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ADSORPTION, DEGRADATION AND RESIDUE ANALYSIS OF AGROCHEMICALS IN AGRICULTURAL SOILS

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Abstract

In modern agriculture agrochemicals are applied to increase crop productivity, manage pest and weeds, and prevent plant diseases. Due to repeated use however soil contamination, persistence of residues, ecological toxicity, groundwater pollution, and transfer into the food chain has become of great concern. The present study discusses the adsorption, degradation, mobility, residue analysis, risk assessment and sustainable management of agrochemicals in agricultural soils. The review brings together recent works on the behavior of agrochemicals in soil systems, highlighting physicochemical properties, adsorption desorption interactions, degradation reaction pathways, environmental fate and degradation, analytical methods for detection, and remediation strategies. The key processes are discussed, including microbial degradation, chemical transformation, photodegradation, leaching, plant uptake and bound residue formation. Chemical properties including solubility, polarity, hydrophobicity, partition coefficient, molecular structure, type of agrochemical formulation and degradation rate in the soil (half-life) control the fate of agrochemicals in soil. The mobility and bioavailability of residues are controlled by adsorption, their persistence and conversion into metabolites by degradation. Strongly bound and non-extractable residues can serve as long term contamination reservoirs. Soil-residue management for sustainability needs to be integrated with monitoring, risk-based regulation, bioremediation, phytoremediation, organic amendments, biochar application, precision agriculture, and integrated pest management to minimize agrochemical persistence and mitigate effects on soil, water, crops, and human health.

KEYWORDS: Agrochemicals; Adsorption; Degradation; Pesticide residues; Agricultural soils

1. INTRODUCTION

Agrochemicals are now a key part of modern agriculture as they are used in crop protection, nutrient management, weed control, pest suppression, and improving yields. Agrochemicals are, in general, any synthetic or biological product used in a field for agriculture, such as pesticides, herbicides, insecticides, fungicides, fertilizers, plant growth regulators, soil conditioners, and others. Pesticides and other crop protection chemicals that are directly associated with soil, crops, water, microorganisms, and non-target organisms are highlighted. The high level of their use has contributed to the enhancement of agricultural productivity; however, it has also sparked significant concerns about soil contamination, persistence in the soil, transfer to the food chain, ecological toxicity, and long-term impacts on human health [1,2].

Agrochemicals can be grouped based on the targeted organism, chemical structure, mode of action, and persistence in the environment. Weed control is managed through the use of herbicides, insect pest management is achieved with insecticides, fungal pathogen management is achieved with fungicides, and nematodes are managed using nematicides. Some compounds can be broad-spectrum, while some are specific to a particular biological target. Other classifications for pesticides include organophosphate, carbamate, pyrethroid, neonicotinoid, triazine, phenoxy herbicide, and organochlorine. The chemical stability, solubility, adsorption properties, degradation routes and toxicity of each group is different. For instance, pyrethroid insecticides are commonly used due to their insecticidal activity, but their persistence and degradation are greatly dependent on microbial transformation and soil properties [3]. Likewise, phenoxy herbicides like 2,4-D are also key in weed management and their environmental fate is closely related to microbial degradation pathways, influencing the persistence of the herbicide in soil as a residue [4]. Agrochemicals are closely linked to the high food demand, the new pests, monoculture systems and the demand for ensuring crop quality under environmental stress in intensive agriculture.

Agrochemicals are commonly applied more than once within a single growing season in high input systems and can be applied as mixtures of active ingredients. This practice can enhance the efficiency of pest control but can also lead to higher levels of chemical resistance in the soil. Soil does not just serve as a passive receptor, but rather a complex reactive system where agrochemicals can be adsorbed, degraded, leached, transformed, immobilized or absorbed by plants. Soil properties, including chemical characteristics, soil texture, pH, organic matter, types of clay minerals, water content, temperature and microbial communities, thus, affect the behavior of pesticides in soil and plants [2].

