidoptera, Coleoptera* and *Hemiptera*, two local plants were selected: *Azadirachta indica* (**Figure 1**) and *Ricinus communis* (**Figure 2**). They were collected in the province of Luanda in the municipalities of Viana, Luanda and Cacuaco.

### 2.2 Obtaining essential oil from A*zadirachta* indica and R*icinus* communis seeds

To obtain the essential oil, the cold pressing method described by Pinheiro (2003) and adapted by Barroso [5, 6] was used, where 900 g of seeds of plant material was

**Figure 1.**
*Leaves and fruits of* Azadirachta indica.

**Figure 2.**
*Leaves and fruits of* Ricinus communis.

placed in the oven at a temperature of 45 ± 2°C for 48 h, then the seeds were crushed in a Britânia Diamante Black 4 blender at a speed of 900 W.

It was pressed manually in an oil press machine. The resulting aqueous material was placed in a container and sealed with parafilm to prevent evaporation. It was allowed to stand in the dark at a temperature of 18 ± 2°C in an oven for 48 h. Subsequently, a heterogeneous compound was obtained with a light phase rich in oil on the surface, an intermediate phase rich in water and a heavy phase rich in insoluble solids. It was decanted to separate the essential oil and then filtered to remove suspended solid particles.

### 2.3 Bioassay

For the Bioensio with eggs, four flasks covered with fine mesh were used, each containing 50 eggs of each species, at a temperature of 25 ± 2°C. For the bioassay with larvae, four flasks were used, each containing 50 eggs, waiting for hatching, where the larvae were obtained. For both cases, 2 ml of *Rinus communis* essential oil, 2 ml of *Azadirachta indica* and 2 ml of the mixture (containing 1 ml of ricinus solution and 1 ml of *Azadirachta indica* solution) were used. The fourth vial was used as a control (**Figure 3**).

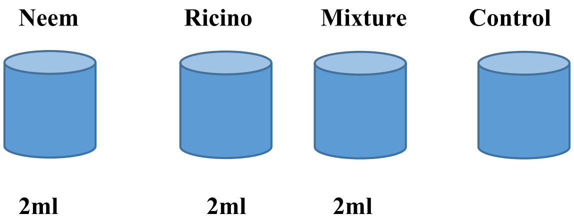

**Figure 3.**
*Schematic illustration of the experimental design of the bioassay used for the essential oils of the two species of plants:* Ricinus communis *and* Azadirachta indica*. Source: The author.*

## 3. Results and discussions

### 3.1 Effect on egg hatching rate

The analysis of the figure below demonstrates a weak correlation between the essential oils of *Ricinus communis* on the occlusion rate of *Bemisia* spp. eggs confirmed by the coefficient of determination ($R^2$ = 0.50). It was observed that the normal periods of occlusion were not altered, with this process occurring between the 9th and 10th day (**Figure 4**).

Similarly, a weak correlation similarity was observed between the essential oils of *Ricinus communis* on the rate of occlusion of eggs of *Bemisia* spp., as confirmed by the coefficient of determination ($R^2$ = 0.62). In this one, it was also verified that the periods of occlusion were not altered, all the eggs occlude between the 9th and 10th day (**Figure 5**).

It was observed that 5% of the population began to occlude on the 6th day of exposure. However, there were still no significant changes since, like the experiments described above, the joint action does not influence the occlusion rates of *Bemisia* spp., as confirmed by the coefficient of determination ($R^2$ = 0.58). In this one, it was also verified that the periods of occlusion were not altered, 95% of the eggs occlude between the 9th and 10th day (**Figure 6**).

Regarding the effect of *Ricinus communis* oil on *Spodoptera* spp., the correlation was even weaker when compared with *Bemisia* spp. We can observe this effect by the coefficient of determination ($R^2$ = 0.49). *Ricinus communis* oil has no effect on hatching, and it was found that the change to the larval stage occurs mostly (about 60%) on the 10th day (**Figure 7**).

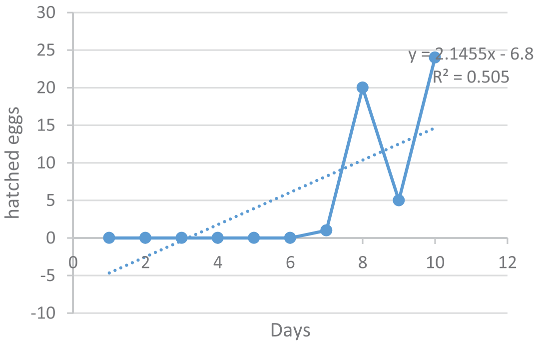

**Figure 4.**
*Graphic illustration of the effect of* Ricinus communis *essential oil on the hatching rate of* Bemisia *spp. eggs after 10 days.*

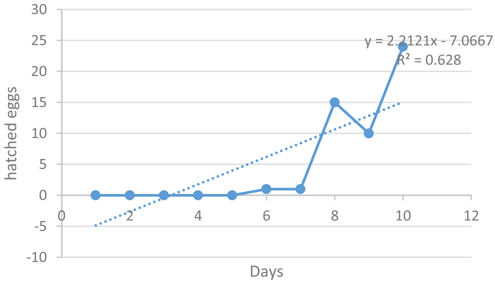

**Figure 5.**
*Graphic illustration of the effect of* Azadirachta indica *essential oil on the hatching rate of* Bemisia *spp. eggs after 10 days.*

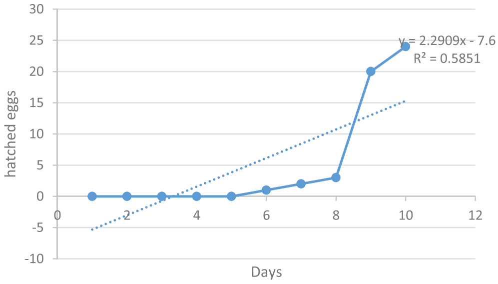

**Figure 6.**
*Graphic illustration of the effect of the joint action of the essential oils of* Azadirachta indica *and* Ricinus communis *on the hatching rate of* Bemisia *spp. eggs after 10 days.*

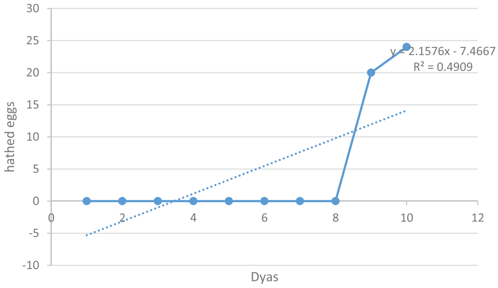

**Figure 7.**
*Graphic illustration of* Ricinus communis *essential oil on the hatching rate of* Spodoptera *spp. eggs after 10 days.*

The effect of *Azadirachta indica* oil on *Spodoptera* spp. demonstrates that the correlation was even weaker when we compare the effect of *Ricinus communis*. It was observed by the coefficient of determination ($R^2 = 0.41$). The change to the larval stage occurs mostly (about 80%) on the 10th day (**Figure 8**).

The effect of the joint action of essential oils on *Spodoptera* spp. demonstrates an even weaker correlation when we compare the isolated effects of *Ricinus communis* and *Azadirachta* indica. It was observed by the coefficient of determination ($R^2 = 0.35$). The change to the larval stage occurs mostly (about 90%) on the 10th day (**Figure 9**).

The effect of *Azadirachta indica* oil on *Sordidus* spp. demonstrates similarity with previous experiments, as regards the coefficient of determination ($R^2 = 0.48$), where

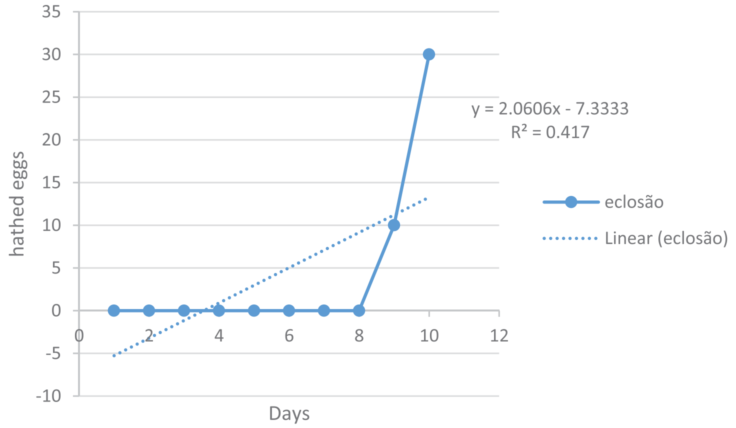

**Figure 8.**
*Graphic illustration of* Azadirachta indica *essential oil on the hatching rate of* Spodoptera *spp. eggs after 10 days.*

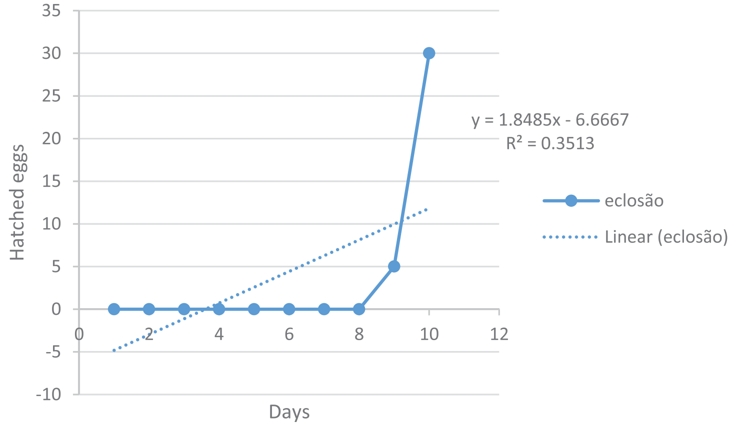

**Figure 9.**
*Graphic illustration of the effect of the joint action of the essential oils of* Azadirachta indica *and* Ricinus communis *on the hatching rate of* Spodoptera *spp. eggs after 10 days.*

there was no influence on the hatching rates of eggs. The change to the larval stage occurs mostly between the 9th and 10th day (**Figure 10**).

