CHAPTER 1: INTRODUCTION

1.1. General

Agriculture constitutes the basis of civilization, and although humankind has changed tremendously, agriculture is still of paramount significance. It has been associated with the production of basic food crops for decades. It forms the backbone of the Indian economy. In India, 58% of the population relies mainly on agriculture for their livelihood (Mohanty, 2017). Global food demand has increased exponentially due to the expanding human population. Many strategies for enhancing crop production have been adopted to increase agricultural yield. The use of agrochemicals is an important element in agriculture. Different types of agrochemicals used for crop yield enhancement have been exemplified in Figure 1.1.

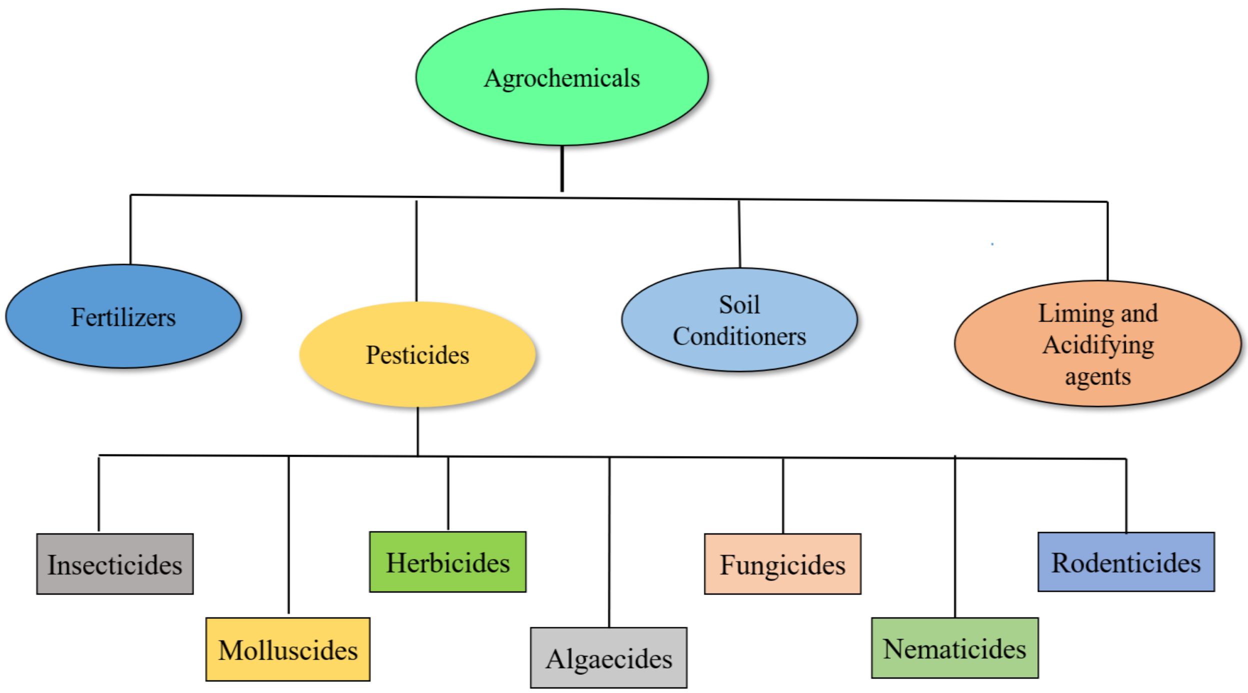


Figure 1.1: Agrochemicals used for enhancement of agricultural production

The development of agrochemicals was aimed to protect crops from pests and enhance agricultural production. The most commonly utilized agrochemicals are chemical fertilizers and pesticides. Pesticides are vital in modern agriculture as they are used in fields to minimize crop losses caused by undesirable insects or pests. Also, due to their effects on agronomic production and profit margin, pesticides play a significant role in contemporary agricultural practices. In addition, the world is currently experiencing a growing urbanization, which implies that less land will be set aside for agriculture, necessitating the enhancement in crop production.

Insect infestation results in considerable losses in food production every year. Effective pest management using chemical pesticides is one of the best strategies to boost crop output. Over the past few decades, there has been a gradual growth in the manufacture and application of pesticides worldwide, especially in developing nations such as Asia and Latin America. Every year, 4 million tons of pesticides are reportedly sprayed on crops worldwide to combat pests (Varah et al., 2020). The usage of various pesticides has a wide range of beneficial effects. The potential advantages are especially significant in developing nations, where agricultural and agricultural-related losses lead to hunger and malnutrition (Cooper and Dobson, 2007). Two categories of benefits are associated with using pesticides: primary and secondary. Primary benefits include the control of nuisance organisms, disease vectors and agricultural pests. Secondary benefits are less intuitively obvious and have long-term consequences such as food security, a wider range of viable crops, increased export revenues, increased habitable areas, etc.

1.2. Pesticides

Pesticides are toxic materials of a biological or chemical origin that are introduced into the environment to prevent, control, reduce, or eliminate the population of weeds, insects, rodents, fungi, and other undesirable pests. The term pest refers to any living thing (plants, animals, or bacteria) that has a detrimental effect on food, human health, comfort, and the economy (Mahmood et al., 2016). Pesticides are accredited in agriculture as effective tools for controlling pests and minimizing harm to crop plants and agricultural losses. The use of chemical pesticides and biological pesticides is widespread around the world. Numerous chemical pesticide classes with various applications and modes of action have been developed. Benzene hexachloride and Dichlorodiphenyltrichloroethane (DDT) were introduced in 1952 as the first insecticides manufactured in India. These pesticides were widely employed in both agricultural and urban environments.

