

# Plant Uptake of Pesticide Residues from Agricultural Soils



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**Abstract** During recent decades, agriculture production has intensified by using a large number of chemical substances as pesticides to protect crops from unwanted fungi, weeds, and insects. It has been reported that long-time exposure of pesticides to different environmental conditions results in persistence of many derivatives of them in the environment. Intense global environmental issues have been raised due to the uptake of those pesticide residues present in agricultural soils by non-target organisms and planted crops. Indeed, the movement of such pesticide residue chemicals through the food chain may still cause potential health risks to humans.

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However, uptake of pesticide residues is more complicated and many factors have promoted the process. The uptake process and bioavailable concentrations of pesticide residues can highly differ depending on environmental conditions, characters of the planted crops, and physicochemical properties of the pesticides. Meanwhile, this chapter summarizes the pesticide residue types and their fate in the agricultural soils, highlighting the mechanisms as well as influencing factors for the plant uptake. Field-based investigations under natural conditions are required for future researches to make reasonable risk predictions for human health.

**Keywords** Agrochemicals, Factors, Human risk, Mechanisms, Persistence

## 1 Introduction

A wide range of chemical compounds is extensively used as pesticides around the world in agriculture to eradicate undesired pests from the cultivations [1]. Pest is a generous word to describe any creature like insects, plant pathogens, weeds, molluscs, birds, mammals, nematodes that have harmful undesirable effects on crops or livestock [2]. It was estimated that annual worldwide pesticide consumption was  $2.7 \times 10^6$  tons [3]. Numerous groups of pesticides, which have different chemical and physical properties from one to another, are continuously used in agriculture. Depending on the function and the target organism, pesticides are categorized into various classes including insecticides, herbicides, fungicides, rodenticides, bactericides, algacides, nematocides, molluscicides, ovicides, etc. [1, 2, 4]. However, among them insecticides, herbicides, fungicides and rodenticides utilize commonly in agriculture [2]. Insecticides are widely used to repel or kill insects in all stages of their growth cycles, while fungicides are used against the fungi and fungal spores, which have the potential to damage high crop yield. Further, herbicides are destroying weeds and other plant species that germinate where they are not wanted. Rodenticides are used to control rodents like mice, rats, woodchucks, beavers whereas they are usually formulated as baits [4]. Besides, they play an important role in preventing the spread of vector-borne diseases in the field.

Moreover, depending on the chemical materials involving in the pesticide manufacturing they can be either inorganic or organic. Pesticides such as copper sulphate, ferrous sulphate and sulphur are simple products that do not contain carbon in their chemical structure hence, they are called inorganic [5]. Comparably, organic pesticides like captan, pyrethrin, and glyphosate are based on chemicals having carbon as the active ingredients. Many feasible ways (modes of entry) are unique for each type of pesticide to enter into target pests such as systemic, contact, stomach poisons, fumigants, and repellents. Some pesticides are ingested to the pest from the mouth and transferred to the rest of the body, heading it to death. In fact, pesticides like malathion are able to attack the larval stomach and kill it [2]. Besides, some pesticides are only effective on target pests, when chemicals are physically contacted

with the epidermis of the organism and entered through the lesion. Moreover, fumigants are forming poisonous vapour and transmitted via the respiratory system of pests which also leads them to death by poisoning.

Despite the beneficial outcome of using pesticides, inappropriate application of those chemicals over few decades may result in soil and water contamination by pesticide residues. Some mechanisms such as photochemical oxidation, photolysis, hydrolysis, and metabolism lead to pesticide degradation while resulting in residue products [4, 6]. Such residues, which are ubiquitous in the agricultural soils, are a major concern as they can persist for a long period in the environment. Pesticide residues contribute to the contamination of aquatic environments and eventually could adversely affect aquatic species. On the other hand, pesticide residue products may have much higher toxicity than the original pesticide even on the non-target organisms. Most importantly, pesticide residues can be uptaken by the non-target edible crops, which will grow in the following seasons [3]. In fact, pesticide residues derived from agricultural soils are found to accumulate in plants at minute levels typically from  $\text{ng kg}^{-1}$  up to  $\text{mg kg}^{-1}$ . Interestingly, 16 different pesticide residues including *p,p'*-DDT, *p,p'*-DDE, *p,p'*-DDD, etc. were detected in agricultural soil samples whereas 11 pesticide residues from them were detected in flora samples according to the study done by Zacharia et al. [7] at a sugarcane plantation in Tanzania. It is clearly shown biota uptake is one of an ultimate destination of pesticide residues in the environment. Further, Neuwirthová et al. [3] found many pesticide residues in soils from arable lands in Czech Republic, which were used as plantation lands many years before. Interestingly, many pesticides including epoxiconazole, tebuconazole, flusilazole, prochloraz, and pendimethalin were detected at increased frequencies and/or concentrations in the soils [3]. Importantly, the transformation product (2-hydroxyatrazine) of atrazine, which was banned decades ago, was frequently reported as a contaminant of agricultural soils in arable lands [3, 8]. These findings are proving the information of the long-time persistence behaviour of pesticide residues in the soil environment [9]. Hence, it was unable to provide the real risk associated with it [3].

However, many parameters have been recognized as governing factors for the behaviour of pesticide residues in soil [10]. Basically, the physicochemical properties of a given pesticide are influencing the fate and binding nature of residues in soils. Further, environmental factors and plant physiology and genotype have a dominating influence on the residue uptake process by plants [11]. Consequently, plant uptake of pesticide residues can be capable of having deleterious effects on wildlife and perhaps human beings through the food chains [7, 12]. This chapter highlights the types of pesticide residues, fate, and plant uptake mechanisms in agricultural soils. The influencing factors for the process of pesticide residues uptake by plants are also discussed alongside their negative effects, particularly on human beings.

## 2 Potential Pesticide Residues in Agricultural Soils

### 2.1 Pesticide Residue Types

Most of the applied pesticides will spread and react with the environment. Pesticides and their degradation products, which remain on and in foods, are known as pesticide residues. Many types of these pesticide residues could be found in the environment. Accumulated concentrations of some pesticide residues in different plants and soils are shown in Table 1. These pesticide residues could be classified by considering many characteristics. As mentioned above, pesticides are categorized based on the nature of active ingredients, their mode of entry, the chemical composition, and the target pest organism and the function [2, 19].

The classification of pesticides based on their chemical composition reflects the chemical and physical properties and effectiveness of the pesticides [2, 19]. Typically, synthetic and plant-originated organic chemicals are widely used as pesticides, however, several inorganic chemicals are also practised as pesticides in the world [2]. Depending on the chemical composition of pesticides, four main groups of pesticides can be recognized such as organochlorines, organophosphorus, synthetic pyrethroids, and carbamates [20–22].