Residues of agrochemicals are both a sink and a transformation medium in agricultural soil. Inorganic and organic compounds can be readily bound and immobilized by carbon-based materials and soil organic fractions, which can affect their mobility and bioavailability [5]. This adsorption can have a beneficial effect on the immediate leaching but also can have a negative effect on the degradation of the residues, thereby increasing the persistence of the residues. Recently, biochar has been used in recent years as a soil amendment due to its high adsorption capacity and ability to decrease the mobility of pesticides in contaminated soil [6].

Another important process that regulates the environmental fate of agrochemicals is degradation. Enzymatic reactions by soil microorganisms, particularly bacteria, fungi and actinomycetes can change or break down the molecules of a pesticide [7]. For pesticides that are commonly used such as pyrethroids, phenoxy herbicides, and others, microbial degradation can diminish toxicity and persistence overtime [3,4]. The movement, transformation, and biological effects of agrochemicals in plant systems have been a topic of concern, such as neonicotinoid pesticides, which need to be understood beyond the soil environment [8]. The synergistic effects of the simultaneous occurrence of pesticides, heavy metals and other contaminants in agricultural soils further compound the ecological and human health risk if they are present in the crops or water sources [1].

Soil systems in agriculture require an integrated approach when considering agrochemicals as this encompasses the classification, intended use, interaction with soil, adsorption, degradation, uptake by plants and risks associated with residues. The objective of the review is to offer a comprehensive knowledge of the behavior of agrochemicals in agricultural soils, connecting adsorption, degradation, residue persistence, analytical detection and risk management. It includes topics on pesticide soil interactions, pesticide residue monitoring, environmental fate, remediation and sustainable strategies for maintaining soil health, water quality, crop safety and human health.

2. Physicochemical Properties of Agrochemicals Influencing Soil Behavior

2.1 Solubility, Polarity, and Hydrophobicity

The physico-chemical characteristics of agrochemicals such as water solubility, polarity and hydrophobicity have a significant influence on their behavior in soils used for agricultural production. Highly soluble and polar compounds are more likely to readily translocate through the soil profile and to enter groundwater or drainage, while hydrophobic compounds are more likely to be retained by soil organic matter, soil clay particles, and carbon based amendments. Rainfall, irrigation and soil properties such as soil texture and water solubility of the active ingredient (AI) may influence the mobility of herbicide residues [9]. The presence of pesticides in the river water samples also highlights that the pesticides may be soluble and transported from fields to rivers via run-off and leaching, as observed in this study [10].

2.2 Partition Coefficient and Organic Carbon Affinity

The aqua octanol and soil organic carbon water partition coefficient are important properties in determining the retention of agrochemicals in soil. Compounds with high organic carbon affinity are more prone to bind to humic substances, crop residues, compost and soil with biochar amendment. Soil organic matter content and microbial activity, which are affected by the presence of organic residues, can also influence the adsorption, desorption, degradation and leaching of pesticides [11]. Likewise, biochar can interact with herbicides as a pore filler, through hydrogen bonding, π–π interactions, electrostatic attraction, and hydrophobic partitioning, which can affect the retention and release of herbicides in soils systems [12]. The key physicochemical characteristics affecting the behaviour of agrochemicals in soil, including their adsorption, degradation, mobility and persistence are summarized in Table 1.

Table 1. Physicochemical properties of agrochemicals influencing adsorption, mobility, degradation, and persistence in agricultural soils

Physicochemical property	Soil-behavior relevance	Expected effect on fate	Reference
Water solubility	Determines movement of agrochemicals in soil water	Highly soluble compounds show greater leaching and groundwater contamination potential	[9]
Polarity	Affects interaction with water, clay, and organic matter	Polar compounds are generally more mobile, while non-polar compounds tend to adsorb more strongly	[11]
Hydrophobicity	Controls affinity toward soil organic matter and carbon-rich amendments	Hydrophobic pesticides may persist due to strong adsorption	[12]
Organic carbon partition coefficient	Indicates binding strength with soil organic carbon	High values suggest stronger adsorption and lower immediate mobility	[11]

Molecular structure and functional groups	Determines ionization, reactivity, and degradation pathway	Chlorinated, aromatic, phosphate, amide, and ester groups influence persistence and transformation	[10]
Half-life	Indicates persistence and dissipation rate	Longer half-life increases residue accumulation risk	[13]
Formulation type	Controls release rate, dissolution, and soil retention	Controlled-release or encapsulated formulations may reduce rapid loss but prolong residue presence	[11]