1.2.1. Generations of pesticides

Pesticides are categorized into five generations. The first generation of pesticides was used before 1940 and included mercury, lead and arsenic. However, they were abandoned due to their low efficacy and high toxicity. The second generation of pesticides included synthetic organic compounds such as organophosphates, organochlorines and carbamates. The late 1940s saw an acceleration in the use of second-generation after the introduction of DDT. During this period, the effects of pesticides like 2,4-dichlorophenoxyacetic acid (2,4-D), aldrin, dieldrin, endrin, chlordane, parathion, and captan were also identified. Since those pesticides were highly effective at controlling pests, they were used extensively. However, gradually, people began to oppose the widespread application of these pesticides, particularly DDT, which kills non-target animals and plants (Umetsu and Shirai, 2020). The issue of residue and the potential health hazards became widely recognized by the public. Third-generation pesticides are altered forms of insect hormones with pest specificity, such as repellents. It includes pyrethroids, neonicotinoids and growth regulators. Biopesticides form the fourth generation of pesticides. Microbial and botanical sources are used to control pests in the fourth generation of pesticides. The fifth generation of pesticides involves genetic modification for the control of pests. Every generation of pesticides has positive and negative aspects. While previous generations were efficient, they frequently had environmental and health concerns. Newer generations, particularly biopesticides and genetically modified crops, seek to provide more specific and sustainable pest control solutions.

1.2.2. Classification of pesticides

Pesticides are classified based on their target pests (insecticides, herbicides, weedicides, rodenticides), mode of action, chemical structure/composition etc. (Hassan and Nemr, 2020). A detailed classification of agrochemicals, particularly pesticides, has been presented in Table 1.1 (Akashe et al., 2018).

Table 1.1: Classification of pesticides based on the target pest, chemical composition, mode of action and mode of entry

Pesticide	Description	Examples
Based on function/target organism		
Insecticides	Chemicals that either eliminate or deter insects and related pests	Malathion, imidacloprid, etc.
Herbicides	Chemical compounds that either eradicate unwanted weeds or inhibit them from growing in the field	Parquet, atrazine, etc.
Fungicides	Chemical agents that remove fungi and molds	Captan, captofol etc.
Rodenticides	Chemical compounds that eliminate moles, rats, mice, and other rodents	Anticoagulants, Arsenic, etc.

Nematicides	Compounds that destroy nematodes	Ethylene bromide,
Acaricides	Chemical substances that eradicate spiders, ticks and mites	Azobenzene, Chlorobenezilate
Molluscicides	Compounds capable of killing molluscs, including slugs and snails	Metaldehyde
Based on the chemical composition		
Organophosphates	Stable compounds that can build up in adipose tissue and are highly persistent in the environment.	Parathion, Malathion, etc.
Organochlorines	Chlorinated hydrocarbons that are extremely hazardous bioaccumulate and breakdown more slowly.	DDT, Endosufan, etc.
Carbamates	Organic substances derived from carbamic acid with the ability to reversibly inactivate acetylcholinesterase enzyme.	Carbofuran, Aldicarb, etc.
Triazines	Herbicidal insecticides that can be used as chemosterilants.	Atrazine, Metribuzin, etc.
Pyrethroids	Natural insecticides derived from pyrethrum extracts of chrysanthemum flowers.	Cypermethrin, Allethrin, etc.
Neonicotinoids	Neuro-active insecticides, chemically analogous to nicotine that are efficacious against certain insects.	Imidacloprid, Acetamiprid, etc.
Based on the mode of action		
Physical poison	Pesticides that kill insects by causing a physical change.	Activated clay
Protoplasmic poison	Pesticides that cause the precipitation of proteins.	Arsenicals
Respiratory poison	Chemical compounds that make respiratory enzymes inactive.	Hydrogen cyanide
Nerve poison	Chemical substances that hinder impulse conduction.	Malathion

Chitin inhibition	Chemicals that inhibit the synthesis of chitin in pests.	Diflubenzuron
Based on the mode of entry		
Systemic Pesticides	Pesticides that seep into untreated tissue after being absorbed by plants or animals and eliminate specific pests.	2,4 –D, imidacloprid
Stomach poisons	Chemicals that penetrate the pest's body via its oral cavity and the gastrointestinal tract.	Malathion
Fumigants	Pesticides that enter a pest's body through the trachea, may kill the target pest by producing a vapor.	Phosphine
Repellents	They are repulsive enough to keep pests away. Additionally, they obstruct the ability of the pest to locate crops.	Methiocarb
Contact pesticides	It acts when pests come into contact with it.	Paraquat, diquat

1.2.3. Production and usage of pesticides

Industrialized and developing nations utilize pesticides in very different ways. Several countries restrict or even prohibit the use of certain pesticides. The United States Environmental Protection Agency (USEPA) states that certain pesticides, such as lindane and carbofuran, are prohibited from being used in the country, while monocrotophos and chlordane are severely limited. Pesticide regulations range from nation to nation as well. In numerous developing nations, pesticides that USEPA has prohibited or outlawed, such as carbofuran, endosulfan, and monocrotophos, remain in use.