Organochlorine pesticides represent one of the initially synthesized pesticide groups, which are used in agriculture. Examples of commonly used organochlorines are heptachlor, endosulfan, chlordane, and dichlorodiphenyltrichloroethane (DDT) [23]. The residual effect of these pesticides on the environment could extend for a long time. For many years, organochlorine pesticides have been used, however, due to their long residual effect many countries have led to the use of alternative pesticides such as organophosphorus and carbamate pesticides, which have a lower residual effect [24, 25].

Due to having multiple functions, organophosphorus pesticides are included in a broad spectrum of pesticides in controlling pests. Also, these pesticides are biodegradable, have slow pesticide resistance, and have reduced environmental pollution [24]. Some of the commonly used organophosphorus pesticides can be listed as glyphosate, malathion, diazinon, acephate, phosmet, and parathion [2, 23]. Carbamates are structurally and functionally similar to organophosphorus pesticides and both pesticide types affect the nerve transmission of pests. Carbamates could be degraded easily with reduced environmental pollution [2, 19]. Examples for carbamates are carbofuran, aminocarb, carbaryl, aldicarb, and pirimicarb [23].

One of the safest organic pesticide groups for food crops is synthetic pyrethroids and these pesticides have longer residual effect and stability than natural pyrethrins. Also, the persistence of most synthetic pyrethroids is negligible and could break due to the light, while the toxicity to mammals and birds is low [2]. Commonly used synthetic pyrethroids are cypermethrin, deltamethrin, and cyhalothrin [23].

The pesticides are classified by indicating the target organism and emphasizing the pesticide activity. The pesticide classes can be specified as herbicides (e.g. glyphosate), insecticides (e.g. chlorpyrifos), fungicides (e.g. chlorothalonil),

**Table 1** Accumulated concentrations of several pesticide residues in different soils and plants

Pesticide type	Concentration range		Plant type	Reference
	Soil $\mu\text{g kg}^{-1}$	Plant $\mu\text{g kg}^{-1}$		
Hexachlorobenzene (HCB)	0.125–0.167	ND–0.033	Potato varieties <sup>a</sup>	[9]
	0.230–1.215	0.050–0.330	Carrot varieties <sup>b</sup>	[9]
$\alpha$ -Hexachlorocyclohexane	ND–87.0	ND–3.66	Potato varieties <sup>a</sup>	[13]
	ND–8.06	ND–2.86	Carrot varieties <sup>b</sup>	[14]
$\gamma$ -Hexachlorocyclohexane	18.5–769.5 dw	1.7–384.7 dw	Radishes ( <i>Raphanus sativus</i> )	[7]
	0.7–19.6	0.4–0.6 fw	Sweet potato	[7]
2,4'-DDT (o,p'-DDT) 4,4'-DDT (p,p'-DDT)	2.76–17.06 dw	2.00–12.89	Mango leaves ( <i>Mangifera indica</i> ), sugarcane ( <i>Saccharum officinarum</i> ), and Guinea grass ( <i>Panicum maximum</i> )	[9]
	1.2–152.4	ND–3.9	Potato varieties <sup>a</sup>	[13]
	0.5–207.8	0.11–47.76	Carrot varieties <sup>b</sup>	[7]
	583.2–2581.4 dw	36–1759.2 dw	Radishes ( <i>Raphanus sativus</i> )	[9]
$\alpha$ -Endosulfan $\beta$ -Endosulfan	1.02–2.0 dw	2.44–4.07	Mango leaves ( <i>Mangifera indica</i> ), sugarcane ( <i>Saccharum officinarum</i> ), and Guinea grass ( <i>Panicum maximum</i> )	[9]
	1.23–13.36	ND–3.23	Potato varieties <sup>a</sup>	[7]
Aldrin	0.57–14.96	ND–6.16	Carrot varieties <sup>b</sup>	[9]
	1.34–13.51 dw	1.67–13.0	Mango leaves ( <i>Mangifera indica</i> ), sugarcane ( <i>Saccharum officinarum</i> ), and Guinea grass ( <i>Panicum maximum</i> )	[9]
	0.001–12.66	ND–0.0019	Potato varieties <sup>a</sup>	[7]
Endrin	1.6–4.3	0.013–2.900	Carrot varieties <sup>b</sup>	[7]
	1.11–5.66 dw	2.26–4.46	Mango leaves ( <i>Mangifera indica</i> ), sugarcane ( <i>Saccharum officinarum</i> ), and Guinea grass ( <i>Panicum maximum</i> )	[9]
4,4'-DDE	0.33–31.0	ND–13.30	Potato varieties <sup>a</sup>	[13]
	0.013–22.70	ND–7.320	Carrot varieties <sup>b</sup>	[7]
	783.9–1081.7 dw	56.9–809.5 dw	Radishes ( <i>Raphanus sativus</i> )	[7]
	1.23–13.49 dw	1.96–11.56	Mango leaves ( <i>Mangifera indica</i> ), sugarcane ( <i>Saccharum officinarum</i> ), and Guinea grass ( <i>Panicum maximum</i> )	[7]

(continued)

Table 1 (continued)

Pesticide type	Concentration range		Plant type	Reference
	Soil $\mu\text{g kg}^{-1}$	Plant $\mu\text{g kg}^{-1}$		
	–	9.47–12.95	Leaf vegetables (spinach – <i>Spinacia oleracea</i> , cabbage – <i>Brassica oleracea</i> , lettuce – <i>Lactuca sativa</i> , dhania – <i>Coriandrum sativum</i> , celery – <i>Apium graveolens</i> , parsley – <i>Petroselinum crispum</i> , and kale – <i>Brassica oleracea</i> )	[15]
	–	9.07–12.75	Root vegetables (carrot – <i>Daucus carota</i> , cauliflower – <i>Brassica oleracea</i> , radish – <i>Raphanus raphanistrum</i> , broccoli – <i>Brassica oleracea</i> , turnip – <i>Brassica rapa</i> , Leek – <i>Allium ampeloprasum</i> , and spring onion – <i>Allium cepa</i> )	
Imidacloprid	–	$1.37 \times 10^3$ – $410 \times 10^3$ dw	Rice plants ( <i>Oryza sativa</i> L.)	[16]
	–	$0.18 \times 10^3$ – $2.64 \times 10^3$	<i>Brassica rapa</i> L. varieties	[17]
Thiamectoxam	–	$3.19 \times 10^3$ – $265 \times 10^3$ dw	Rice plants ( <i>Oryza sativa</i> L.)	[16]
Difenoconazole	–	$0.23 \times 10^3$ – $79.1 \times 10^3$ dw	Rice plants ( <i>Oryza sativa</i> L.)	[16]
Clothianidin	$0.02 \times 10^3$ – $0.5 \times 10^3$	$0.07 \times 10^3$ – $7.0 \times 10^3$	Rice plants ( <i>Oryza sativa</i> L.)	[16]
Chlordecone	–	0.8–262.7 dw	Radish plants	[18]

ND Not Detected, dw dry weight, fw fresh weight

<sup>a</sup>Potato varieties – Cara, Valour, Kestrel, and Desiree

<sup>b</sup>Carrot varieties – Nairobi, Major, and Autumn Kings

rodenticides (e.g. warfarin), bactericides (e.g. copper complexes), larvicides (e.g. methoprene), virucides (e.g. scytovirin), nematocides (e.g. aldicarb), molluscicides (e.g. metaldehyde), algacides (e.g. copper sulphate), acaricides (bifenazate), termiticides (e.g. fipronil), lampricides (e.g. trifluoromethyl nitrophenol), and ovi-cides (e.g. benzoxazin) [19, 26].