2.3 Molecular Structure and Functional Groups

Reactivity, binding and transformation potential are determined by the molecular structure of an agrochemical. Polarity, ionization, adsorption and susceptibility to chemical or microbial degradation is influenced by functional groups like chlorine, phosphate, amide, carboxyl, and aromatic rings. The persistence of organochlorine pesticides can be higher due to their chemical stability and hydrophobicity whereas organophosphorus and pyrethroid pesticides may be hydrolyzed, oxidized, or degraded by any microorganisms with environmental conditions [14].

2.4 Persistence, Half-Life, and Transformation Tendency

Persistence is generally measured by half-life, that is the length of time needed to break down or dissipate 50% of the applied agrochemical. The compounds with long half-lives tend to persist in the soils and therefore pose a long-term ecological risk. The degradation can take place via microbial metabolism, hydrolysis, photo-, oxidation and advanced oxidation processes. Due to the highly reactive oxidative pathways, hydroxyl-radical-based advanced oxidation processes (AOPs) are potential methods for remediating soils contaminated by organic compounds and have been investigated [15]. Bioaugmentation can also help pesticides degrade by introducing or stimulating microorganisms that can degrade specific chemicals [16].

2.5 Influence of Formulation Type on Soil Retention and Release

The way the agrochemical is formulated affects its dissolution, spreading, adsorption, degradation, and availability in soil. Granules, emulsifiable concentrates, wettable powders, encapsulated and controlled-release products differ in their release of product and in their residue. Retention and transformation can also be influenced by the interactions of formulations with soil moisture, soil microbial populations, and organic amendments. So, the fate of agrochemicals is influenced by molecular characteristics, soil properties, formulation type, and amendments treatment applied during their use [11]. The link between agrochemical properties, environmental fate processes and environmental effects is shown in Figure 1.