The amount of pesticides used globally per hectare of cropland increased from 2.1 kg/ha in the 2000s to 2.6 kg/ha in 2019. Pesticide use in India is roughly 0.5 kg/hectare, with organochlorine pesticides accounting for a significant portion of this usage (Kaur et al., 2022). India currently ranks 12th in the world and is the major producer of pesticides (Nayak and Solanki, 2021). The most widely used pesticides in India include those that are registered for use, such as atrazine, butachlor, carbendazim, chlorpyrifos, fipronil, imidacloprid, malathion, mancozeb, monocrotophos and quinalphos (Ministry of Agriculture and Farmers Welfare, Government of

India (2023), https://agricoop.gov.in/). Because of variables, including weather patterns, pest outbreaks, and modifications to farming methods, the amount of pesticides used each year may differ considerably. Figure 1.2 shows a graphical representation of the consumption of chemical pesticides and biopesticides in India in recent years (2017-2023).

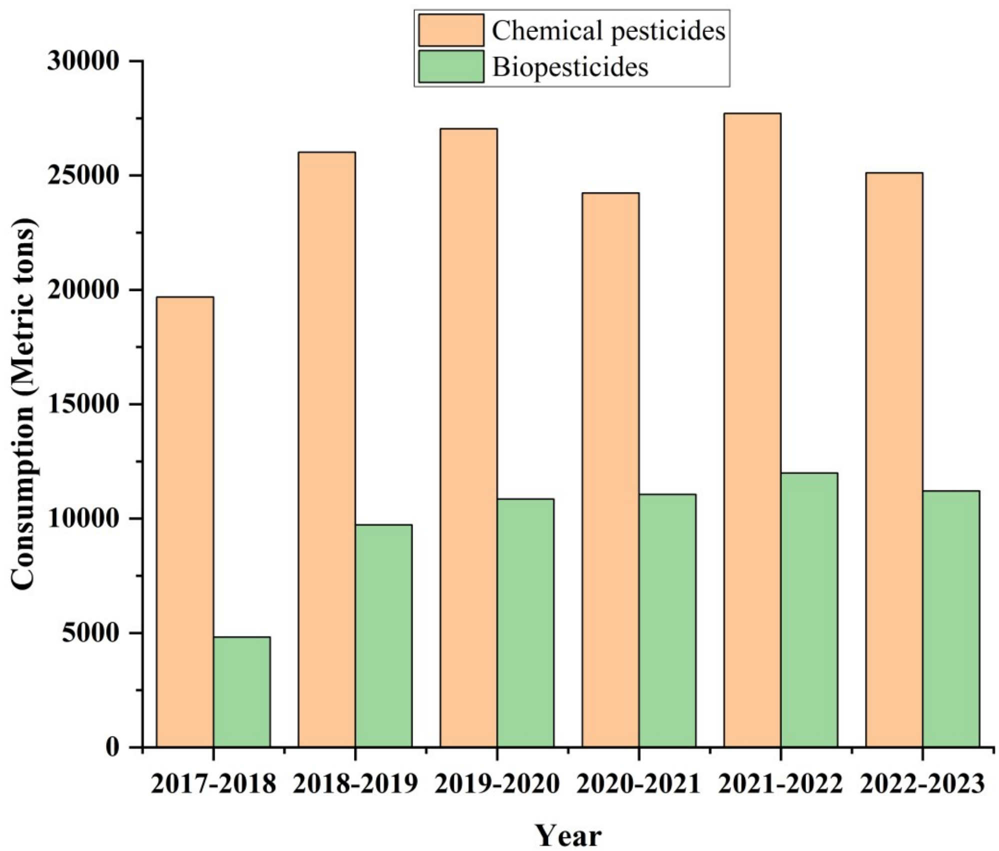


Figure 1.2: Consumption of chemical pesticides and biopesticides in recent years

According to Abhilash and Singh (2009), the world's pesticide usage has reached 2 million tons, of which 45% is used in Europe, 24% in the USA, and 25% in other parts of the world. According to the Food and Agriculture Organization, the use of pesticides worldwide increased by 36% between 2000 and 2019, reaching 4.2 million tons. Asia contributed the most (52-53%), followed by America, Europe, Africa, and Oceania. Over time, the proportions of each region in the global total varied slightly, but Asia continued to contribute the most. With 1.8 million tons or 42% of the global total, China was the largest consumer of pesticides in 2019, far more than the combined use of the US and Brazil (0.4 million tons each). In Asia, China is the largest consumer of pesticides, followed by India, Korea and Japan (Yadav et al., 2015). Herbicide is the most commonly used pesticide worldwide, but insecticide consumption is higher in India and other tropical nations (Abhilash and Singh, 2009). This results from an increase in insect pest attacks, mostly brought on by warm and humid weather.

Maharashtra, Uttar Pradesh, Punjab, Haryana, and Telangana are the leading pesticide-consuming states in India. A graphical representation of the state-wise pesticide consumption in India has been illustrated in Figure 1.3.