Herbicides are used in agricultural fields to control weeds without harming the crop (selective herbicides) or control all the vegetation (total herbicides). These pesticides could be absorbed through roots or leaves, respectively, into the plants and the pesticide selectivity may depend on the differences in plant uptake, metabolism, and translocation mechanisms. Herbicides are classified based on their chemical composition. For example, glufosinate and glyphosate (organophosphorus herbicides), molinate and propanil (carbamate herbicides), dicamba and chloramben (benzoic acid herbicides), alachlor and propanil (amide herbicides), and pyridate and norflurazon (pyridine and pyridazinone herbicides) can be presented [27].

Insecticides are applied to soil or plants to control pests such as insects in the crops. Insecticides also could be grouped according to the chemical composition, such as DDT and endosulfan (organochlorine insecticide), chlorpyrifos and fenitrothion (organophosphorus insecticides), methomyl and carbaryl (carbamate insecticides), permethrin (pyrethroid insecticide), and acetamiprid (neonicotinoid insecticide) [27, 28].

Fungicides are used in agriculture to protect fruits, vegetables, and cereals from fungal diseases [29]. Fungicides are classified according to their chemical composition. Examples of commonly used fungicides are chlorothalonil (organochlorine fungicide), fenpropimorph (morpholine fungicide), thiabendazole (benzimidazole fungicide), and cyproconazole (azole fungicide) [28].

## ***2.2 Fate and Transport in Soil***

As mentioned above, most of the applied pesticides on the plants or the soil would be dispersed in the surrounding environment. Even the pesticide application area is comparatively small, eventually, pesticides may spread into a larger area by adsorption into the soil, volatilizing into the air, or dissolving in water. Soil-applied pesticides may lead to unintended dispersal and non-target contamination in soil and surface water bodies through pathways such as surface runoff and flooding [30]. Further, groundwater and lower soil layers may be contaminated through percolation [2]. After the pesticide application, the fate and behaviour of the deposited pesticides on soil and plant surfaces may be influenced by many factors such as volatilization, adsorption, photochemical decomposition, chemical decomposition, microbial decomposition, movement, and organism uptake [31–33]. Physically, the soil has a heterogeneous nature while the soil structure varies laterally and vertically resulting in a complex water flow through the soil profile. Soil properties, pesticide properties, and environmental conditions determine the pesticide movement rate through the soil [34].

Adsorption plays a major role in affecting the interactions taking place between soil colloids and pesticides, because it directly or indirectly influences the extent of the other affecting processes [35]. Adsorption is the association of an atom, ion, or molecule from a dissolved solid, liquid, or gas to a surface. The adsorption of pesticides onto soil surfaces depends on many factors such as physicochemical characteristics of the adsorbent and the adsorbate, soil reaction, surface acidity, and temperature. In the case of the physicochemical characteristics of the adsorbent, the surface area and the total charge are more important than the surface charge density in most situations. When considering the physicochemical characteristics of the adsorbate, the adsorption process may be subjected to the water solubility, acidity and basicity of the molecule, shape and configuration, size of the molecule, polarity, charge distribution, and polarizability. The properties of adsorbent and adsorbate are influenced by the soil reaction in the clay-water system. Also, the degree of attachment and separation of adsorbate would be determined by the soil solution pH. The surface acidity as an important property in the soil system determines the adsorption and desorption of organic compounds. The temperature of soil systems may affect the adsorption processes since adsorption is an exothermic process, while desorption is an endothermic process. Distinct adsorption mechanisms could be identified as physical adsorption, chemical adsorption, and hydrogen bonding. As a result of short-range dipole-dipole interactions, van der Waals forces could be created between adsorbent and adsorbate to form physical adsorption. Mechanisms such as ion exchange could lead to chemical reactions between adsorbent and adsorbate to form chemical adsorption [34, 35].

The behaviour, distribution, and fate of pesticides could be strongly influenced by the physical and chemical properties of soil [36]. Topsoil is the area where pesticides could frequently be found [37]. Soil constituents with highly reactive surfaces mainly determine physical and chemical properties. These constituents could be divided into two fractions as the mineral fraction and the organic fraction. Crystalline clay minerals and amorphous and crystalline oxides/hydroxides represent the mineral fraction, while humic acid represents the organic fraction. Humic acid has a higher cation exchange capacity than clay minerals, because functional groups such as amino, carboxyl, phenolic hydroxyl, and alcoholic hydroxyl in humic acid contribute to form hydrogen bonds with pesticide molecules [35]. As an example, Yu et al. [33] showed that the adsorption and desorption processes of three pesticides, namely chlorpyrifos, myclobutanil, and butachlor were strongly controlled by soil organic matter (OM).

The pesticide mobility could be controlled by many factors related to the soil such as vegetation, preferential flow, soil moisture, amendment, soil tillage, and facilitated transport. The OM resulted from vegetation could adsorb hydrophobic pesticides through van der Waals forces, while phenolic hydroxyl and carboxyl groups in the OM could form hydrogen bonds with hydrophilic pesticides [34]. The transport of pesticides in the soil may occur through the downward and upward moving water, through the diffusion in soil airspace, and through the diffusion in soil water. Relatively non-volatile pesticide movement could be happened through percolating water, while air diffusion is more important in high volatile pesticide movement. In



high evapotranspiration present areas, the upward movement of pesticides could be a factor [35]. Eventually, diffused or transported pesticides would be partitioned in the soil matrix.