The effect of *Ricinus comunis* oil on *Sordidus* spp. demonstrates similarity with previous experiments, as regards the coefficient of determination ($R^2$ = 0.40), where there was no influence on the hatching rates of eggs. The change to the larval stage occurs mostly on the 10th day (**Figure 11**).

The effect of the joint action of essential oils on *Spodoptera* spp. demonstrates an even weaker correlation when we compare the isolated effects of *Ricinus communis* and *Azadirachta indica*. It was observed by the coefficient of determination ($R^2$ = 0.37). The change to the larval stage occurs mostly (about 90%) on the 10th day (**Figure 12**).

## 3.2 Effect on larval mortality

Regarding the effect of *Azadirachta indica* oil on the mortality of *Bemisia* spp., a strong correlation was observed in the experiment by the coefficient of determination

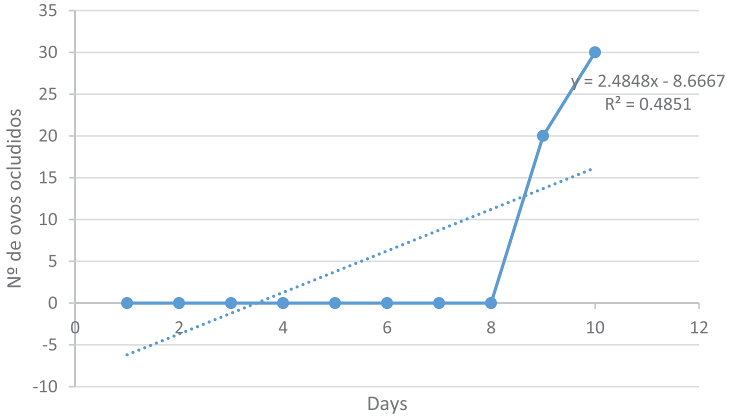

**Figure 10.**
*Graphic illustration of* Azadirachta indica *essential oil on the hatching rate of* Sordidus *spp. eggs after 10 days.*

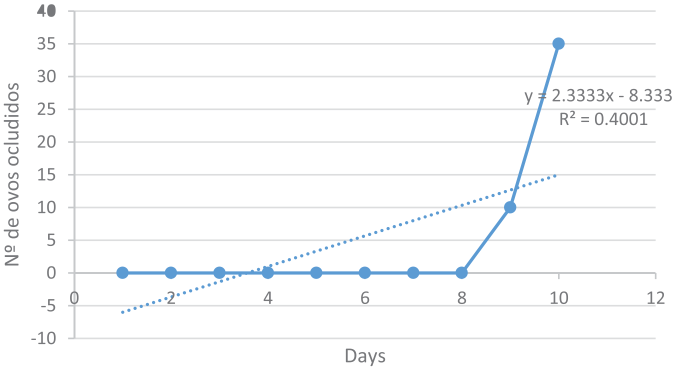

**Figure 11.**
*Graphic illustration of* Ricinus communis *essential oil on the hatching rate of* Sordidus *spp. eggs after 10 days.*

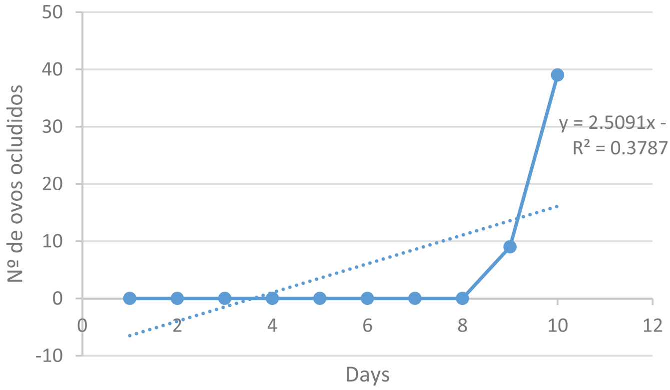

**Figure 12.**
*Graphic illustration of the effect of the joint action of the essential oils of* Azadirachta indica *and* Ricinus communis *on the hatching rate of* Sordidus *spp. eggs after 10 days.*

($R^2 = 0.85$). Fifty percent of the population of *Bemisia* spp. larvae dies on the 2nd day of exposure. Total mortality is finalized on the 7th day of exposure (**Figure 13**).

Regarding the effect of *Ricinus communis* oil on the mortality of *Bemisia* spp., a weak correlation was observed in the experiment by the coefficient of determination ($R^2 = 0.025$). Fifty percent of the population of *Bemisia* spp. larvae dies on the 6th day of exposure. Weak effect if we compare with the previous experiment, as the entire population of larvae dies on the 9th day of exposure. Total mortality is finalized on the 7th day of exposure (**Figure 14**).

The combined action demonstrates a similar effect as the isolated action of *Azadirachta indica*. It was observed that 50% of the population dies on the second day of exposure, but the entire population disappears between the 5th and 6th day of exposure. A strong positive correlation was also observed by the coefficient of determination ($R^2 = 0.82$) (**Figure 15**).

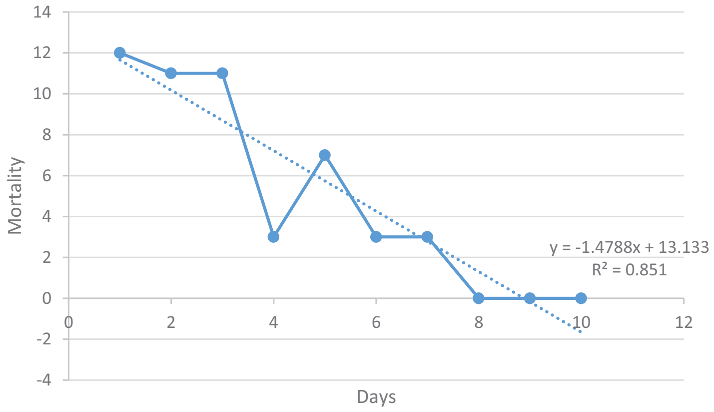

**Figure 13.**
*Graphic illustration of the effect of the essential oil of* Azadirachta indica *on the mortality of* Bemisia *spp., during 10 days.*

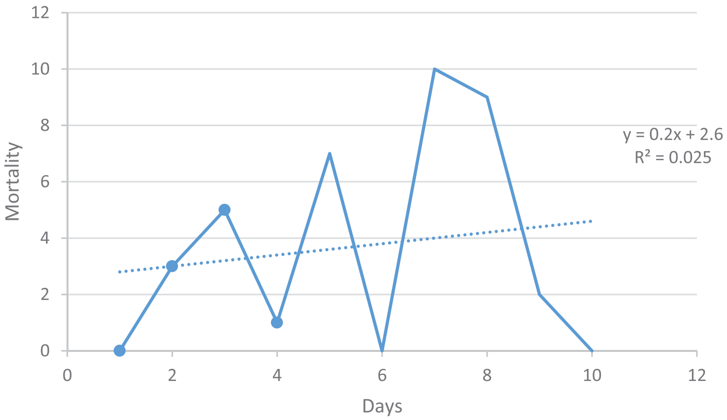

**Figure 14.**
*Graphic illustration of the effect of* Ricinus communis *essential oil on the mortality of* Bemisia *spp., during 10 days.*

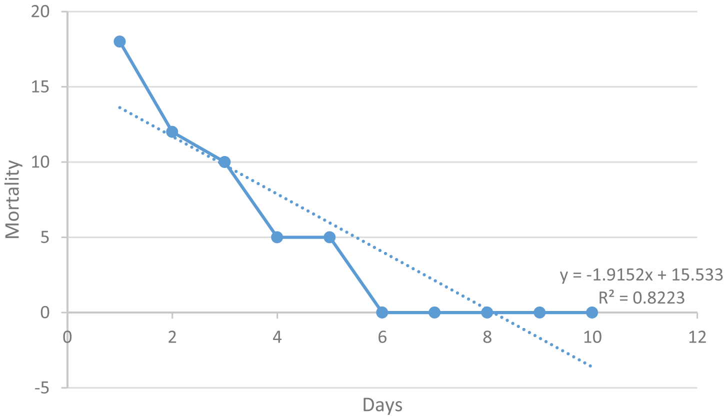

**Figure 15.**
*Graphic illustration of the effect of the joint action of* Azadirachta indica *and* Ricinus communis *essential oils on the mortality of* Bemisia *spp. after 10 days of exposure.*

The effect of *Azadirachta indica* oil on the mortality of *Spodoptera* spp. was similar to the effect on *Bemisia* spp., where a strong correlation was observed in the experiment due to the coefficient of determination ($R^2$ = 0.73). It was observed that around 50% of the population of *Spodoptera* spp. larvae dies on the 2nd day of exposure. Total mortality ends between the 7th and 8th day of exposure (**Figure 16**).