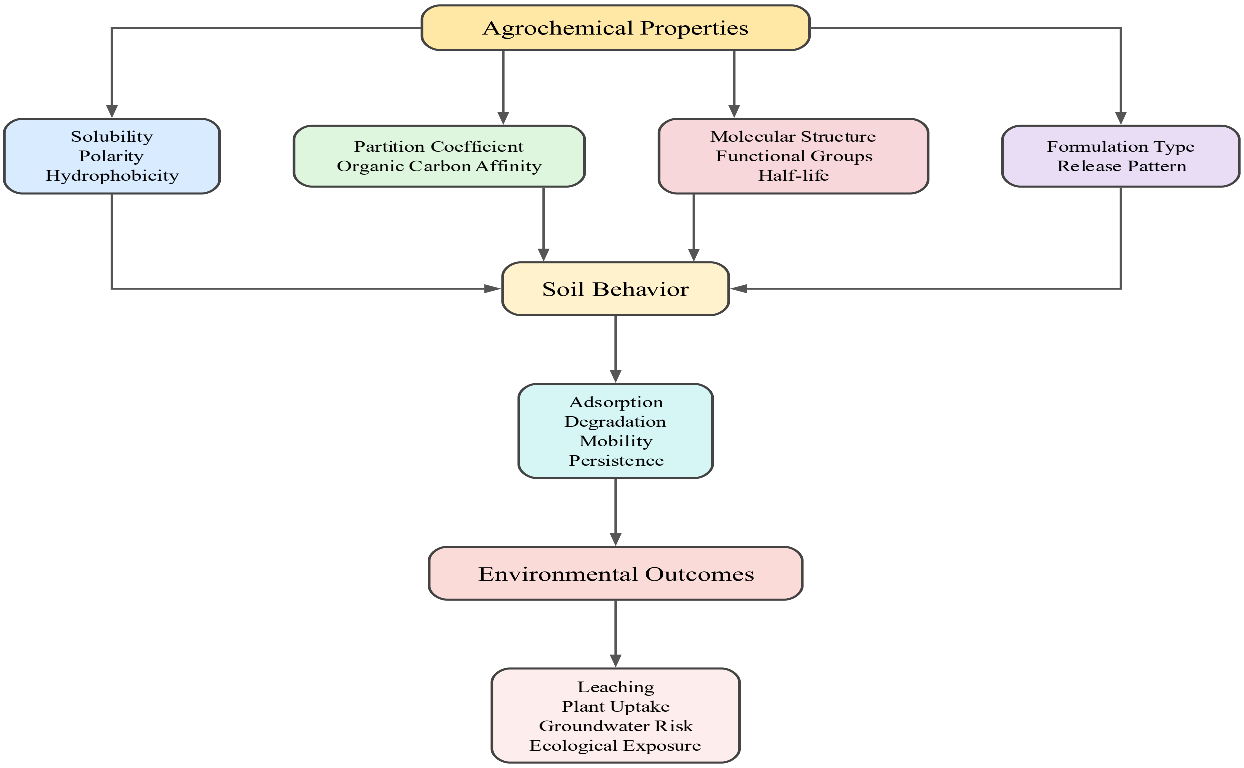

Figure 1. Conceptual framework showing how agrochemical physicochemical properties regulate soil fate processes

3. Adsorption of Agrochemicals in Agricultural Soils

3.1 Concept and Significance of Adsorption in Soil Systems

Adsorption is a phenomenon of utmost significance in the fate of agrochemicals in agricultural soils. The process of binding or sticking of pesticide molecules to soil surfaces such as organic matter, clay minerals, oxides and other reactive soil particles. The adsorption will be a determinant of the fate of the pesticide in the application area or of its susceptibility for microbial degradation, its migration into the groundwater or the formation of a bound residue. The adsorption characteristics of agrochemicals are different for different soil systems because these agrochemicals are categorized based on their chemical structure, polarity, hydrophobicity and persistence [17]. Advanced extraction and chromatography-based analytical studies also showed that pesticide residues in environmental and food related samples can be monitored for a long period of time, and adsorption is playing an important role in the monitoring of residues and risk assessments [18].

3.2 Mechanisms of Adsorption

There are several mechanisms of agrochemical adsorption, such as: hydrophobic bonding, hydrogen bonding, ion exchange, van der Waals forces, electrostatic attraction and ligand exchange. The tendency of hydrophobic pesticides to attach to soil organic matter and of ionizable pesticides to attach to charged clay surfaces, or metal oxides. The strength and type of binding depends on functional groups on the pesticide molecule. Pyrethroids, for example, are degraded in soil under a variety of conditions, and degradation could be a change in molecular structure or change in polarity of pyrethroids and their metabolites [19]. These adsorption mechanisms not only influence the stability of the residues but also play an important role in pesticide soil remediation technologies [20].

3.3 Role of Soil Organic Matter, Clay Minerals, pH, Texture, and Cation Exchange Capacity

Intensity of adsorption is strongly affected by soil properties. The adsorption of ionic or polar pesticides is usually enhanced by clay minerals and oxides, while the absorption of hydrophobic pesticides is generally enhanced by organic matter. The pH of the soil can influence the ionization of weakly acidic and basic pesticides, and either enhance or reduce adsorption depending on the chemical structure. Texture may also be important since a soil with a high clay and organic matter percentage will have a higher pesticide holding capacity than a sandy soil. The binding of positively charged or polar agrochemicals is related to cation exchange capacity [21]. Table 2 presents the main adsorption mechanisms of interaction between agrochemicals and soil organic matter, clay minerals, oxides and amendments.

Table 2. Major adsorption mechanisms of agrochemicals in agricultural soils and their environmental implications

Adsorption mechanism	The main soil component involved	Environmental implication	Reference
Hydrophobic bonding	Soil organic matter, biochar, humic substances	Reduces mobility but may increase long-term persistence	[12]
Hydrogen bonding	Organic matter, clay minerals, pesticide functional groups	Enhances retention of polar pesticides	[22]
Ion exchange	Clay minerals and charged soil surfaces	Important for ionizable herbicides and insecticides	[23]
Van der Waals forces	Organic matter and mineral surfaces	Supports weak to moderate surface adsorption	[24]
Ligand exchange	Metal oxides and mineral surfaces	Influences binding of compounds with reactive functional groups	[2]
Pore filling	Biochar and porous organic amendments	Immobilizes residues and lowers leaching potential	[25]
Electrostatic attraction	Charged clay minerals, oxides, and organic matter	Affects adsorption depending on soil pH and pesticide charge	[26]