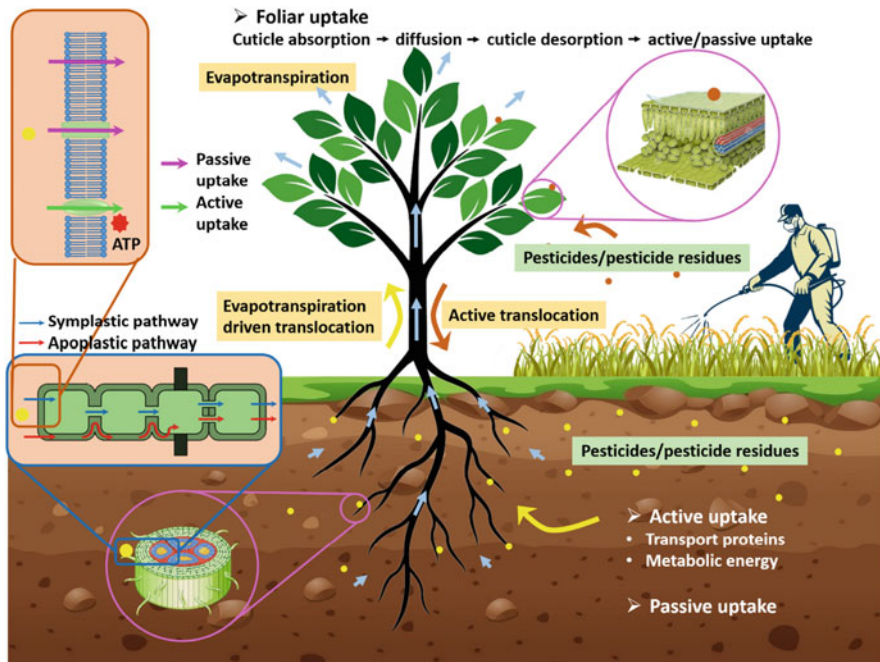
The release of pesticides into the soil solution is identified as leaching. It could be resulted from the pesticide dissolution from an original form or through the pesticide desorption from soil surfaces. The leaching of pesticides is determined by the pesticide properties (sorption, degradation, and solubility) and soil properties (type, texture, and structure) [34, 38, 39]. For example, the leaching of nicosulfuron herbicide from clay minerals is strongly limited due to the rapid sorption [40]. Furthermore, due to the low degradation rate and low mobility, mesotrione has no movement lower than 20 cm in soil [41]. Pesticide leaching is strongly influenced by the soil type while pesticide properties have a partial contribution [26]. Also, leaching could be influenced by the soil moisture level and the evapotranspiration ratio. Both soil texture and structure could affect the pesticide movement and leaching because the degree of pesticide leaching is high in light-textured soils than in heavy-textured soils and the changes in soil texture usually affect the changes in soil structure. Due to the small-diameter pores in the high clay content soil, the molecular diffusion of pesticides may be restricted [35]. The fate of pesticides in the soil strongly determined by the climatic parameters such as appearance time of the first rainfall after pesticide application and the intensity and duration of the rainfall event [42].

Another important process for controlling the transport of pesticides and their residue levels in the soil is the degradation of pesticides. As mentioned above, pesticides could be degraded photochemically, chemically, or biologically [43]. Processes such as photolysis, photochemical oxidation, hydrolysis, and metabolism are contributing to the overall degradation of pesticides [12]. According to Si et al. [44] and van der Linden et al. [45], the degradation could be pH-dependent for certain pesticides which are susceptible to dissociation and hydrolysis. Soil microorganisms play an important role in pesticide degradation [46, 47]. The rhizosphere which has high biomass and microbial activity enhances pesticide degradation [34]. Pesticides could be degraded inside plant tissues either by enzymatic reactions of the plant [48] or due to activities of endophytic bacteria [49]. An example of abiotic pesticide degradation is the degradation of atrazine to form hydroxyatrazine and according to Wang et al. [50], this conversion is catalysed by the soil colloidal surface Bronsted acidity.

Soil macro-organisms such as earthworms could accumulate some pesticide residues in their bodies [24]. Usually, the uptake of pesticide residues such as myclobutanil and butachlor by earthworms is increased with the decreasing amount of soil OM. Pesticide residues could be accumulated in earthworm bodies via two pathways such as passive diffusion through the earthworm dermis and contaminated soil ingestion [51]. Due to the strong sorption of chlorpyrifos pesticide onto soils, earthworms are incapable of accumulating the pesticide from the soil surface via their dermis [33]. Besides soil macro- and micro-organisms, pesticides and pesticide residues could be degraded, translocated, and accumulated in plant tissues. The process involved in pesticide movement into vegetation is identified as plant uptake.

### 3 Mechanisms of the Uptake, Translocation, and Bioaccumulation of Pesticide Residues in Plants

Food crops and other plants in the environment are vulnerable to pesticide residue contamination. Pesticides remaining in the air and soil can be absorbed by plants through the plant aerial parts (leaves, fruits, and shoots) and roots, respectively (Fig. 1) [12, 52]. Herbicides are absorbed into plants through both leaves and roots, while some other organic pollutants are absorbed into plants only through roots from soil [53]. Organic pesticides are less volatile and their uptake into plants is generally happening through the plant root because usually it is the first tissue that soil pesticides come in contact with [53, 54]. Pesticide uptake from plants occurs in two processes, namely passive uptake and active uptake [52, 55]. In the passive uptake process, pesticide molecules are diffused into the plant roots in the direction of a reducing chemical potential within several plant components [52, 55]. For example, passive uptake is the major process of uptake of fungicides (e.g. imazalil and tebuconazole), herbicides (e.g. phenylurea), and insecticides (e.g. o-methylcarbamoyloxime) [55]. In the active uptake process, pesticide absorption occurs for some organic pesticides (e.g. phenoxy acid herbicides) against a chemical potential gradient with the assistance of carriers in root cell membranes



**Fig. 1** Mechanisms of the uptake, translocation, and bioaccumulation of pesticide residues in plants

[52]. Transport proteins on the cell membrane and energy metabolism are key components in the plant root uptake [54]. The efficiency and degree of pesticide uptake from the soil is depending on the factors such as pesticide concentration in soil, physicochemical properties of pesticides, interaction between soil microorganisms and pesticides, plant species, exposure time, temperature, and other system variables [18, 56, 57].