Similar to **Figure 10**, it was observed that the effect of *Ricinus communis* oil on the mortality of *Spodoptera* spp. is relatively smaller when compared to the effect of *Azadirachta indica*. For this experiment, 50% of the population dies on the 7th day, ending mortality on the 9th day of exposure (**Figure 17**).

The joint action proved to be very efficient on *Spodoptera* spp., as it appears that around 90% of the population dies on the 2nd day of exposure. Final mortality occurred on the 4th day of exposure (**Figure 18**).

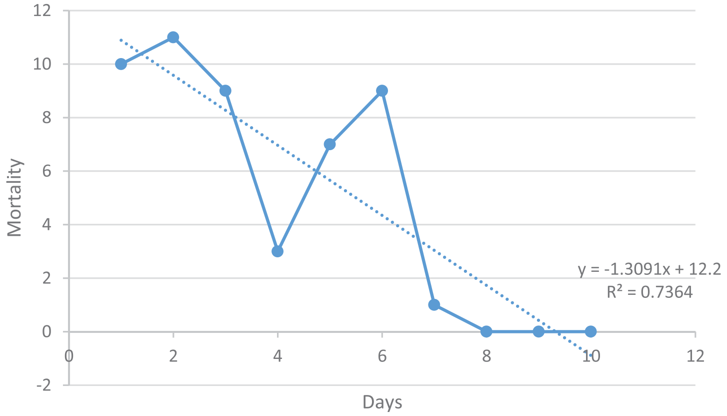

**Figure 16.**
*Graphic illustration of the effect of* Azadirachta indica *essential oil on the mortality of* Spodoptera *spp., for 10 days.*

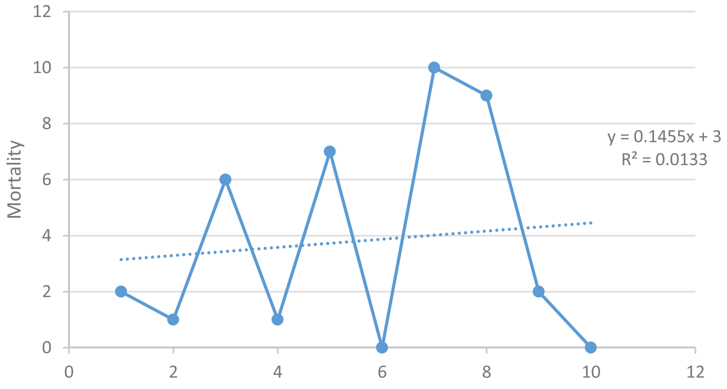

**Figure 17.**
*Graphic illustration of the effect of the essential oil of* Ricinus communis *on the mortality of* Spodoptera *spp., during 10 days.*

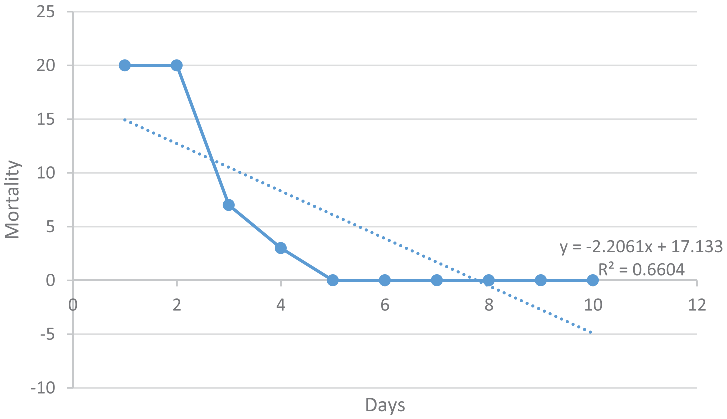

**Figure 18.**
*Graphic illustration of the effect of the joint action of the essential oils of* Azadirachta indica *and* Ricinus communis *on the mortality of* Spodoptera *spp. after 10 days of exposure.*

The effect of *Azadirachta indica* oil on the mortality of *Sordidus* spp. was similar to the effect on *Benisia* spp., a strong correlation was observed in the experiment by the coefficient of determination ($R^2$ = 0.89). It was observed that around 50% of the population of *Spodoptera* spp. larvae dies on the 2nd day of exposure. Total mortality is finalized on the 6th day of exposure (**Figure 19**).

Similar to previous *Ricinus communis* experiments. it was observed that the effect of *Ricinus communis* oil on the mortality of *Sordidus* spp. is relatively lower when compared to the effect of *Azadirachta indica*. For this experiment, around 50% of the larval population dies between the 7th and 8th day, with mortality ending on the 9th day of exposure (**Figure 20**).

The joint action proved to be very efficient on *Sordidus* spp., as it appears that around 90% of the population dies on the 2nd day of exposure. Final mortality occurred on the 5th day of exposure. A relatively minor result when compared to the graphs in **Figure 14** (**Figure 21**).

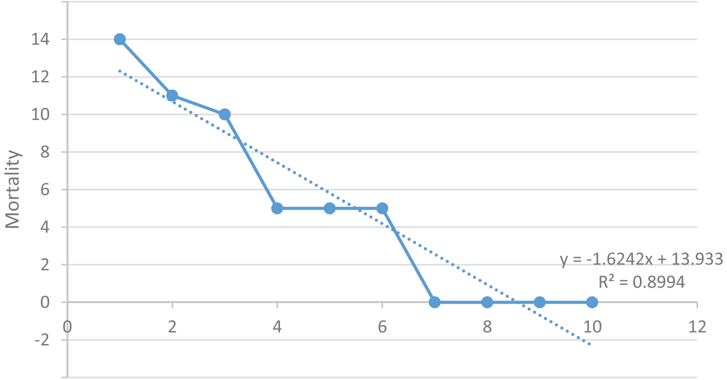

**Figure 19.**
*Graphic illustration of the effect of* Azadirachta indica *essential oil on the mortality of* Sordidus *spp. for 10 days.*

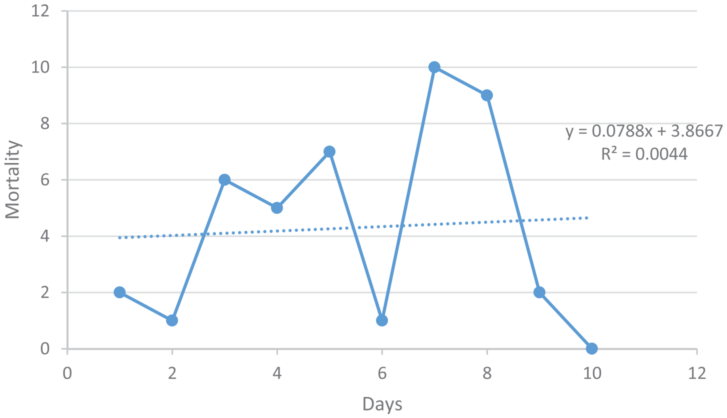

**Figure 20.**
*Graphic illustration of the effect of* Ricinus communis *essential oil on* Sordidus *spp. mortality, during 10 days.*

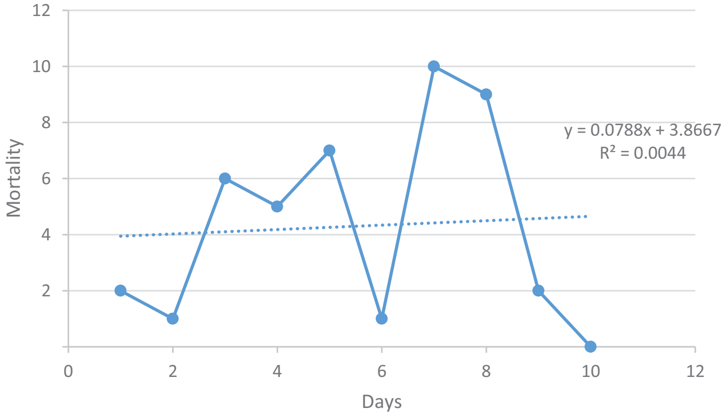

**Figure 21.**
*Graphic illustration of the effect of the joint action of* Azadirachta indica *and* Ricinus communis *essential oils on the mortality of* Sordidus *spp. after 10 days of exposure.*

## 4. Discussion

The effects of these plants have already been tested by other authors, like Peron and Ferreira [8], who evaluated the efficiency of *Ricinus communis* extract in controlling corn caterpillars, being more efficient at a concentration of 75%, where after eight days 75% of the caterpillars had died. Note that in this study similar results were obtained with *Ricinus communis* essential oil.

At higher concentrations of *Ricinus communis* extract, more precise results would be obtained, especially on occlusion rates. Santos et al. [9], when using an aqueous extract of castor bean leaves on eggs and fifth instar nymphs of the predator *Podisus nigrispinus*, showed that mortality from the extract was observed at concentrations of 7 and 10%, with the lowest survival rates being observed, with 30 and 10%, respectively.