3.4 Adsorption Isotherms

Isotherm models are frequently used to study adsorption. The Freundlich model is applied for heterogeneous soil surface whereas the Langmuir model assumes that adsorption takes place in a monolayer on a finite number of binding sites. Temkin models take into consideration changes in interaction energy when adsorption occurs. These models quantify the adsorption capacity, binding affinity and nonlinearity for pesticides which facilitates prediction of pesticide mobility and the persistence of pesticide residues. Such modelling will also be helpful in the interpretation of residue data from techniques like QuEChERS, gas chromatography, mass spectrometry, solid phase extraction, and LC-MS/MS [27].

3.5 Desorption, Hysteresis, and Bioavailability

Desorption refers to the release of previously adsorbed molecules of pesticides back into soil solution. In many soils, the process of desorption is slower and less complete than adsorption, creating hysteresis. This means that the residues can be associated for a long time but can be released under varying soil conditions. Lower desorption can result in decreased acute toxicity but can also help to preserve pesticide persistence from microbial degradation. Bioavailability plays a part in microbial degradation of pesticide residues, meaning that residues that are tightly bound might not be available for microorganisms to degrade [19].

3.6 Impact on Leaching, Runoff, and Groundwater Contamination

Adsorption directly influences leaching, runoff and contamination of groundwater. Percolation is more likely to transport weakly adsorbed pesticides, and erosion during runoff is more likely to transport strongly absorbed pesticides. Monitoring of surface waters and wastewater has shown that the presence of pesticide residues in aquatic ecosystems can be traced back to agricultural areas, where sensitive analytical detection methods are needed [27]. Thus, knowledge of adsorption is crucial for pesticide mobility prediction, design of remediation measures and minimizing agrochemical residues in soil environments [20]. Figure 2 depicts the adsorption/desorption process of agrochemical residues between soil particles and soil solutions.

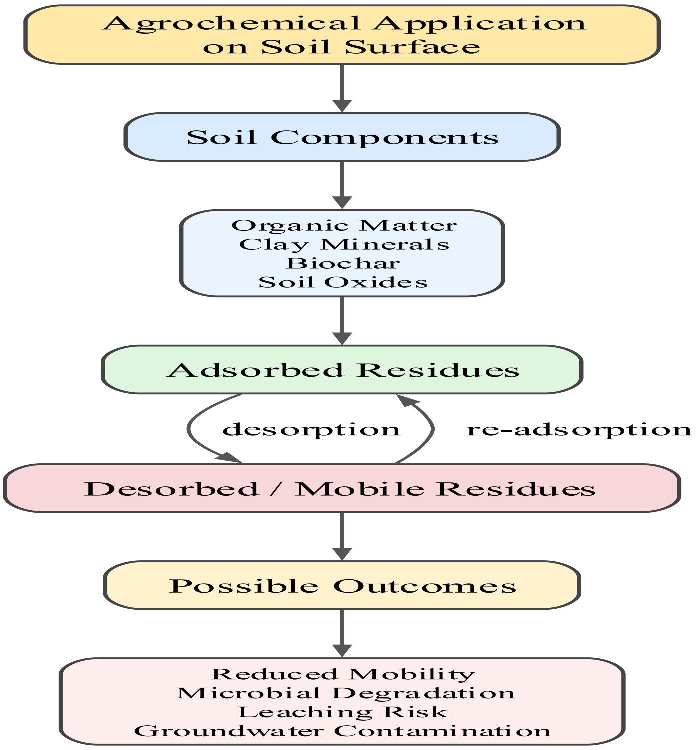

Figure 2. Schematic representation of adsorption and desorption of agrochemicals in agricultural soil

4. Degradation and Transformation of Agrochemicals in Soil

4.1 Overview of Degradation and Transformation Processes

Once agrochemicals are added to agricultural soils, they undergo several degradation and transformation reactions which control their persistence, toxicity, and environmental fate. The degradation can occur through biological, chemical and photochemical processes, and the transformation can include the formation of metabolites or intermediate products. The significance of these processes lies in the fact that some residues can volatiles quickly while others can remain in soil, sediment or water bodies and impact non-target species. For instance, pyrethroids are among the insecticides extensively found in sediment samples, and have been linked to adverse effects on benthic invertebrates, highlighting the potential for ecological risks from incomplete degradation and environmental transport outside of the agricultural arena [28].