Organic pesticide residue movement from soil to plant and translocation of them are primarily driven by the evapotranspiration process in the plants [55]. Contact pesticides neither penetrate the plant tissue nor translocate via the vascular system of the plants. Also, partially soluble organic pesticides are usually accumulated in plant roots due to the difficulty of moving to the shoots. Pesticides such as systemic herbicides (e.g. glyphosate) can be absorbed into plants and translocated into untreated tissues. This pesticide movement in plant tissues could be multidirectional or unidirectional which means that some pesticides can be moved either downwards or upwards in the plant while other pesticides can only move upwards [2]. The pesticide movement through plant tissues happens via two pathways, namely the symplastic pathway and apoplastic pathway. The symplastic pathway is identified as the route which lies through the protoplasts of the plant cortex, while the apoplastic pathway represents the route via the intercellular space and cell walls of the plant cortex [58–60]. According to previous studies, the uptake and translocation pathways of pesticides can differ depending on the physicochemical characteristics of pesticides and plants. Therefore, polar organic pesticides (e.g. atrazine, imidacloprid, and carbendazim) are most likely to be translocated via symplastic pathway, whereas non-polar organic pesticides (e.g. propiconazole and phenanthrene) are usually being translocated through the apoplastic pathway [54, 61]. Further, physicochemical properties of these molecules determine their long-distance transportation pathway inside the plant. For example, small organic molecules transported through either xylem or by phloem, whereas large organic molecules with low membrane permeability will be transported via phloem [53].

The lipid content of plant roots has a crucial role in organic pesticide uptake and storage because high lipid content leads to elevated uptake of hydrophobic organic pesticides [52, 54]. As mentioned in Ju et al. [62], the hydrophobicity and subcellular fraction concentration factor (SFCF) of pesticides determine their bioconcentration in plant roots. The SFCF reflects the ratio between pesticide concentration in total plant solid-phase components (root cell organelles and cell walls) and the water-soluble root cellular components (cell organelles and cell walls). It has been observed that organochlorine pesticides such as chlordecone insecticide can be translocated in plants (i.e. radish) via different routes. One route is the root absorption followed by evapotranspiration-driven translocation through diffusion from xylem vessels and the other route is the periderm adsorption followed by diffusion towards underlying tissues [18]. Lipophilic pesticides prefer diffusion through the periderm than root absorption. Also, chlordecone contamination is facilitated by organic acids produced in courgette roots through pesticide desorption from soil [18, 63].

Pesticides could be taken up through foliar parts of a plant and plant cuticle plays a major role in this process by acting as a potential barrier for pollutant penetration. A plant cuticle is a complex extracellular structure that covers the external surface of the plant's aerial parts. The behaviour of pesticide drops on plant surface could be influenced by the cuticle physicochemical properties and ultimately it affects the efficiency and rate of penetration. This penetration is a diffusion-controlled process that consists of three parts such as absorption into the cuticle, diffusion through it, and desorption from it. Cuticle hydration can increase the hydrophilic compound penetration, while hydrophobic compound transportation through the cuticle could be enhanced by factors that decrease wax viscosity [64]. When pesticides (e.g. chlorantraniliprole (CAP)) reach the apoplast of the leaf through cuticle and epidermis penetration, further they could penetrate the symplast through the plasma membrane with the involvement of carrier-mediated transportation (amino acid transporters) [65]. Active translocation of foliar uptaken pesticides can occur through phloem tissues to stems and roots. When pesticide uptake is high, crosswise diffusion of pesticides could be happening from phloem to xylem. These processes can be driven by diffusion resulted from concentration difference or transpiration [65]. These processes ultimately lead to pesticide residue accumulation in different parts of plants such as leaves, fruits, seeds, stems, roots, and tubers.

Bioaccumulation of organic pesticide residues in plant tissues can depend on the physicochemical properties of the pesticide such as lipophilicity and low water solubility. Increment of these factors may increase the bioaccumulation of the pesticides because non-polar contaminant molecules are less soluble in water while they can dissolve in plant lipids. The size of the contaminant molecule also important in the pesticide accumulation because the passage capability through biological membranes is increasing with the decreasing molecule size. The low biodegradability of the pesticides also leads to bioaccumulation in plant tissues. The biodegradation process resulted from the plant metabolic activities acts as a counter-reaction for the bioaccumulation by changing the chemistry of the pesticides [66].

According to many previous studies, the presence of pesticide residues in food items was in quantifiable amounts. Organophosphate and carbamate pesticide residues such as chlorpyrifos, 3-hydroxyl carbofuran, and methiocarb have been detected in considerable amounts in food samples in Nigeria. The comparison of pesticide residue presence between cereals, fruits, and vegetables indicated that cereals had much lower residue than in fruits and vegetables. Vegetables had the highest pesticide residues and the surface area to size ratio could be the reason for the relatively high contamination of vegetables [67].

## 4 Factors Influencing the Uptake of Pesticide Residues by Plants

The factors affecting the uptake of pesticide residues from the soil by plants are of great importance, especially for the health of herbivores and/or human. As shown in Fig. 2, several factors are recognized, which influence the pesticide residues uptake through roots and the translocation to the aerial parts of plants or accumulation in plant roots grown under irrigated soils in real agricultural systems [13, 68]. Basically, predicting the uptake of pesticide residues from agricultural soil by plants is complex hence, environmental factors, plant physiology factors, and physicochemical properties of pesticide residues or a combination of these are effective for the uptake of residue into plants.

### 4.1 Environmental Factors

In general, properties of the agricultural environments (i.e. soil, climate) largely shape and determine the uptake and accumulation of the pesticide residues by crop plants [69]. Furthermore, the magnitude of bioavailability/bioaccessibility of pesticide residues within the rhizosphere plays a vital role in plant uptake. It has been