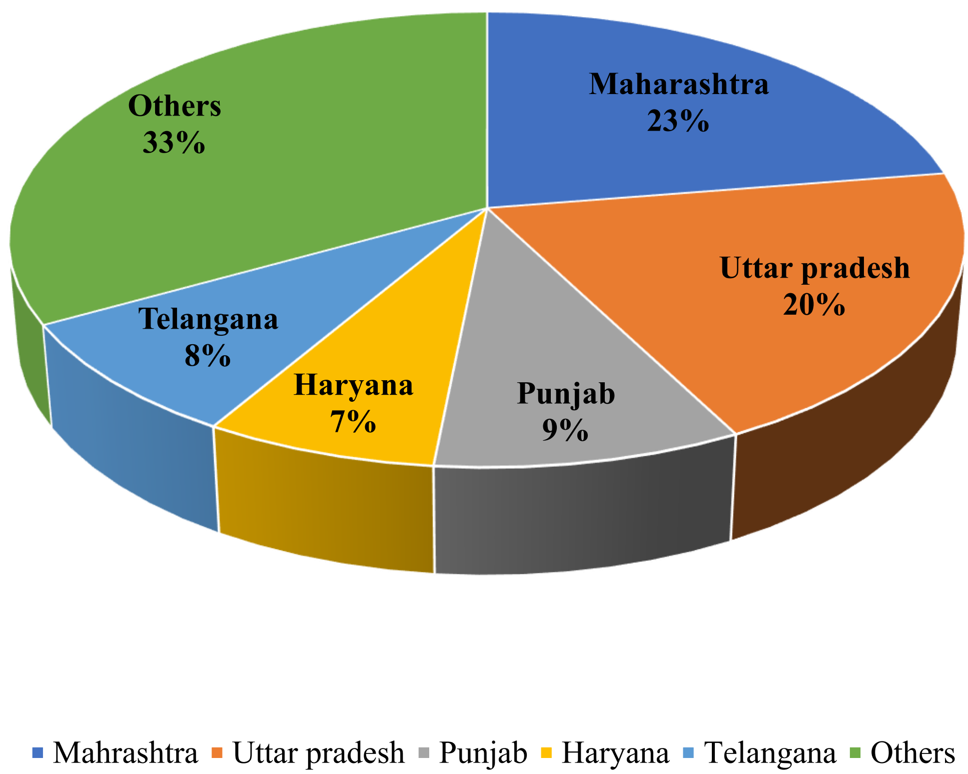


Figure 1.3: State-wise pesticide consumption in India (Ministry of Agriculture and Farmers Welfare, Government of India, 2023, https://agricoop.gov.in/)

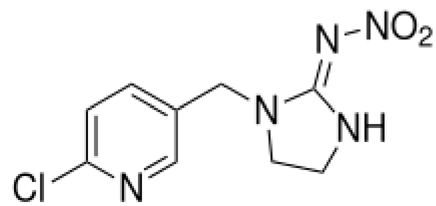
The export of agricultural commodities has been impacted in recent years by pesticide residue in several crops. In this context, some of the most significant strategies for reducing human exposure to pesticides and preserving soil fertility for appropriate productivity are integrated pest management, pesticide safety, regulation of pesticide use, along with suitable application technologies. Agricultural pests and diseases are managed with the use of biopesticides, which are derived from naturally occurring substances such as plants, animals, and microorganisms like bacteria, cyanobacteria, and microalgae. Because biopesticides are host-specific and environmentally friendly, they are significantly more advantageous to utilize than conventional chemical pesticides (Thakur et al., 2020).

Contrary to organochlorine insecticides, organophosphorus insecticides have recently surged due to the prohibition of certain organochlorine pesticides. Due to their extensive use in plant protection, neonicotinoid insecticides are now among the most popular pesticides (Bonmatin et al., 2015). Neonicotinoids represent a significant and prevalent chemical class of insecticides introduced to the international market. They are comparatively newer and are currently preferred because of their low toxicity and capability to target many pests. With an incredibly favorable toxicological profile, they account for around 25% of the global pesticide industry and have a very selective pest profile with relatively minimal threat to nontarget species (Zhang et al., 2023). Among the neonicotinoids, imidacloprid is one of the most widely used insecticides across the globe, especially in India.

1.3. Imidacloprid

Imidacloprid is a member of the class of nicotine-related insecticides known as neonicotinoids. It is a systemic insecticide that penetrates all plant sections at different growth phases, protecting the entire plant from insects during growth. Its strong insecticidal action at low application rates and physical characteristics have made it a widely accepted pesticide; however, since it is often sprayed over fields to protect crops, it is released into the environment. These compounds are becoming increasingly popular since they work differently from pyrethroid and organophosphate insecticides, helping prevent insect pests from developing a resistance to pesticides (Bass et al., 2015). Some physicochemical properties of imidacloprid have been represented in Table 1.2.

Table 1.2: Physico-chemical properties of Imidacloprid

Structure	

Chemical formula	$C_9H_{10}ClN_5O_2$
IUPAC name	1-(6-chloro-3- pyridylmethyl)-N-nitroimidazolidin-2-ylideneamine
Molar mass	255.661 g/mol
Appearance	Colorless crystals or Beige powder
Melting point	136.4 to 143.8°C
Solubility in water	0.61 g/L (20°C)
Density	1.54 g/cm^3
Soil sorption coefficient	156-960 (Mean value ranges from 249-336)

1.3.1. Mode of action

According to Jeschke et al. (2013), neonicotinoid pesticides are highly selective agonists of nicotinic acetylcholine receptors (nAChR) with targeted action against insect nervous systems. Because of their distinctive mode of action, these compounds are very effective at controlling insects that have become resistant to pyrethroids, carbamates, and organophosphates. In insects, imidacloprid affects motor neurons, overstimulates the nervous system, and ultimately results in insect death. Additionally, tests for reproductive toxicity revealed that imidacloprid is an agonist of the acetylcholine receptors, which control the endocrine system of the brain.