The effect of *Ricinus communis* on other Hymenoptera has already been described, when Burg and Mayer [10], when studying the effect of *R. communis* seed oil on aphids and lice, described it as efficient in controlling these insects. The bioinsecticide activity of this vegetable was also studied by Murdue [11], in leaf-cutter ants, verifying its efficiency in combating them. Barroso [5, 6], when studying the effect of the aqueous extract of green castor beans on larvae and pupae of *Spodoptera frugiperda*, observed a reduction in the life span of these stages, and Góes et al. [12] identified a toxic effect of *R. communis* leaf extracts on *Apis mellifera* worker larvae, using castor oil.

The efficacy of *A. indica* seed oil on three stages of development of *Lutzomyia longipalpis* was evaluated, demonstrating insecticidal activity on all stages tested. With regard to ovicidal activity, Abdel-shafy and Zayed [13] observed, when treating eggs of the tick *Hyalomma anatolicum excavatum*, a significant deleterious effect on the embryonation of eggs with the compound Neem-Azal F with hatching rates varying from 34 to 60%, 15 days after treatment. Regarding the larvicidal effect, 67.75 ± 2.21% of the larvae did not reach the pupal stage. The lethal concentration 50 (LC50) verified in these studies for larvae was 60.98 (45.93–91.62) mg $mL^{-1}$.

Several studies have been carried out in recent years to elucidate the changes in the endocrine control mechanism induced by azadirachtin, which cause the effects observed in growth inhibition. These studies made it possible to identify changes in the levels of morphogenetic hormones such as ecdysone [14].

A marked structural similarity was identified between ecdysone and azadirachtin; however, it is not clear whether the effects on these hormonal levels are direct or indirect [14].

Some evidence indicates that azadirachtin can block the release of several substances located in the central nervous system, as well as the formation of chitin, a polysaccharide that forms the exoskeleton of insects, in addition to preventing sexual communication, causing sterility and decreasing intestinal motility [14].

Barroso [5, 6, 15] demonstrated that there is greater effectiveness of the joint action of essential oils, causing 96, 100 and 100%, in concentrations of 1, 1.5 and 2.0 ml, respectively, in 24 h. A relatively smaller difference when Azadirachta essential oil was used alone indicates that it caused mortality of 65, 97 and 100% at concentrations of 1, 1.5 and 2 ml, respectively. The lowest efficacy observed was that of *Ricinus communis* essential oil, causing mortality of 10, 63 and 100% at the same concentrations described and at the same time, but still with great significance.

Barroso's studies [5, 6, 15] also corroborate the results of Amer and Mehlhorn [16], where the authors evaluated the larvicidal potential of 41 essential oils, analyzing this effect after 1, 12 and 24 h. More than 48% of these oils only acted after 12 h of exposure, that is, not during the first few hours.

After this approach, it is logical to conclude that the fight against pests will be directed toward sustainability if we fully exploit the properties of *Ricinus communis* and *Azadirachta indica*. In the reported studies, it was possible to note that both have general effects against insects. More studies should be carried out on *Ricinus communis* and on the joint action of both plants.

Another fact is the abundance of these vegetables, where we can find them widely distributed, in most continents. This will allow, from an economic point of view, to promote and use more sustainable practices in the management and control of pests in agriculture.

## 5. Conclusion

After the experiments, the following was concluded:

The essential oils of *Ricinus communis* are effective on the mortality of *Bemisia* spp., *Spodoptera* spp. and *Sordidus* spp. larvae, reaching 100% mortality in 7, 9 and 9 days of exposure, respectively.

The essential oils of *Azadirachta indica* are effective on the mortality of *Bemisia* spp., *Spodoptera* spp. and *Sordidus* spp. larvae, reaching 100% mortality in 9, 7 and 6 days of exposure, respectively.

The *Azadirachta indica* and *Ricinus communis* solution was the most effective in achieving mortality on *Bemisia* spp., *Spodoptera* spp. and *Sordidus* spp. in 5, 4 and 5 days, respectively.

No significant effects of the essential oils on the hatching rates of eggs of the three evaluated species were observed, but the bibliography admits this possibility if the concentration of the active principle of azadirachtin or ricin is increased.

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## Chapter 5

# Pesticide Exposure and Neurobehavioral Performance among Paddy Farmers

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## Abstract

The study aims to assess the potential risks and impacts of pesticide exposure on paddy farmers. Specifically, it focuses on evaluating the knowledge, attitude, and practices of these workers regarding pesticide exposure, as well as determining their neurobehavioral performance. This study adopted a questionnaire on knowledge, attitude, and practice and the workers were interviewed for their demographic information, health symptoms, and chemical exposure factors. The Neurobehavioral Core Test Battery assessment tools were used to evaluate neurobehavioral performance. About 43.9% of respondents had high knowledge of the pesticide used, 53.7% of them showed a concern level of attitude toward pesticide usage, and 68.3% of them indicated good practice while handling the pesticide. 48.8% of the workers showed underperformed neurobehavioral performance. The chi-square test revealed significant associations between neurobehavioral performance and spraying frequency ($p = 0.005$) and frequency of changing personal protective equipment (PPE) ($p = 0.05$). Overall, the study seeks to shed light on the level of risk, knowledge, attitudes, and practices among paddy rice workers regarding pesticide exposure. This information can guide the development of interventions and strategies to promote worker safety, minimize pesticide-related risks, and protect both human health and the environment.

**Keywords:** neurobehavioral, paddy farmers, pesticide exposure, knowledge, attitude, practices

## 1. Introduction

Pesticide is the most common and widely used in agriculture work which gives many benefits to the crops by giving high product quality yield and helps in preventing and controlling pests from causing any damage to the crops. The term pesticide covers a wide range of compounds including insecticides, fungicides, herbicides, rodenticides, molluscicides, nematicides, and others [1]. Pests, weeds, and plant diseases are responsible for considerable yield loss of various crop production in tropical Asian countries. World Health Organization (WHO) defined pesticides as chemical compounds used to protect crops from pests and plant diseases as well as to control weeds [2]. Based on statistical data, there are nearly 2.7 million metric tons of pesticides globally used in 2020 [3]. Malaysia itself recorded the usage of 44.1 thousand tons of pesticides in 2018, mainly on paddy, rubber, vegetables, fruits, and palm oil plantations [4]. Farmers, agricultural workers, and pesticide operators, in most parts of the world, were exposed to high incidences of poisoning and health hazards due to working with chemical pesticides in the past [5, 6]. Pesticide exposure was shown to correlate with adverse health effects, such as vomiting, diarrhea, skin irritation, and dizziness [6]. Various factors can impact the extent of pesticide exposure in real-field settings. These factors encompass the kind of crop cultivated, the specific pesticide utilized along with its physical and chemical characteristics, the spraying machinery employed, the adoption of personal protective gear, storage practices for pesticide products, proper disposal of empty containers, and the behaviors and expertise of those working with these substances [7]. Toxic chemical from pesticides gradually accumulates in body fat through dermal, oral, and respiratory routes due to improper handling, and it may pose long-term and chronic effects on human health [8]. On the other hand, it was estimated that 6.7% of agricultural workers in Malaysia are poisoned each year [9]. According to the report by the World Health Organization and the United Nations Environment Program, there are over 3 million chemical poisonings reported annually and 200,000 pronounced deaths worldwide due to pesticide exposure [10]. Chemicals also can alter neurobehavioral performance. Beyond the age of 28, there is a decline in nerve function every 5 years. This decline is attributed to the impact of harmful chemicals from pesticides, which can enter brain cells through various biological mechanisms. Consequently, nerve cell deterioration occurs, resulting in altered neurobehavioral functions [11]. The previous study has indicated that pesticides can lead to changes in neurotransmitter systems, ion channels, mitochondrial function, cholinergic mechanism, and free radical production, all of which contribute to impaired neurobehavioral functions in individuals. Furthermore, individuals with abnormal nutritional status have been found to exhibit poorer neurobehavioral performance compared to those with adequate nutritional conditions, likely due to endocrine disruption [11].

Moreover, previous studies highlighted the significant influence of insufficient training or education when handling pesticides. Despite the Malaysian government offering free certification in Good Agricultural Practices (GAP) to promote sustainable farming methods, there is a low uptake among rice farmers in obtaining MyGAP certification. Consequently, this low certification rate contributes to a decrease in the percentage of farmers adopting safe agricultural techniques for their crops [12]. Furthermore, providing comprehensive guidance to farmers regarding the use of chemical pesticides is crucial in mitigating the adverse effects of rice farming practices on human health, environmental impact, and the sustainability of paddy cultivation techniques. Besides, a study conducted in Bangladesh revealed that trained farmers, in contrast to their untrained counterparts, demonstrated increased adherence to safety protocols during pesticide handling [13]. This included actions like properly covering their bodies, changing and washing contaminated clothing used during spraying, and taking a bath after completing pesticide application. Delivering comprehensive training regarding pesticide knowledge, attitudes, and safety measures can positively impact both workers and the environment. Malaysia has prioritized its self-sufficiency policy concerning rice and paddy production. Throughout the Eleventh Malaysian Plan (2016–2020) and the National Agro-Food Policy (2011–2020), Malaysia has consistently implemented proactive and forward-thinking strategies to foster the growth of its paddy and rice sectors [14]. In Malaysia, paddy holds utmost significance within the food subsector for two primary reasons. Firstly, rice stands as the staple food for the majority of the population, with Malaysian adults consuming an average of 2.5 plates of white rice daily [15]. Secondly, within the paddy farming community, the crop serves as the primary source of income and sustenance, especially for small-scale farmers and landless agricultural workers. A study conducted in Kelantan revealed that it is the second state with significant granary areas in Malaysia, following Kedah. The Kemubu Agricultural Development Authority (KADA) was established in 1968 as part of the concerted efforts to bolster national food security and achieve self-sufficiency, aligning with the objectives outlined in the Agro-Food Policy (2011–2020) [16].