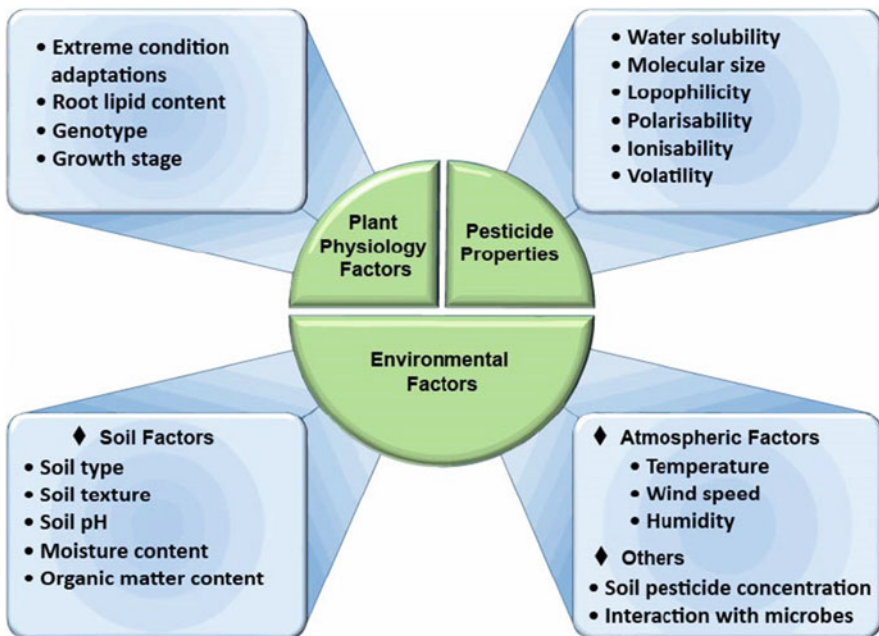


Fig. 2 Factors influencing the uptake of pesticide residues by plants

previously proven that the crops grown in sandy soils with a lower proportion of OM and clay have a higher potential to uptake pesticide residues than in soils enriched with clay and OM [11]. Moreover, soil texture can also have a huge impact on the persistence of pesticide residues in soil and plant uptake [69]. For example, loamy soil texture is responsible for limiting the bioavailability of pesticide residues in the soil thus, leading to reduced plant uptake. Whereas, Xu et al. [70] have argued that sandy soils are capable of fast infiltration and percolation of contaminants thus providing less bioavailability of pesticide residues around the rhizosphere. Moreover, higher humic acid content, a major component of soil, can influence the bioavailability of pesticide residues in the soil. In addition, soil pH can also have a huge influence on the uptake of pesticide residues by plants [57]. Biodegradation of pesticide residues is increased at the alkaline pH by limiting their bioavailability in soil. In fact, the acidic pH of soil usually favours the sorption of the pesticide residues onto the soil, while impacting positively to the uptake of residues by plants [11]. However, acidic soil facilitates the formation of neutral form of residues thus, giving the appropriate conditions for the plant uptake [11]. Furthermore, crops growing in well-aerated soils (under aerobic conditions) compared to compacted and waterlogged soils may have higher potential to upgrade the functionality of roots in the rhizosphere, while enhancing the ability of the uptake of pesticide residues through water and nutrients [11, 71].

In addition to the aforementioned factors, ambient temperature, wind speed, and air humidity can also act as influencing factors for the uptake and accumulation of pesticide residues into crop plants. High temperature, high wind, and low humidity of the environment positively shape the evapotranspiration rate of plants thus facilitating enhanced pesticide residues uptake. It is highlighted that agricultural sites located in dry and hot climatic regions compared to cold or humid regions highly favour pesticide residues uptake from soil. Furthermore, owing to the high temperature, vapour pressure, and volatility of pesticide molecules are noticeably altered which results in increased evapotranspiration rate leading to the plant uptake [72]. Whereas, in the case of crop plants grown under adequate soil moisture conditions, the evapotranspiration rates are expected to exhibit excessive potential for pesticide residues uptake. However, it was reported that plants grown in outdoor agricultural lands accumulate fewer residues compared to the plants grown under greenhouses, which might be due to the pesticide exposure to some particular environmental conditions like air currents, photodegradation, and soil dispersion [57, 73].

## ***4.2 Plant Physiology Factors***

Generally, plant physiology properties have a decisive role in the overall uptake from the soil and translocation through the plant, nevertheless, the process driven by transpiration is also plant-specific. In addition, as uptake of residues from the soil is inextricably linked to the evapotranspiration process, there are some adaptive

mechanisms of plants to minimize transpiration rate [74]. Most importantly, the plants grown in drought conditions (under stress) exhibit less potential for residue uptake from soil, because they have evolved many mechanisms for reducing consumption of resources compared to the plants exposed to the optimum conditions. Therefore, various defence mechanisms, such as stomatal closure, hormone regulation, antioxidants generation, induction of stress proteins, and osmotic adjustment, have been found in plants to cope with such adverse abiotic environmental conditions [75–77]. Moreover, the genotype of the plant is affecting the potential for pesticide residues uptake [68]. It was found that the uptake ability of pesticide residues is exerting different patterns within the crop plant varieties even belonging to the same genus [78]. Furthermore, the accumulation of residues in plants from soil may vary according to their different growth stages as seedling stage (S-stage), rapid growth stage (R-stage), and maturation stage (M-stage). The total amount of the insecticide imidacloprid taken up by leafy vegetables was investigated by Li et al. [17] whose results demonstrate that concentration of imidacloprid could increase with vegetative growth. Similarly, Ge et al. [16] compared the capacity of rice plants (*Oryza sativa* L.) to uptake and distribute imidacloprid (IMI) and thiamethoxam (THX) pesticides from soil and found out that the capability of accumulation of those pesticide residues is much greater in above-ground parts (IMI-10.0 and 410 mg kg<sup>-1</sup> dw; THX-23.0 and 265 mg kg<sup>-1</sup> dw) than in roots (IMI-1.37 and 69.3 mg kg<sup>-1</sup> dw; THX-3.19 and 30.6 mg kg<sup>-1</sup> dw). However, some previous studies reported that root crops like carrot, potato, beet, and radish have more susceptibility to accumulate residues of many organochlorines, such as DDT, chlordane, endrin, from agricultural soils to a greater extent [9, 68]. Interestingly, uptake concentration of organochlorine residues was noticed much higher in carrots compared to other root crops, such as radish, beet, potato, etc. [79]. In fact, leafy vegetables are highly vulnerable to uptake than succulent crops with small root system [11].

In addition, pesticide residues accumulation in root is governed by the plant root lipid content thereby, partitioning into the lipids is considered as primary sorption mechanism of poorly soluble pesticide residues [52, 80, 81]. The potential uptake of pesticide residues from agricultural soil into aerial parts of the plants highly differs depending on the growing season of crops. Crops that are growing during the rainy period do not favour the uptake of pesticide residues from soil, thus the summer season positively influences the uptake. Once these residues are taken up by the plant, they are translocated to aerial parts of the plant such as shoots, leaves, or fruits [82].

### **4.3 Physicochemical Properties of Pesticide Residues**

The persistence of the pesticide residues in the environment and toxicity on non-targeted species depend upon several physicochemical characteristics of pesticides [7, 82]. Molecular size, ionizability, water solubility, lipophilicity,

polarizability, and volatility act as dominating factors to determine the pesticide's interaction with the environment. The physical and chemical parameters of some selected pesticide residues are listed in Table 2. Long-time persistence (long half-life) of pesticide residues is not much desirable where residues can be uptaken via the root system of non-targeted species. Further, active adsorption of pesticide residues through the roots is influenced by the water solubility of residues [83]. Pesticides are available from high soluble to insoluble compounds. Solubility property is influencing the mobility of the residues in the soil environment. High soluble pesticide residues could dissolve well with rainwater and leach downwards while reducing the bioavailability around the rhizosphere [84]. Insoluble residues can be retained in soil whereby are adsorbed tightly on various inorganic and organic soil fractions for a long period.