1.3.2. Production and application

The first neonicotinoid insecticide to enter the market was imidacloprid, also known as 1-(6-chloro-3-pyridylmethyl)-N-nitroimidazolidin-2-ylideneamine. Nihon Bayer Agrochem introduced imidacloprid in 1991, initiating the modern era of neonicotinoid insecticides. It is currently the most commonly used insecticide, applied to over 140 crops in over 100 nations (Liu et al., 2013; Drobne et al., 2008). Since imidacloprid is a Category II acute toxicant, it falls under the general-use pesticide category. Applications of imidacloprid as a foliar application, soil treatment, and seed dressing are widespread across a wide variety of crops worldwide. Initially designed for agricultural use in the 1990s, they are currently used to protect lawns, grains, cereals, fruits, and vegetables from a range of insects. After germination, imidacloprid is applied to the seeds to protect the roots of crops and seedlings.

1.4. Fate and disposition of pesticides in the environment

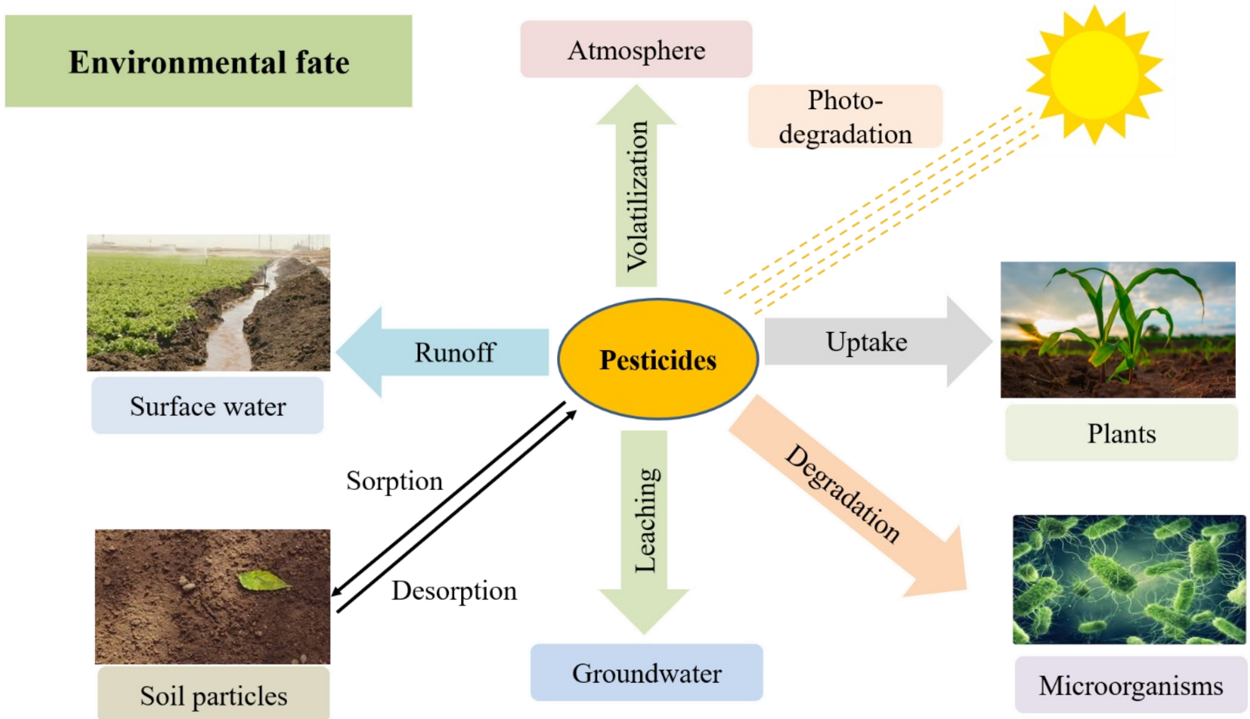


Figure 1.4: Fate of pesticides in the environment

Pesticides have a long-term effect on the environment; hence, it is particularly important to understand their fate in the soil. Only around 0.1% of the total amount of pesticides applied reach the target species; the remaining chemicals seep into the environment and disrupt the ecological balance (Bhende et al., 2023). Many pesticides leave behind low-concentration residues in the natural environment, although their use is only permitted if it can be shown that they do not linger in the environment. The physical and chemical characteristics significantly impact their persistence in the soil. Approximately 95% of applied herbicides and 98% of applied insecticides reach non-target soil microorganisms rather than their target pest since pesticides are sprayed proportionately throughout the entire field, regardless of the affected areas (Meena et al., 2020). The environmental fate of pesticides is represented pictorially in Figure 1.4.

Pesticide mobility and degradation processes can be affected by a range of biotic and abiotic factors, such as the amount of pesticide applied, physicochemical properties of the soil, degradation capacity of the soil microorganism, microbial diversity, behavior of pesticides in the soil, pesticide solubility in water and solvents, etc. (Khalid et al., 2020). Even after spraying in trees, some insecticides will invariably come in contact with soil flora and fauna. Thus, it can contaminate both surface and ground water through leaching and thereby accumulate in the food chain. A large portion of the pesticide applied gets released into the environment, leading to serious issues like accumulation and toxicity to organisms that are not the intended targets. As a consequence of direct or indirect exposures, contaminated soil, surface waters, and groundwater present risks to human health and the environment (Li et al., 2021).