Evaluating the knowledge, attitude, and practice (KAP) regarding pesticide use among paddy farmers holds immense importance. This study seeks to gauge the KAP levels specific to this group, serving as a baseline dataset. The insights garnered aim to pinpoint interventions capable of improving farmers' KAP. Furthermore, the study outcomes could aid governmental agencies in understanding the KAP of paddy farmers, facilitating the development of more impactful training and educational initiatives tailored to this demographic.

## 2. Methodology

This cross-sectional study focused on paddy farmers in Kota Bharu district, Kelantan who utilized chemicals in their agricultural work. The inclusion criteria encompassed paddy farmers aged 18 years and above, actively engaged in full-time paddy field work and exposed to chemicals, while the exclusion criteria involved those with less than a year's experience in paddy farming and individuals unable to communicate in Bahasa Malaysia.

Data collection spanned from November 2022 to April 2023, aiming for a 5% margin of error and a 95% confidence level. Anticipating a 20% dropout rate, the estimated sample size was 120 respondents. The study employed a simple random sampling technique, selecting participants from a roster provided by KADA using a random number generator.

The written consent and a directory of farmers and farms in the Kota Bharu district were acquired by KADA. The study employed simple random sampling to choose the study location, while purposive sampling identified eligible paddy farmers who met the inclusion criteria. Subsequently, these individuals received a set of questionnaires in the Malay language. The questionnaires were distributed by the researchers at the paddy farmers' common gathering areas after their work hours, minimizing the need for them to travel elsewhere to participate. Questionnaires and neurobehavioral assessments, including the Neurobehavioral Core Test Battery (comprising various tests like Simple Reaction Time, Minnesota Manual Dexterity, Digit Span, Digit Symbol, Benton Visual Retention, Pursuit Aiming, and Trail Making), were administered in various paddy fields at the selected location. The time taken was 40–60 minutes. Before the assessment was conducted, explanation was given to make sure that all of the respondents understood what the tests were all about.

Ethical approval was obtained from both KADA and the University's Human Research Ethics Committees (USM/JEPeM/21010081 and USM/JEPeM/KK/23010025). Upon approval, researchers contacted unit leaders via WhatsApp apps to randomly select and approach paddy farmers. Participants received research information and consent forms before engaging in the questionnaire. The study ensured participant confidentiality, handling all identifiable information provided by participants with utmost confidentiality unless explicit consent was given for identification. No incentives or tokens were offered to participants, and there were no conflicts of interest. The collected data underwent analysis using IBM Statistical Package for Social Sciences version 27.0, following the completion of all questionnaires and assessments. Subsequently, data entry was performed for analysis. The socio-demographic information and health symptoms data of the respondents underwent univariate analysis. Descriptive statistics, including frequencies and percentages, were employed to present these findings. In evaluating the percentage of correct answers regarding knowledge, attitude, and practice on pesticide usage, Spearman's correlation analysis was utilized. Additionally, Pearson's Chi-square test analysis was conducted to ascertain the significance of association between selected chemical exposure factors and neurobehavioral performances among paddy farmers.

### 2.1 Questionnaire

The questionnaire utilized in this study, adapted from a previous study [17], comprised 53 questions divided into five sections:

i. Section A—Social Demographics: This section consists of 13 questions gathering personal information like age, gender, race, educational level, work experience period, frequency of pesticide spraying, and type of pesticide used (fungicide, rodenticide, or insecticide).

ii. Section B—Health Symptoms: Encompassing queries about 14 types of health symptoms experienced by participants in the past three months due to pesticide use, such as dizziness, nausea, vomiting, and blurred vision.

iii. Section C—Knowledge of Pesticide Usage: Assessing respondents' understanding of pesticide hazards, health effects, and long-term implications. Questions were structured as yes/no options and multiple-choice queries with scoring based on correct responses.

iv. Section D—Attitudes Toward Pesticide Usage: Exploring attitudes regarding personal protective equipment (PPE) use, safe handling procedures, and actions in response to visible symptoms. It includes yes/no queries and picture-based questions.

v. Section E—Practices Regarding Pesticide Usage: Evaluating practices related to safety precautions, training attendance, pesticide labeling, storage, and disposal. Questions were scored on a yes/no scale, and one question involved providing the correct answer.

The questionnaire's reliability was assessed using Cronbach's Alpha, yielding scores for knowledge ($\alpha = 0.669$), attitude ($\alpha = 0.800$), and practice ($\alpha = 0.657$) [17]. Additionally, a feasibility study was conducted to assess participants' comprehension and timing for questionnaire completion. **Table 1** depicts the classification for total scores in knowledge, attitude, and practice [18].

| Variables | Level | Score | Total Score (%) |
|---|---|---|---|
| Knowledge | High | 18–22 | 81–100 |
| | Moderate | 13–17 | 61–80 |
| | Low | 0–12 | 0–60 |
| Attitude | Concern | 17–20 | 81–100 |
| | Neutral | 13–16 | 61–80 |
| | Not concern | 0–12 | 0–60 |
| Practice | Good | 15–18 | 81–100 |
| | Fair | 11–14 | 61–80 |
| | Poor | 0–10 | 0–60 |

**Table 1.**
*Classification for knowledge, attitude, and practice total scores.*

## 2.2 Neurobehavioral core test battery (NCTB)

The health effects of farmers were evaluated through a neurobehavioral core test battery (NCTB). NCTB test estimated to take around 40–60 minutes included seven tests, which were Digit Symbol, Digit Span, Pursuit Aiming, Trail Making, Benton Visual Retention, Simple Reaction Time, and Minnesota Manual Dexterity. The assessment conducted through operational guidelines from the World Health Organization was used as a reference document to ensure a standard manner of assessment (WHO, 1986). All of these tests measure different domain functions, are independent of each other, and are done in series. The neurobehavioral raw test scores were computed using a formula developed by WHO (1986) to make them comparable to the tests and scores from other studies. **Table 2** depicts the neurobehavioral test components and the functional domains tested.

$$Standard\ score = \frac{(Raw\ \text{score} - \text{mean})}{\text{Standard deviation}}\, x\, 10 + 5 \qquad (1)$$

| Test | Domain tested |
|---|---|
| Benton visual retention | Visual perception/memory |
| Reaction time | Attention/response speed |
| Pursuit aim | Motor steadiness |
| Digit symbol | Perceptual-motor speed |
| Digit Span | Short-term auditory memory |
| Trail making | Motor and visual coordination/steadiness |
| Santa Ana manual dexterity | Manual dexterity |

**Table 2.**
*Neurobehavioral tests and the domain tested.*

## 3. Results

### 3.1 Socio-demographic information of the respondents

Out of the intended participants, only 41 farmers opted to take part in the study (response rate of 34.2%). The frequency distribution of responses indicates that the majority of respondents were male, accounting for 82.9% of the total participants. The remaining 17.1% were female. **Table 3** shows that the largest proportion of participants (41.5%) fell within the age range of 18 to 39, followed by the age range of 40 to 59 (34.1%), and 60–79 (24.4%). It was evident that the participants in this study varied in terms of age. In terms of body mass index (BMI), the majority of participants (58.5%) had a normal BMI, while 7.3% were underweight, 34.2% were overweight or obese. Regarding education level, 61.0% of the paddy farmers had completed upper secondary education, 34.1% had higher education, and 4.9% had no formal education. Among the participants, the majority (43.9%) had 1–10 years of work experience, followed by 22.0% participants with 21–30 years of experience, 19.5% participants with 11–20 years of experience, and 14.6% participants with 31–40 years of experience. Regarding pesticide handling training, 39.0% of individuals attended the program, while the remaining participants did not receive any training. In terms of pesticide usage, herbicides, fungicides, and rodenticides were the most used types (63.4%). 19.5% of participants used two types of pesticides, 9.8% of participants used only insecticides, and one participant (2.4%) used rodenticides. Regarding health problems, 56.1% of the paddy farmers reported having no health issues. The frequency of pesticide spraying varied among participants, with the "other" category being the most common response (24.4%). Some participants sprayed their crops every day and once a week (22.0%), once a month (19.5%), and once every two months (2.4%). The majority of participants (61.0%) only changed their protective equipment (PPE) when it was worn out. Others changed their PPE when it expired (24.4%) or based on other methods such as "two times in a year," "sometimes," and "when needed to change PPE" (7.3%). A small percentage changed their PPE once a year (4.9%), while some participants reported never changing their PPE (2.4%).