4.2 Microbial Degradation and Enzymatic Transformation

Microbial degradation is one of most important pathways of degradation of agrochemicals in soil. Pesticides are capable of being metabolized by bacteria, fungi and actinomycetes, particularly via the use as carbon, nitrogen, phosphorus or energy source. Hydrolases, oxidoreductases, dehalogenases, esterases and oxygenases are enzymes involved in the breakdown of chemical bonds and the conversion of pesticide molecules to less persistent forms. Recent studies indicate that microbial communities play a crucial role in the degradation of soil organic contaminants, with microbial adaptation, contaminant bioavailability, soil characteristics, and ecological disturbance influencing the efficiency of degradation [29]. A better diversity and increased enzymatic activity in microbial communities can improve natural remediation of agrochemical residues by sustainable land management practices [30].

4.3 Hydrolysis, Oxidation-Reduction, and Chemical Degradation

Chemical degradation involves hydrolysis, oxidation, reduction, dehalogenation and splitting of functional groups. Hydrolysis plays a particularly significant role in the case of ester, amid, carbamate or organophosphate bonds; oxidation-reduction reactions occur frequently in soils that vary in moisture and aeration conditions. For example, neonicotinoid insecticides have different adsorption and degradation characteristics in agricultural soils depending on soil properties and environmental conditions, including their retention and transformation [31]. The degradation of chemicals is, therefore, closely related to pH, redox state, mineral surfaces and organic matter. The main degradation and transformation pathways of agrochemicals in agricultural soils are summarized in Table 3.

Table 3. Degradation and transformation of agrochemicals in soil systems

Degradation pathway	Main process	Major influencing factors	Environmental significance	Reference
Microbial degradation	Bacteria, fungi, and actinomycetes metabolize pesticide molecules	Microbial diversity, soil moisture, temperature, pH, organic matter	Reduces parent compound concentration and supports natural attenuation	[19]
Enzymatic transformation	Enzymes break chemical bonds through hydrolysis, oxidation, and reduction	Enzyme activity, substrate availability, microbial adaptation	Converts agrochemicals into metabolites or less toxic products	[3]
Hydrolysis	Water-mediated cleavage of ester, amide, or phosphate bonds	Soil moisture, pH, temperature	Important for organophosphates, carbamates, and some herbicides	[31]
Oxidation-reduction	Electron-transfer reactions transform pesticide structure	Aeration, redox potential, mineral surfaces	Alters persistence, toxicity, and mobility	[15]
Photodegradation	Sunlight breaks or transforms residues on soil surface	Light intensity, exposure time, soil cover, moisture	Important immediately after field application	[2]
Amendment-assisted degradation	Biochar, compost, or organic residues modify degradation environment	Amendment type, carbon content, microbial stimulation	May enhance degradation or immobilize residues	[32]

4.4 Photodegradation on Soil Surfaces

Photodegradation occurs when agrochemicals are in the sun on or close to the soil. Chemical bonds can be directly broken by UV and visible radiation, or UV and visible radiation can create reactive species that alter the structure of pesticide molecules. Photodegradation typically occurs in the top soil layer but may still be significant shortly after field application in dry soils or in unburied residues after field application prior to rain or tillage [3].

4.5 Formation of Metabolites and Transformation Products

Not all degradation occurs through the process of Agrochemical degradation. Metabolites of the parent compounds can be formed which can be biologically active, mobile or toxic. This is especially critical for products whose breakdown compounds can remain in the soil under certain conditions such as insecticides and herbicides. Rice straw biochar amendment significantly influences the persistence of triazine herbicide parent compounds and the formation or persistence of degradation products as well as their adsorption, thereby altering the persistence [32]. Hence, parent agrochemicals and relevant metabolites should be taken into consideration for residue analysis.