The soil sorption processes that regulate pesticide transfer and bioavailability also play a significant role in determining the fate of pesticides in the environment. Pesticide behavior in soils is dependent on its persistence and retention in the soil. According to Singh et al. (2020), a significant number of frequently applied pesticides can accumulate and remain in the soil ecosystem or seep into groundwater. Furthermore, organic matter from plants that are can subsequently introduce pesticides into soil systems. Biological data, such as the abundance of bacteria and fungi, can also evaluate the fate of pesticides since microorganisms transform the toxic pesticides into non-toxic simpler compounds (Wang et al., 2022).

Several environmental factors, including pH, temperature, soil type, and soil organic content influence the degradation process of neonicotinoids. Among neonicotinoid pesticides, imidacloprid is the most persistent in soil. As imidacloprid and its metabolic byproducts bind to soil particles more firmly over time, the probability of their persistence in the environment is increased (Hussain et al., 2016; Bonmatin et al., 2015). Imidacloprid is consumed more and more worldwide every day due to its strong insecticidal action and low toxicity to mammals. As a result, there has been an increase in the accumulation of these pesticides in soil and water. High toxicity to honey bees, high stability, high water solubility, bioaccumulation, environmental persistence, wind transport, and dust accumulation are all characteristics of imidacloprid (Guan et al., 2008). The fate of imidacloprid and its products in the environment and drinking water is of concern to the public. Subsequently, it is essential to evaluate the possible negative effects that pesticide application may cause to ecosystems.

The environmental fate of imidacloprid needs to be better documented. Imidacloprid has been reported to be relatively stable in soil by some authors (Hulbert et al., 2020; Tišler et al., 2009), but subsequent studies demonstrate the contrary (Aliste et al., 2021; Leiva et al., 2017). Both biotic and abiotic variables influence the fate of pesticides in the environment. Imidacloprid is primarily released into the environment and water sources as wastewater from agricultural operations and industries. Imidacloprid has a high solubility in water, making it a high potential contaminant of aquatic environments. It may enter water bodies by spray drift or run-off, even though it is not meant for use in aquatic environments. In several water sources, imidacloprid has been found in concentrations ranging from 2.09 to 3625 parts per billion (ppb) (Bradford et al., 2018).

The rate at which imidacloprid dissipates in the field varies greatly and has occasionally been observed to breakdown slowly in soil with half-lives longer than 180 days in non-vegetated soil (Anhalt et al., 2007). The physicochemical and biological characteristics of the soil control the fate of pesticides and further influence their movement within the natural environment. The sorption-desorption processes, volatilization, plant uptake, run-off, leaching, and physicochemical characteristics of pesticides play significant roles in the rate of dissipation and half-life of pesticides in the environment (Barizon et al., 2020).

The half-life of imidacloprid in the soil ranges between 27–229 days under field conditions, depending on sorption, pH, amount of organic matter present, formulation type, and vegetation present (Didović et al., 2022; Phong et al., 2009). Gao et al. (2021) estimated that the half-life of Imidacloprid in soil was 25-1250 days, whereas it was 156 days in tropical soil, as per Dankyi et al. (2018). It was reported by Pietrzak et al. (2020) that the variation ranged from 35.9 to 1230 days, with a degradation rate of 0.019 L/d.

1.5. Impacts of pesticides

Due to their widespread presence in the environment, the benefits of pesticide use are outweighed globally. Even though many nations have banned some of the least biodegradable and ecologically persistent pesticides, their use is steadily increasing. Pesticide use on a large scale has led to several toxicological effects on living things due to direct and indirect exposure to pesticides and residues. The stability and presence of less soluble active components are the primary cause of the detrimental effects of pesticides. Numerous incidents involving the diverse toxicological effects of pesticides have been reported worldwide (Hernández et al., 2013). Pesticides are labeled with relative symbols according to these classifications: highly toxic, moderately toxic, and slightly relatively harmless. Pesticides can be dangerous to people, other living things, and the environment in case of prolonged exposure, even when considered harmless or mildly toxic. Field application, operational hazards during manufacturing, direct and indirect toxic effects resulting from hazardous residues in food and the environment, and various other factors contribute to the toxicological effect (Damalas & Eleftherohorinos, 2011; Parra-Arroyo et al., 2022).

1.5.1. Environmental impacts

Most pesticides pollute the air, land, and water when sprayed in significant amounts. Numerous studies have demonstrated that pesticides adversely impact the natural environment, putting all life forms at risk (Zhang et al., 2023). Overusing these pesticides leaves a significant amount of residues with their effects on crops. These residues lead to nutritional imbalances and lower agricultural produce quality (Alengebawy et al., 2021). In addition to entering food systems, the continuous use of pesticides has raised their concentration in streams and soils.

Previous studies provide strong evidence that pesticides can have negative impacts on the environment, including soil contamination, water pollution, harm to non-target species, pesticide resistance, pesticide drift, and bioaccumulation (Kalyabina et al., 2021; Damalas and Eleftherohorinos, 2011). Pesticides impact the environment in several ways. Pesticides can contaminate soil and reduce soil quality. Soil microorganisms play a crucial role in controlling soil quality due to their complex activities and significant role in generating soil enzymes. Pesticide overuse can decrease the diversity of microorganisms in the soil, indirectly impacting soil fertility (Mahmood et al., 2016). Because of this, microorganisms may be a helpful indicator of changes in soil health (Meena et al., 2020). In addition to disrupting soil biodiversity, this haphazard use of pesticides harms soil microcosms as well as the amount of microbial biomass in soil (Prashar and Shah, 2016).