### 3.2 Health symptoms of the participants

Based on **Table 4**, approximately, 11 participants (26.8%) reported experiencing excessive sweating in the preceding three months. The second most prevalent health issue was skin redness, with 19.5% of participants reporting this symptom. Cough was reported by 17.1% of participants, while headache and numbness in the legs were experienced by 14.6% of participants. Stomach pain, redness of eyes, and blurred vision were each reported by 12.2% of participants. A sore throat was reported by 9.8% of participants. Chest pain, numbness in the hand, and breathing difficulty were each experienced by 7.3% of participants, while a runny nose was reported by 4.9% of participants.

### 3.3 Distribution of levels of knowledge, attitude, and practice on pesticide usage

**Table 5** depicts the distribution of scores for knowledge, attitude, and practices. In the knowledge category, 18 participants (43.9%) demonstrated high to moderate levels, while 5 participants (12.2%) exhibited a low level of knowledge.

| Variables | Mean ± SD | n | Percentage (%) |
|---|---|---|---|
| Gender | | | |
| Male | | 34 | 82.9 |
| Female | | 7 | 17.1 |
| Age (years old) | 45.17 ± 14.731 | | |
| 18–39 | | 17 | 41.5 |
| 40–59 | | 14 | 34.1 |
| 60–79 | | 10 | 24.4 |
| BMI | 23.5211 ± 4.47450 | | |
| Underweight | | 3 | 7.3 |
| Normal | | 24 | 58.5 |
| Overweight/obese | | 14 | 34.2 |
| Race | | | |
| Malay | | 41 | 100 |
| Chinese | | 0 | 0 |
| Indian | | 0 | 0 |
| Nationality | | | |
| Malaysian | | 41 | 100 |
| Education level | | | |
| No formal education | | 2 | 4.9 |
| Primary level | | 0 | 0 |
| Secondary level | | 25 | 61.0 |
| Tertiary level | | 14 | 34.1 |
| Working experience (years) | 17.61 ± 11.563 | | |
| 1–10 | | 18 | 43.9 |
| 11–20 | | 8 | 19.5 |
| 21–30 | | 9 | 22.0 |
| 31–40 | | 6 | 14.6 |
| Attend training program on pesticide handling | | | |
| Yes | | 16 | 39.0 |
| No | | 25 | 61.0 |
| If YES, the agency involved | | | |
| Department of Occupational Safety and Health | | 0 | 0 |
| State department of agriculture | | 1 | 2.4 |
| State health department | | 0 | 0 |
| NIOSH | | 0 | 0 |
| Department of KADA | | 3 | 7.3 |
| Two agencies | | 9 | 22.0 |
| Three agencies | | 2 | 4.9 |
| Others | | 1 | 2.4 |

| Variables | Mean ± SD | n | Percentage (%) |
|---|---|---|---|
| Types of pesticide used | | | |
| Herbicide | | 2 | 4.9 |
| Insecticide | | 4 | 9.8 |
| Rodenticide | | 1 | 2.4 |
| Two types of pesticide | | 8 | 19.5 |
| Three types of pesticide | | 26 | 63.4 |
| Health problems | | | |
| One disease | | 14 | 34.2 |
| Two diseases | | 3 | 7.3 |
| Three diseases | | 1 | 2.4 |
| No disease | | 23 | 56.1 |
| Frequency of spraying pesticide | | | |
| Everyday | | 9 | 22.0 |
| Once a week | | 9 | 22.0 |
| Once a month | | 8 | 19.5 |
| Once per two months | | 4 | 9.8 |
| Once per six months | | 1 | 2.4 |
| Other | | 10 | 24.4 |
| Frequency in changing of PPE | | | |
| Worn out | | 25 | 61.0 |
| Expired | | 10 | 24.4 |
| Once a year | | 2 | 4.9 |
| Never | | 1 | 2.4 |
| Others | | 3 | 7.3 |

**Table 3.**
*Socio-demographic distribution of the respondents (N = 41).*

| Health symptoms | n | Percentage (%) |
|---|---|---|
| Headache | 6 | 14.6 |
| Cough | 7 | 17.1 |
| Nausea/vomiting | 2 | 4.9 |
| Redness of skin | 8 | 19.5 |
| Breathing difficulty | 3 | 7.3 |
| Blurred vision | 5 | 12.2 |
| Seizure | 0 | 0 |
| Runny nose | 2 | 4.9 |
| Chest pain | 3 | 7.3 |
| Sore throat | 4 | 9.8 |

| Health symptoms | n | Percentage (%) |
|---|---|---|
| Redness of eyes | 5 | 12.2 |
| Stomach pain | 5 | 12.2 |
| Numbness in legs | 6 | 14.6 |
| Numbness in hands | 3 | 7.3 |
| Excessive sweating | 11 | 26.8 |

**Table 4.**
*Health symptoms on the use of pesticides (N = 41).*

| Variables | Level | n | Frequency (%) |
|---|---|---|---|
| Knowledge | High | 18 | 43.9 |
| | Moderate | 18 | 43.9 |
| | Low | 5 | 12.2 |
| Attitude | Concern | 22 | 53.7 |
| | Neutral | 10 | 24.4 |
| | Not concern | 9 | 22.0 |
| Practice | Good | 28 | 68.3 |
| | Fair | 9 | 22.0 |
| | Poor | 4 | 9.8 |

**Table 5.**
*Distribution of knowledge, attitude, and practice levels (N = 41).*

Concerning attitudes toward pesticide usage, 22 individuals (53.7%) reached a concern level, while 10 participants (24.4%) achieved a neutral level, and 9 participants (22.0%) showed no concern.

Regarding practices, 28 people (68.3%) demonstrated good levels of pesticide usage, while 9 participants (22.0%) exhibited fair levels, and 4 participants (9.8%) showed poor levels of practices. Overall, fair levels (53.7%) were predominant among the participants, followed by high levels (46.3%) in the combined assessment of knowledge, attitude, and practices.

### 3.4 Correlation between knowledge, attitude, and practice

**Table 6** presents Spearman's correlation analysis, indicating that there was no significant correlation (p = 0.097) between the level of knowledge and attitude toward pesticide usage among paddy farmers. However, a moderate positive and statistically significant correlation (r = 0.426, p = 0.005) emerged between knowledge and practices related to pesticide usage. This suggests that a higher level of knowledge was associated with greater adherence to safe practices, indicating a significant correlation between knowledge and practices.

The analyses supported a notable relationship between knowledge and practices, implying that an increase in knowledge might lead to higher adherence to safe practices regarding pesticide usage. Additionally, the correlation analysis unveiled a moderate positive and statistically significant correlation (r = 0.380, p = 0.014)

| Variables | | Knowledge | Attitude | Practice |
|---|---|---|---|---|
| Knowledge | r | — | 0.263 | 0.426* |
| | p-value | — | 0.097 | 0.005 |
| Attitude | r | 0.263 | — | 0.380* |
| | p-value | 0.097 | — | 0.014 |
| Practices | r | 0.426* | 0.380* | — |
| | p-value | 0.005 | 0.014 | — |

**Significant at $p < 0.05$, Statistical test Spearman's correlation.*

**Table 6.**
*Distribution scores of knowledge, attitude, and practice on pesticide usage (N = 41).*

between attitudes and practices concerning pesticide usage. This finding signifies that a stronger adherence to positive attitudes was linked to safer practices regarding pesticide usage. The analyses also supported a significant correlation between practices and attitudes, suggesting that an increase in positive attitudes might result in higher levels of safe practices in the context of pesticide usage among paddy farmers.

### 3.5 Neurobehavioral performance

**Table 7** highlights that the majority of respondents exhibited abnormal performances in Minnesota Manual Dexterity (Preferred Hand) and Pursuit Aiming (48.8%), while most obtained normal scores in Minnesota Manual Dexterity (Nonpreferred Hand) (68.3%). The mean score (mean = 50) derived from the Neurobehavioral Core Test Battery (NCTB) test can serve as an indicator of each participant's neurobehavioral performance.

| Neurobehavioral Test | Neurobehavioral performance | | | |
|---|---|---|---|---|
| | Normal | | Abnormal | |
| | n | % | n | % |
| Simple Reaction Time | 27 | 65.9 | 14 | 34.1 |
| Minnesota Manual Dexterity (Preferred Hand) | 21 | 51.2 | 20 | 48.8 |
| Minnesota Manual Dexterity (Non-preferred Hand) | 28 | 68.3 | 13 | 31.7 |
| Digit Span | 22 | 53.7 | 19 | 46.3 |
| Digit Symbol | 17 | 41.5 | 24 | 58.5 |
| Benton Visual Retention | 26 | 63.4 | 15 | 36.6 |
| Pursuit Aiming | 21 | 51.2 | 20 | 48.8 |
| Trail Making (Part A) | 24 | 58.5 | 17 | 41.5 |
| Trail Making (Part B) | 23 | 56.1 | 18 | 43.9 |
| **Neurobehavioral Performance** | **21** | **51.2** | **20** | **48.8** |

**Table 7.**
*The distribution of neurobehavioral performance among respondents.*

### 3.6 The association between selected chemical exposure factors and neurobehavioral performances among paddy farmers

The study did not establish significant associations between several exposure factors, such as the type of chemical used, spraying time, duration, working experience, smoking habits, and changing clothes after handling chemicals with neurobehavioral performance ($p > 0.05$) (**Table 8**). Similarly, the practices of washing hands and taking a bath after handling chemicals did not yield statistically significant data due to consistent responses. However, amidst these factors, two variables exhibited notable statistical relevance.