In addition, lipophilicity denoted by octanol/water partition coefficient ( $\log K_{ow}$ ) is one of the most important physicochemical properties to screen pesticide translocation within the tissues of plants particularly through xylem [16, 85]. It is noteworthy that pesticide residues with high  $\log K_{ow}$  values ( $>1.8$ ) have weak translocation performance in plants [17]. Thus pesticide residues with low solubility usually can accumulate in the root system hence, very difficult to be transported to the aerial parts [69]. For example, pesticide IMI ( $\log K_{ow} = 0.57$ ) and THX ( $\log K_{ow} = -0.13$ ) were detected in high concentration in leaves rather than those in roots, while it was differing from the difenoconazole ( $\log K_{ow} = 4.4$ ) residue which could have been attributed to their octanol/water partition coefficient [16, 52]. Moreover, it has been recognized that high molecular weight chemicals are difficult to be uptaken by plants than chemicals with lower molecular weight [72]. The basic chemical structure of the compound plays a critical role as it can influence the persistence of the pesticide in the soil. On the other hand, pesticide molecules in their ionic form might have increased desirability to be taken up by the plant in low soil pH condition [86]. Nevertheless, they are tightly bound to negatively charged soil fractions and persist for a year or more [87]. Moreover, most of the pesticides are easily broken down into another product, which can be either more stable or transient and complex than their parent compounds. Contrary to this, those newly evolved products may become less toxic chemicals. However, volatilization and photochemical transformation of pesticide residues are of particular interest, because they are among the factors affecting the uptake of the residue by plants [72, 88]. Pesticides with high volatility would completely disappear within a short period, hence reducing the presence of residue in the soil environment. Besides volatilization, pesticides are subjected to photochemical processes by exposing to UV radiation thus, the transformation of the structure is depending upon the complexity of the pesticide compound [88]. It was reported that about 80–90% of pesticides applied into the agricultural fields get volatilized within few days [86].



**Table 2** Physicochemical properties of several pesticides that determine their translocation capacity within the plant

Pesticide	Activity	Formula	Octanol water partition coefficient (Log $K_{ow}$ )	Water solubility (mg L <sup>-1</sup> ) at 25°C except noted below	Molecular weight (g mol <sup>-1</sup> )
Imidacloprid	Insecticide	C <sub>9</sub> H <sub>10</sub> ClN <sub>3</sub> O <sub>2</sub>	0.57	510 (20°C)	255.66
Thiamethoxam	Insecticide	C <sub>8</sub> H <sub>10</sub> ClN <sub>3</sub> O <sub>3</sub> S	-0.13	4,100 (20°C)	291.71
Difenoconazole	Fungicide	C <sub>19</sub> H <sub>17</sub> C <sub>12</sub> N <sub>3</sub> O <sub>3</sub>	4.4	3.3 (20°C)	406.3
Clothianidin	Insecticide	C <sub>8</sub> N <sub>5</sub> H <sub>8</sub> SO <sub>2</sub> Cl	0.905	327 (20°C)	249.678
Chlordecone	Insecticide	C <sub>10</sub> Cl <sub>10</sub> O	4.5	2.7	490.633
Chlordane	Insecticide	C <sub>10</sub> H <sub>6</sub> Cl <sub>8</sub>	4.74	2.78	409.8
Aldrin	Insecticide	C <sub>12</sub> H <sub>8</sub> Cl <sub>6</sub>	6.50	0.027	364.90
Endrin	Insecticide, rodenticide	C <sub>12</sub> H <sub>8</sub> Cl <sub>6</sub> O	5.2	0.230	380.90
Hexachlorobenzene (HCB)	Fungicide	C <sub>6</sub> Cl <sub>6</sub>	5.73	0.005 (20°C)	284.8
Endosulfan	Insecticide	C <sub>9</sub> H <sub>6</sub> Cl <sub>6</sub> O <sub>3</sub> S	3.83	0.32 (22°C)	406.93
Dichlorodiphenyldichloroethylene (4,4'-DDE)	Insecticide	C <sub>14</sub> H <sub>8</sub> Cl <sub>4</sub>	6.51	0.260	318.03
Dichlorodiphenyltrichloroethane (4,4'-DDT)	Insecticide	C <sub>14</sub> H <sub>9</sub> Cl <sub>5</sub>	6.91	0.025	354.49
Dichlorodiphenyldichloroethane (DDD)	Insecticide	C <sub>14</sub> H <sub>10</sub> Cl <sub>4</sub>	6.02	0.09	320.04
Malathion	Insecticide	C <sub>10</sub> H <sub>19</sub> O <sub>6</sub> PS <sub>2</sub>	2.75	145	330.358
α-Hexachlorocyclohexane (α-HCH)	Insecticide	C <sub>6</sub> H <sub>6</sub> Cl <sub>6</sub>	3.08	2.00	287.86
β-Hexachlorocyclohexane (β-HCH)	Insecticide	C <sub>6</sub> H <sub>6</sub> Cl <sub>6</sub>	4.14	31.40	287.86

(continued)

Table 2 (continued)

Pesticide	Activity	Formula	Octanol water partition coefficient (Log $K_{ow}$ )	Water solubility (mg L <sup>-1</sup> ) at 25°C except noted below	Molecular weight (g mol <sup>-1</sup> )
γ-Hexachlorocyclohexane (γ-HCH)	Insecticide	C <sub>6</sub> H <sub>6</sub> Cl <sub>6</sub>	2.67	10.0	287.86
Glyphosate	Herbicide	C <sub>3</sub> H <sub>8</sub> NO <sub>5</sub> P	-1.0	12,000	169.073
Trifluralin	Herbicide	C <sub>13</sub> H <sub>16</sub> F <sub>3</sub> N <sub>3</sub> O <sub>4</sub>	4.69	<1 (27°C)	335.28

## 5 Major Impacts on Human Health and the Environment

The excess and widespread use of pesticides has triggered many environmental and health-related issues worldwide. As stated in Bhandari et al. [37], more than two million people living in developing countries have a higher health risk due to excessive pesticide use. Also, previous estimations stated that the annual death rate of pesticide poisoning was about 5,000–20,000 [2]. Many chemical pesticides and their residues released into the surroundings have led to environmental pollution. Specifically, pesticide residues can spread in soil, water, and air resulting in the increase of soil, water, and air pollution by reducing their quality. Ultimately, these pesticides and their residues can end up in the human body and may cause diseases especially in the renal, reproductive, nervous, respiratory, endocrine, immune, and cardiovascular systems [19, 89]. According to Golge et al. [28], pesticides may result in genotoxic, neurotoxic, and carcinogenic activities in the human body.