Pesticides can pollute groundwater and surface water, impacting aquatic life and reducing water quality. Owing to the process of rainwater infiltration, residual pesticides could become sources of pollution and constitute a major risk to the soil and groundwater environment (Arias-Estévez et al., 2008). Pesticides can harm non-target species, including birds, fish, and beneficial insects such as pollinators. The extensive usage of pesticides has disastrous effects on wildlife as well (Karimi et al., 2022). Certain pesticides do more harm to non-target organisms because they interfere with metabolic processes shared by a wide variety of plants, animals, and microbes.

Pesticides can drift from their intended target area and impact non-target areas, including wildlife habitats, homes and parks. In addition to killing pests, pesticides eliminate beneficial species in the environment and gradually develop pest resistance, thus reducing their long-term efficacy (Goulson, 2013). Pesticides can bioaccumulate in the food chain, leading to potential health risks for wildlife and humans. Improper utilization of these low-biodegradable chemicals enhances their availability and accumulation in soil as well as in water. Bioaccumulation of these persistent, toxic compounds imbalances the ecosystem functioning and is a key factor in the loss of biodiversity of flora and fauna.

Excessive use of imidacloprid on crops may alter the native microbial community, change the biochemical composition of the soil, and decrease the combined activity of alkaline phosphatase and dehydrogenase. Additionally, treatment with imidacloprid has a negative effect on several soil enzymes, such as urease, acid phosphatase, β-glycosidase, and fluorescein diacetate hydrolase (Mahapatra et al. 2017). Long-term use of imidacloprid can be harmful to ammonia-oxidizing archaebacteria, soil microbes, and soil enzymes such as phosphatases, ureases, and dehydrogenase (Cycoń and Piotrowska-Seget 2015).

Imidacloprid enters the soil and contaminates the environment when it is used excessively on crops. Numerous reports indicate that imidacloprid has an adverse effect on ecosystems. Imidacloprid treatment has also been found to alter the structure of the soil microbiome (Hussian et al., 2016). Recent reports indicate that it is potentially toxic to non-target organisms (Zhang et al., 2023; Zhu et al., 2019). A significant amount of the pesticide enters the soil after spraying, which may pose certain risks to the soil (Damalas & Koutroubas, 2016). It persists in soil for a year or more and is highly mobile, eventually moving into surface waters or leaching into groundwater (Bonmatin et al., 2015).

Although imidacloprid is detected in surface water in minute quantities, it acts as an insect neurotoxin and is toxic even at low concentrations and may pose a serious threat to aquatic environments (Bashir et al., 2020; Borsuah et al., 2020; Grung et al., 2015). It has a significant negative impact on fish and other aquatic species, especially when it enters water bodies (Chen et al. 2019). Imidacloprid has been reported to adversely affect zebrafish and shrimp (Pang et al., 2020).

1.5.2. Human health

It is important to address pesticides since they can significantly affect humans directly and indirectly. Numerous adverse effects in humans have been linked to widespread pesticide exposure. There are three possible ways that pesticides might affect people. First, the most significant way these substances might be exposed is through food or ingestion. Second, the use of pesticides in homes has led to an increase in dermal contact. Finally, it could happen from breathing contaminated air, especially for people close to agricultural areas (Meftaul et al., 2020; Rani et al., 2021).

Pesticides are responsible for causing both acute and long-term health impacts in humans, including cancer, central nervous system disorders, and genetic mutations (Mostafalou and Abdollahi, 2013). Several variables, such as the kind of pesticide used, quantity and length of exposure, age, sex, and general health of the person exposed, affect the impact of pesticides on human health. Acute health effects of pesticides include skin and eye irritation, respiratory problems, and digestive disturbances. There is an increasing indication that acute pesticide exposure causes immunosuppression, neurobehavioral syndromes and progressive toxicity. In severe cases, exposure to high levels of pesticides can result in poisoning, which can cause symptoms such as headache, dizziness, nausea, vomiting, seizures, and even death (Ye et al., 2013). Studies show that there is a close link between pesticides and cancer in humans. Some of the chronic and acute toxicological effects of pesticides are endocrine and reproductive disorders, chronic liver damage, inhibition of choline esterases, Burkitt's lymphoma, leukemia, Parkinson's and Alzheimer's diseases, etc. (Mostafalou and Abdollahi, 2013).

Pregnant women and children are particularly vulnerable to the effects of pesticides, as exposure to these chemicals can interfere with fetal development and cause neurodevelopmental effects in children (Dahiri et al., 2021). Children may also have increased exposure to pesticides through hand-to-mouth contact with contaminated soil or surfaces and through consuming contaminated food. Chronic exposure to pesticides has been linked to an increased risk of certain types of cancer, including non-Hodgkin lymphoma, prostate cancer, and childhood leukemia. Pesticides have also been shown to have neurological effects, including decreased cognitive function, motor skills, and attention (Lushchak et al., 2018).