The frequency of pesticide spraying and the frequency of changing personal protective equipment (PPE) demonstrated significant associations. Neurobehavioral performance correlated significantly with the frequency of pesticide spraying, ($p = 0.005$). Additionally, the frequency of changing PPE exhibited a noteworthy relationship, although slightly less significant ($p = 0.05$). These findings, as detailed in **Table 8**, underscore the importance of these particular factors concerning the studied outcomes.

| | **Neurobehavioral performance** | | | | |
|---|---|---|---|---|---|
| **Factors of pesticide exposure** | **Normal, n (%)** | **Abnormal, n (%)** | **Total, n (%)** | **p-value** | **$X^2$** |
| Frequency of chemical type | | | | | |
| Used 1–2 chemical | 5 (71.4%) | 2 (28.6%) | 7 (100%) | 0.168[a] | 3.928 |
| Used 3–4 Chemical | 3 (27.3%) | 8 (72.7%) | 11 (100%) | | |
| Used >4 Chemical | 13 (56.5%) | 10 (43.5%) | 10 (43.5%) | | |
| Spraying time | | | | | |
| Morning | 8 (42.1%) | 11 (57.9%) | 19 (100%) | 0.422[a] | 3.314 |
| Evening | 1 (3.33%) | 2 (66.7%) | 3 (100%) | | |
| Morning and Evening | 10 (58.8%) | 7 (41.2%) | 17 (100%) | | |
| Morning, Afternoon and Evening | 2 (100%) | 0 (0%) | 2 (100%) | | |
| Spraying frequency | | | | | |
| Everyday | 2 (22.2%) | 7 (77.8%) | 9 (100%) | 0.005a* | 0.010 |
| Once a week | 8 (88.9%) | 1 (11.1%) | 9 (100%) | | |
| Once a month | 1 (12.5%) | 7 (87.5%) | 8 (100%) | | |
| Once every 2 months | 3 (75%) | 1 (25%) | 4 (100%) | | |
| Once every 6 months | 1 (100%) | 0 (0%) | 1 (100%) | | |
| Others | 6 (60%) | 4 (40%) | 10 (100%) | | |
| Frequency of changing personal protective equipment | | | | | |
| Broken | 9 (36%) | 16 (64%) | 25 (100%) | 0.050[a,*] | 7.490 |
| Expired | 7 (70%) | 3 (30%) | 10 (100%) | | |
| Once a year | 1 (50%) | 1 (50%) | 2 (100%) | | |
| Never | 1 (100%) | 0 (0%) | 1 (100%) | | |
| Others | 3 (100%) | 0 (0%) | 3 (100%) | | |

| | Neurobehavioral performance | | | | |
|---|---|---|---|---|---|
| **Factors of pesticide exposure** | **Normal, n (%)** | **Abnormal, n (%)** | **Total, n (%)** | **p-value** | **$X^2$** |
| Spraying duration | | | | | |
| <1 hours | 3 (50%) | 3 (50%) | 6 (100%) | 0.910[a] | 0.309 |
| 1–2 hours | 8 (57.1%) | 6 (42.9%) | 14 (100%) | | |
| ≥2 hours | 10 (47.6%) | 11 (52.4%) | 21 (100%) | | |
| BMI | | | | | |
| Normal | 15 (62.5%) | 9 (37.5%) | 24 (100%) | 0.312 | 5.412 |
| Underweight | 2 (66.7%) | 1 (33.3%) | 3 (100%) | | |
| Overweight | 2 (20%) | 8 (80%) | 10 (100%) | | |
| Obesity | 2 (50%) | 2 (50%) | 4 (100%) | | |
| Smoking habit | | | | | |
| Active Smoker | 10 (62.5%) | 6 (37.5%) | 16 (100%) | 0.721[a] | 1.543 |
| Passive Smoker | 1 (50%) | 1 (50%) | 2 (100%) | | |
| Ex-smoker | 3 (37.5%) | 5 (62.5%) | 8 (100%) | | |
| Non-smoker | 7 (46.7%) | 8 (53.3%) | 15 (100%) | | |
| Change cloth after handling chemical | | | | | |
| Yes | 11 (44%) | 14 (56%) | 25 (100%) | 0.341 | 1.336 |
| No | 10 (62.5%) | 6 (37.5%) | 16 (100%) | | |

[a] *Using Fisher's Exact Test as Expected count <5 is more than 20% of the cells.*
**Significant at p-value <0.05.*

**Table 8.**
*The association between selected chemical exposure factors and neurobehavioral performances among paddy farmers.*

## 4. Discussion

The demographic findings from this study reveal that the majority of paddy farmers possess a secondary education level, indicating a considerable level of knowledge among this group. Their understanding of the effects of pesticides on human health aligns with earlier studies, supporting the notion that farmers with higher knowledge levels are aware of the negative impacts of pesticides on health [19, 20]. Interestingly, most farmers in this study had not undergone specific pesticide handling instruction, a trend observed in prior research where experienced farmers rely on past experiences rather than formal training [7].

Moreover, the data from this study indicated that a significant proportion (56.1%) of paddy farmers had over a decade of experience in paddy field agriculture. This finding is consistent with previous research where respondents had substantial experience in farming, indicating a deep understanding of agricultural practices and pesticide use [21]. Experience in the rice farming sector for more than ten years has been associated with expertise in agricultural techniques and pesticide use, further emphasizing the significance of experience in shaping knowledge and practices related to pesticide management [22].

Collectively, these findings underscore the importance of both education and extensive experience in shaping farmers' knowledge, understanding, and practices regarding pesticide usage. While formal training may not be prevalent among experienced farmers, their accumulated practical knowledge plays a pivotal role in pesticide management, highlighting the valuable contribution of hands-on experience to effective pesticide handling and agricultural practices.

Pesticide mishandling poses significant health risks to agricultural workers, as indicated by previous studies that reported that 58.8% of farmers experienced pesticide-related poisoning symptoms like headaches and vomiting [23]. Similar symptoms, such as headaches, vomiting, dizziness, and abdominal discomfort, were corroborated by other studies [24]. Extensive research on the hazards of pesticides likely contributes to the farmers' comprehensive understanding of these health risks. However, it is crucial to note that these symptoms could also stem from various factors like weather conditions, prolonged sunlight exposure, or underlying medical conditions. In this study, excessive sweating (26.8%) was the most reported symptom, potentially influenced by the hot weather during data collection in Kelantan. Additionally, using multiple products on a single spraying day, whether in combination or separately, could result in cumulative or combined exposures to various chemicals with similar toxicological effects. This multi-product use might elevate toxicity compared to employing a single active chemical alone.

Increased knowledge and improved attitudes toward pesticide handling may enhance the workers' capacity to self-report health symptoms associated with pesticides. Despite this awareness, some workers neglect to wear a full set of Personal Protective Equipment (PPE) while handling pesticides. Ndayambaje et al. discussed the low frequency of wearing PPE among farmers, citing reasons such as boots getting stuck in mud, and hindering compliance with recommendations [25].

While self-reported symptoms are considered unreliable predictors of pesticide poisoning [26], monitoring blood acetylcholinesterase (AChE) levels is suggested. However, interpreting AChE levels can be challenging as they primarily reflect organophosphate and carbamate exposure. Moreover, conducting blood tests in field locations with a high prevalence of blood-borne illnesses poses risks to researchers, such as exposure to HIV and HepB.

Overall, these findings emphasize the multifaceted challenges in mitigating pesticide-related health risks among agricultural workers, ranging from symptom attribution to the practical limitations of using biomarkers for exposure assessment in field settings.

The findings of this study suggest a relatively uniform level of knowledge among paddy farmers, with 43.9% demonstrating a "high" or "moderate" level. However, concerns arise regarding potential risks due to inadequate information about pesticide hazards [27] and insufficient education on appropriate pesticide usage procedures, encompassing storage, handling, and disposal [23]. Addressing these gaps is crucial through the implementation of educational initiatives and recycling programs focused on the proper management of empty pesticide containers and chemical waste.

Comprehensive knowledge plays a pivotal role in fostering safe and sustainable pesticide management and preventing subterranean water contamination [28]. Notably, the study highlights diverse sources of knowledge acquisition among farmers, primarily through interactions with retailers (52.63%), fellow farmers (25.73%), and consultancies (21.64%) [22].

Regarding attitude, incidents occurring in paddy fields have discouraged poisoned farmers from reporting injuries to healthcare facilities due to factors such as financial constraints, perceived mild severity, or inadequate access to healthcare services [29]. In terms of practices, while the general population mostly faces pesticide exposure through contaminated food and water, individuals living near pesticide-using areas or carrying contaminated items home may also experience significant exposure [30].

The ability of farmers to make informed decisions and execute proper practices relies heavily on their knowledge regarding pesticide classification, application rates, re-entry periods, and storage. A study on the Gaza Strip indicated that without adequate knowledge and practice on these aspects, farmers struggle to make informed choices and adopt proper practices [31].