The degree of the harmful health impact of pesticides and their residues can be determined by the toxicity of pesticide chemicals, the magnitude of exposure, and the exposure time. Exposure is the contact of pesticide substance with the human body and it can happen through ingestion of contaminated water and food, inhalation of pesticide containing dust and air, and the direct dermal absorption of pesticides [2, 90]. When the pesticide exposure level surpasses the acceptable dosage level, harmful effects can take place in the human body [28]. The toxicity of pesticides can be either acute or chronic. Acute toxicity is defined as the capability of a chemical substance to cause harmful health effects right after exposure. This acute toxicity can occur from the pesticide exposure during the application, pesticide drift from croplands, accidental or intentional poisoning [91]. Chronic toxicity reflects the capacity of a chemical substance to generate harmful health effects during long-time exposure. This chronic toxicity can result from the pesticides and their residues containing in the harvest. Due to pesticide poisoning, many symptoms in the human body can appear such as nausea, headaches, faintness, body aches, weakened vision, skin rashes, and muscle cramps [2]. Many chronic effects caused by pesticide poisoning can be listed as different types of cancer, neurodegeneration, blood disorders, reproduction effects, birth defects, genetic alteration, endocrine disruption, and respiratory, digestive and renal problems [19, 92].

Pesticides that are significantly hazardous for humans are identified as priority substances. For example, herbicides such as atrazine, triazine, simazine, and terbutryn have been characterized as priority substances by the water policy directive draft by European Union (2013/39/EU) [93]. However, due to good weed controlling ability in crops such as cereal, cotton, and sugarcane these herbicides are currently being used extensively [94]. Carbamate pesticides are suspected as mutagenic and carcinogenic substances that can be enormously toxic to animals and humans [67]. As stated in Saini et al. [95], carbofuran is a toxic carbamate insecticide that can cause embryotoxic and teratogenic effects on humans through cholinesterase inhibition. Pesticides such as metalaxyl-M can possess low to moderate toxicity while acetamiprid insecticide causes relatively low toxicity in mammals [28]. Also, a

study of chronic dietary exposure to pesticides in a Greek population showed that organochlorines and pyrethrins residues in vegetables and fruits caused negligible effects on humans [96].

According to many research findings, humans can be exposed to pesticides mainly via contaminated food ingestion [96, 97]. Analysis of dried brown beans and watermelons in Nigeria identified dichlorvos, chlorpyrifos, dimethoate, and diazinon pesticide amounts higher than the acceptable residue limits [67]. Many cowpeas, millet, soybeans, white pepper, egusi seeds, and maize samples collected from Cameroon had one or more pesticide residues of dimethoate, acetamiprid, imazalil, carbofuran, malathion, metalaxyl, and DDT higher than the European Union maximum residue limits [98]. Gherkin plant is susceptible to many insects, bacterial, and fungal infections and the samples analysed in Turkey showed the residues of applied pesticides such as metalaxyl, chlorothalonil, and acetamiprid [28]. Also, pesticides such as acetamiprid, aldicarb, carbofuran, metalaxyl, pirimicarb, carbaryl, and isoprocarb are often inspected in cucumber and Chinese cabbage samples in China [99].

Apart from the health effects to humans, pesticide residues can pose adverse effects on the environment as well. Extensive use of pesticides can intensify the soil accumulation of residues and ultimately it can affect the soil microorganisms and soil structure. The degradation products of pesticides can alter the biochemical reactions, microbial diversity, and enzymatic activities. Also, it may reduce soil fertility and soil biomass [2]. According to Chandran et al. [23], the toxicity of degradation products of pesticides is more toxic than the parent pesticide. Pesticides remaining in the soil for long periods can be a threat to the ecosystem by spreading via food chains [92]. Intensive pesticide application can lead to the increase of pesticide resistance of pests and also, it can affect non-target organisms in the environment [99]. For example, populations of pollinators, natural predators (important for pest control), and earthworms can be reduced by pesticides such as carbamates and some organophosphorus pesticides [24]. It has been reported that the volatilized herbicides can affect the primary producers by damaging non-target plants including some rare species [19]. Pesticides can accumulate and pollute surface water bodies through surface runoff, irrigation, leaching from treated soil, pesticide spray equipment washing, and accidental spillage [2]. Lv et al. [55] stated that tebuconazole fungicide can pose health effects on humans via aquatic organism contamination.

## 6 Future Outlook and Considerations

The rapidly growing population creates a demand in approximately 70% increment of food production worldwide. Anthropogenic chemicals are quite frequently using to control pest effects on crop production thereby remarkably increasing agricultural productivity [72]. Despite advances that have been made, excessive usage of pesticides leads to the introduction of pesticide residues to agricultural soils. Perhaps the

most challenging part is the cultivation of safe crops using contaminated lands [100]. Laboratory experiments have proven enough that the soil acts as a primary sink for pesticide-based soil contaminants and uptake of them by various plant species. Pesticide residues accumulated in edible plants are of great concern due to the dietary ingestion of them via food chain can harm to human health. As the basis for the most food productions being linked with the soil quality, it is important to assess dissipation patterns and pathways of pesticides in agricultural ecosystem qualitatively and quantitatively. Even so, laboratory experiments are limited to few conditions, hence it may be difficult to predict the potential risk of plant uptake. Therefore, it is obvious to conduct studies under realistic field conditions to compensate for such limitations and to make reasonable risk predictions for human health which should be taken into account [53]. Further, the effect of the pesticides and the uptake of residues by plants may vary in different locations in the world. The statistics may significantly differ in the tropics compared to their counterparts in the temperate. Thus, comprehensive studies should be carried out in tropical and subtropical agricultural regions where intensive research has not been carried out yet in the field of ecotoxicology [101]. Additionally, introducing soil quality standards and prospective risk assessment schemes for commonly used pesticides will bring up control in pesticide application rate and thereby lowering the effect to the agroecosystems [101].

There are many different types of pesticides to manage the population of pests nevertheless, based on their coverage they can be either narrow-spectrum or broad-spectrum. In the future, it would be interesting to have an understanding of how that wide range of chemical mixtures in the field conditions influence plant uptake [102]. It is assumed that the association of botanical pesticides derived from the same essential oil may have synergistic as well as antagonistic effects on a selected pest and its ecosystem [103]. However, utilization of the same land for various seasonal plants has a risk for the production of safer agricultural crops, whereas uptake patterns of soil persistent pesticides are depending on the plant species. In the meantime, it is required to conduct experiments using different soil types with various textures to access the potential risk for plant uptake of pesticide residues. Perhaps, in some risk assessment studies calculate the bioconcentration factor (BCF) to measure the tendency of pesticide residues accumulation in crops. Very high BCF values suggest that uptake of residues from contaminated soil is increasing for the particular plant. However, the plant could accumulate residue from the mode of application thus BCF value is not suitable for all the situations to measuring the potential of plant uptake effect [104]. Importantly, proper eco-toxicological risk assessments should be undertaken at each stage of cropping to ensure safe food production thereby reducing health risks for humans [105].

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