In humans, imidacloprid is linked to reproductive and mutagenic effects and is considered neurotoxic (Gibbons et al., 2015). According to Silvia et al. (2020) imidacloprid exposure results in thyroid lesions, impaired reproduction, decreased human weight gain, and miscarriages. Imidacloprid inhalation can result in severe respiratory issues, neuropsychiatric issues, and severe gastrointestinal symptoms. Imidacloprid induces DNA damage in HepG2 cells and human lymphocytes, lymphocytic cell death, and genetic toxicity in TK6 human lymphoblastoid cells (Bhende et al., 2023; Guo et al., 2018).

1.6. Treatment technologies

The elimination of pesticides from the environment is essential because they harm humans and non-target organisms, as well as contaminate groundwater. Various physicochemical techniques, such as Fenton oxidation, adsorption, flocculation, hydrolysis, ultrasound, illumination, etc., have been developed for the removal of pesticides (Pang et al. 2020; Erguven and Yildirim 2019; Qurie et al. 2021; Hassaan & El Nemr, 2020; Saleh et al., 2020; P. Zhang et al., 2018; Jatoi et al., 2021). However, these techniques have their disadvantages, such as high energy consumption, higher processing and equipment costs, sludge generation and production of toxic byproducts (Marican & Durán-Lara, 2018; Saleh et al., 2020). The physical treatment methods for pesticide-contaminated sites are costly, and the chemical methods are known to transfer the compound from one phase to another only; hence, they are not eco-friendly. Advanced oxidation processes have also been adopted for the removal of pesticides (Bakshi et al., 2021). To overcome these problems, several researchers have focused on safer methods, such as photolysis-based physiochemical approaches and biological methods for a wide range of recalcitrant pesticide residues (Kaur et al., 2023). Among biological methods, microorganisms as well as plants have been used for reducing the pesticide contamination (Kaur et al., 2022)

Microorganisms with effective degradation capabilities are being investigated as one of the biological approaches. Microorganisms are capable of metabolizing pesticides by utilizing them as nutrients for their growth (Shahid et al., 2023). The application of natural bioremediation for removing such chemicals is a relatively recent development. One of the key mechanisms in nature governing the fate and transformation of pesticides is microbial degradation. Bioremediation involves the complete removal of organic toxic pollutants into innocuous or naturally occurring compounds, such as carbon dioxide, water, and inorganic compounds that are safe for terrestrial and aquatic life (Abatenh et al., 2017). Bioremediation can also remove low-concentration contaminants that chemical or physical methods cannot remove.

In addition to biodegradation, other bioremediation techniques for insecticides have also been developed, including biosorption and biotransformation. Biosorption involves the use of microbial biomass, such as fungal or algal biomass, to remove insecticides from the environment by adsorption or accumulation. Biotransformation involves the use of microorganisms to convert insecticides into less toxic or non-toxic compounds. Therefore, biological techniques offer the most effective and suitable method for removing these chemicals from the soil. Microorganisms readily degrade some pesticides, while others have proven to be recalcitrant. Major reactions in pesticide degradation include mineralization and co-metabolism.

Microorganisms play an important role in the removal of toxic substances from the environment because they contain enzymes that allow them to consume environmental contaminants as food. For the biodegradation of different organic compounds, numerous mechanisms and pathways have been established (Wang et al., 2022). Microorganism diversity offers a potential richness in biodegradation. While microbes can catalyze metabolic reactions similar to plants and mammals, they are unique since they are capable of completely mineralizing a wide variety of organic compounds (Gilani et al., 2016; Singh & Walker, 2006). Since microbial degradation techniques have the benefits of complete degradation, economic viability, and reliability, among other advantages, they have become an essential technique for removing pesticide residues from the environment (Azubuike et al., 2020; Benjamin & Wesseler, 2016; Boopathy, 2016).

1.7. Organization of the thesis

This thesis consists of nine chapters, followed by references at the end.

Chapter 1 provides a brief introduction to pesticides, their fate in the environment, their impacts on health and the environment and the technologies adopted for the abatement of these chemicals. The chapter ends with highlighting the research objectives and organization of the thesis.

Chapter 2 focuses on the review of literature on bioremediation, factors influencing bioremediation, the different microorganisms used in the bioremediation of pesticides and the insecticide imidacloprid, toxicity studies conducted using different organisms and metagenomic studies on imidacloprid biodegradation.

The details of the materials and methodology adopted in the studies conducted have been discussed in **Chapter 3.** This chapter discusses the different chemicals and media required, analytical techniques, the experimental setup and the methodologies implemented for different bioremediation and toxicity studies conducted.

Chapter 4 deals with the isolation and identification of imidacloprid-degrading bacteria, the preparation of bacterial consortium and their application in imidacloprid degradation at varying concentrations of imidacloprid in batch bioreactors. Stirred-tank batch reactor was also implemented for imidacloprid biodegradation using the bacterial consortium.

Chapter 5 presents the studies conducted for the assessment of phytotoxicity using *Cicer arietinum* seeds, anti-oxidative enzyme assay and study of plant photosynthetic pigments. In addition, it also includes bacterial toxicity assessment, bioluminescence inhibition and cytotoxicity assessment.

Chapter 6 consists of imidacloprid biodegradation in slurry and soil microcosm, identification of metabolites and kinetic study.

Chapter 7 includes the metagenomic analysis of samples.

Chapter 8 includes the application of lyophilized and encapsulated bacteria for imidacloprid-degradation in soil microcosm.

Chapter 9 presents a summary of the thesis with major conclusions drawn from the study and further scope for research.