Attending safe pesticide handling training emerges as a crucial factor in enhancing understanding among paddy farmers. Participation in such programs facilitates comprehension of various exposure routes (e.g., inhalation, ingestion, skin absorption) and the potential harm pesticides can cause. Furthermore, past research indicates that individuals with higher knowledge levels are more likely to adhere to prescribed recommendations for personal protective measures when using pesticides [18]. These insights underscore the pivotal role of education and training in shaping attitudes, and practices, and ultimately, ensuring safer pesticide handling among farmers.

The correlation analysis within this study did not reveal any significant relationship between the knowledge and attitudes of paddy farmers regarding pesticide usage, aligning with previous research findings. Despite considerable awareness among participants about the pesticides they use and their associated harmful effects, a notable percentage still refrained from using any pesticide applicator, potentially exposing themselves to health hazards [22]. This discrepancy in practices may stem from a lack of trust in information disseminated through media marketing compared to the guidance received from retailers and co-farmers [22].

The inefficacy of farmers' attitudes toward the use of personal protective equipment was highlighted in the previous study, indicating an absence of significant associations between knowledge, attitudes, and the actual use of protective equipment [32]. A high level of knowledge among farmers does not necessarily translate to a similarly high degree of positive attitude. Instances such as the erroneous placement of insecticides by some farmers (13.9%) might reflect a deficiency in technical knowledge and insufficient training in pesticide safety management [20].

Interestingly, a significant correlation was observed between the knowledge and practices of paddy farmers in pesticide usage, in line with prior research indicating that good knowledge typically translates into good practices in pesticide use [33]. However, findings contrasting high knowledge levels with poor practices among farmers, as observed in rural villages in Karnataka, suggest a disconnect between awareness and practical implementation. Despite understanding the harmful effects of pesticides, a significant percentage engaged in unsafe practices such as mixing pesticides with bare hands, not wearing protective clothing during spraying, and carelessly disposing of leftover pesticides [22].

This study accentuates the need for education and awareness programs specifically tailored to the local context, considering the distinct economic, social, and individual characteristics of the Malaysian farming community. Moreover, the significant correlation between attitudes and practices in pesticide usage implies that improving attitudes can positively influence the implementation of safer practices. Notably, the disposal methods of empty pesticide containers need revision, as burning or burying such containers poses risks to both human health and the environment, requiring an expansion of participants' knowledge of the appropriate waste management practices [33]. Additionally, the influence of peer learning and community experiences on pesticide users' attitudes and practices emphasizes the importance of peer influence in shaping their work-related techniques [18].

The study explored various factors associated with chemical exposure among paddy farmers and their potential impacts on neurobehavioral performance. Surprisingly, despite a significant number of respondents being smokers (39%) [34], no clear relationship between smoking and neurobehavioral performance was established. Nevertheless, previous studies have highlighted the detrimental effects of nicotine on brain function, nerve health, and arterial walls, which are aspects linked to neurobehavioral issues [34].

Regarding pesticide application, the timing and frequency significantly influence exposure levels and subsequent neurobehavioral effects [35]. Farmers predominantly applied pesticides during cooler periods like early mornings and evenings to ensure rapid drying and avoid vaporization, preventing unintended spread onto non-target surfaces [35]. The frequency of pesticide application varied among respondents, with many farmers spraying daily or infrequently [36]. This frequency correlated with the type of crop, pesticide variety, and pest infestation [36]. Higher pest prevalence necessitated more frequent spraying, leading to increased chemical exposure and elevated risks to neurobehavioral performance [37].

Notably, the duration of pesticide spraying did not exhibit a direct association with neurobehavioral performance in this study, despite the majority of farmers spending more than 2 hours spraying daily [38]. The World Health Organization recommends limiting lengthy spraying to 5–6 hours a day, emphasizing regular health checks due to increased chemical exposure and absorption during prolonged spraying [38].

Regarding personal protection equipment (PPE), while farmers wore it over their work clothes, it is essential to note that chemicals can still linger on clothing [39]. However, this study did not establish a significant relationship between washing clothes after handling chemicals and neurobehavioral performance [11]. This contrasts with previous research, highlighting the importance of proper clothes washing post-chemical exposure to prevent health symptoms or diseases among farmers who handle chemicals [39].

These findings emphasize the nuanced relationships between various factors like smoking, pesticide application timing, frequency, duration, and clothes washing concerning neurobehavioral performance among paddy farmers.

## 5. Conclusions

The primary objective of this study was to evaluate the knowledge, attitude, and practices concerning pesticide usage among paddy farmers in Kelantan. The findings underscored that 43.9% of the participants exhibited a commendable "high" and "moderate" level of knowledge, while 53.7% expressed a "concerned" attitude, and a majority, comprising 68.3%, demonstrated "good" practices in pesticide handling. Despite the predominant absence of health issues reported by most participants (56.1%), notable symptoms like excessive sweating (26.8%), skin redness (19.5%), cough (17.1%), headache, and numbness in the legs (14.6%) were observed, likely attributed to prevailing hot weather conditions. Statistically significant, moderate, and positive correlations were discerned between knowledge and practices ($r = 0.426$, $p = 0.05$), as well as between practice and attitude ($r = 0.380$, $p = 0.014$) among the paddy farmers about pesticide use. The study also noted that nearly half of the respondents displayed normal neurobehavioral outcomes (51.2%). Among the factors associated with pesticide exposure, both the frequency of spraying and the regularity of changing personal protective equipment (PPE) emerged as significant association with neurobehavioral performance ($p < 0.05$). The research highlighted that a significant proportion of respondents engaged in daily chemical application, a pattern associated with a higher incidence of abnormal neurobehavioral functioning. Moreover, those who reported changing their PPE only when it was damaged or broken exhibited elevated rates of abnormal neurobehavioral outcomes compared to individuals who consistently adhered to a routine replacement of protective gear. These findings underscore the critical need for interventions and enhanced safety measures among paddy farmers to mitigate the risks associated with frequent pesticide exposure, emphasizing the importance of both prudent spraying practices and regular replacement of personal protective equipment to safeguard neurobehavioral health.

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## Conflict of interest

The authors declare no conflict of interest.

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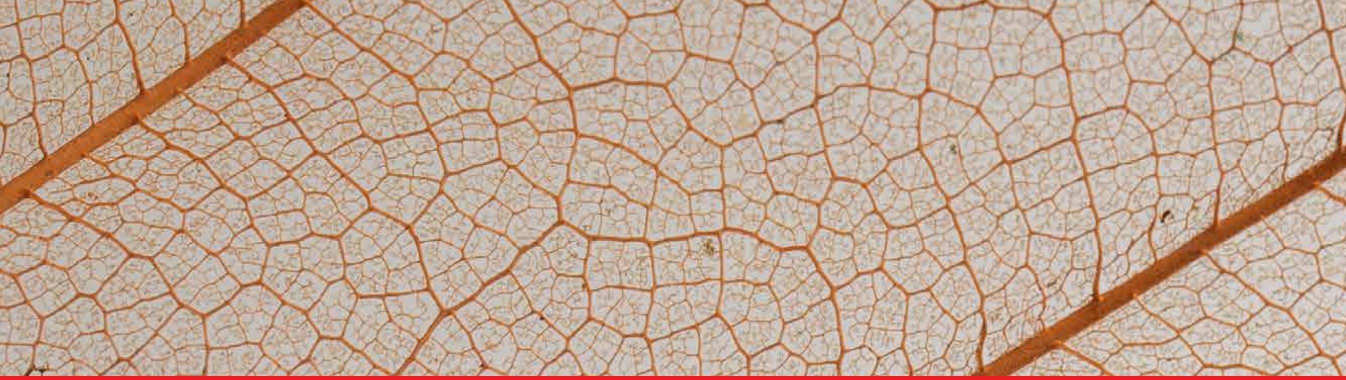

*Edited by Kassio Ferreira Mendes*

*Pesticides - Agronomic Application and Environmental Impact* is a seminal work that navigates the delicate balance between the indispensable role of pesticides in modern agriculture and the critical need for environmental preservation. In an era where food security and ecological sustainability are paramount, this book emerges as a beacon of knowledge and understanding. This volume encapsulates a comprehensive exploration of the world of pesticides, shedding light on their vital function in ensuring crop health and abundance. It addresses the core concerns surrounding the application of these chemicals, highlighting innovative approaches and strategies to reduce their ecological impact. The reader is guided through the intricacies of pesticide chemistry, application techniques, and the latest developments in minimizing environmental risks. Crafted with the expertise of leading professionals in the field, this book offers a holistic view of the subject matter. It is designed to cater to the interests of a diverse readership, including agricultural practitioners, environmental scientists, policymakers, and students. The content is rich with information yet accessible, making it an invaluable resource for anyone seeking to understand the interplay between agricultural productivity and environmental stewardship. The advantage of this book lies in its balanced perspective. It does not shy away from discussing the challenges and controversies surrounding pesticide use. Instead, it offers well-rounded insights and potential solutions, contributing significantly to the ongoing dialogue in this critical area. *Pesticides - Agronomic Application and Environmental Impact* stands as a testament to the possibility of harmonizing human agricultural needs with the imperative of ecological conservation, making it a must-read for those who are navigating these complex and essential topics.

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