4.6 Factors Affecting Degradation

The agrochemical degradation process is affected by soil moisture, temperature, pH, aeration, organic content, soil texture, organic matter content, and type of the amendment. Microbial activity tends to be higher at elevated temperatures and optimum moisture and enhances degradation, while extreme dryness, acidity, alkalinity or lack of aeration can slow transformation. Organic amendments can promote microorganisms and can create adsorption and decrease bioavailability. Sandy loam soils have been demonstrated to have different degradation rates depending on temperature and organic amendments, showing the importance of soil management practices on the degradation rate [33].

4.7 Degradation Kinetics and Half-Life Assessment

A frequently used method for estimating the rate of the degradation of agrochemicals in soil is called degradation kinetics. Half-life is the amount of time it takes for pesticide to be reduced to 50% of the application. Usually first order kinetic models are used, but sometimes a biphasic or multi-compartment model can be more appropriate for field use. Altering degradation kinetics by modification of biochar can be achieved by modifying the adsorption, microbial habitat, moisture retention and contaminant availability. So, modified biochar is proposed as an effective amendment for the pesticide-contaminated soils as it can enable immobilization, transformation, and remediation processes [25]. The process of agrochemicals being degraded, forming metabolites and mineralized and the residue's persistence is summarized in Figure 3.

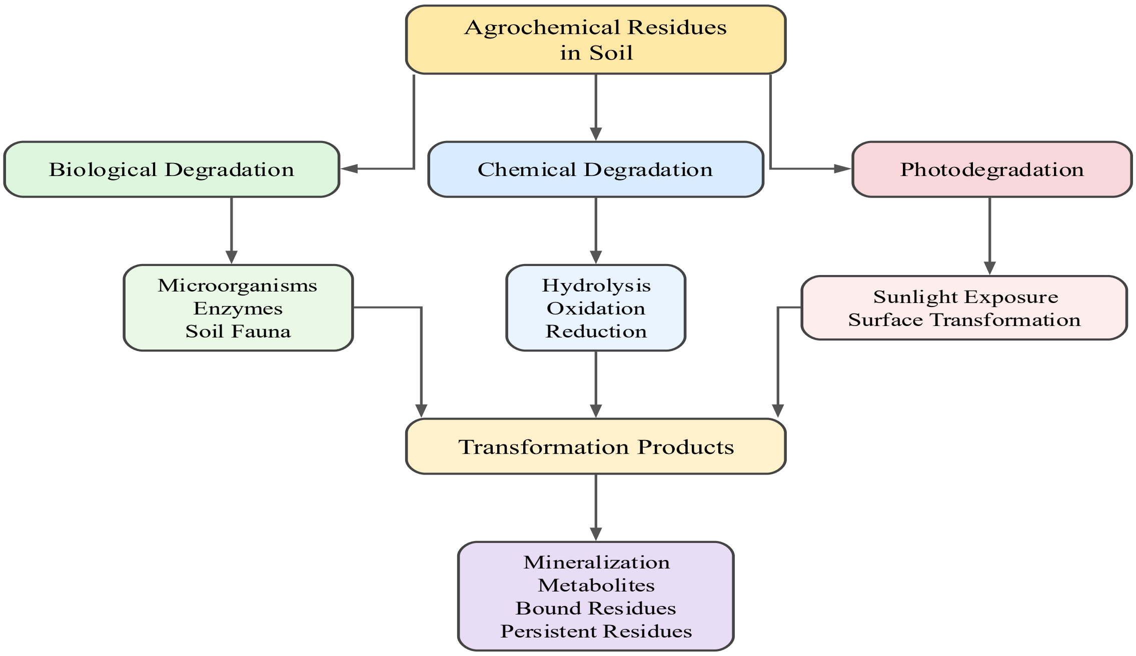

Figure 3. Integrated degradation pathway of agrochemicals after entry into agricultural soil

5. Persistence, Mobility, and Environmental Fate of Agrochemical Residues

5.1 Soil Persistence and Residue Ageing

The number of agrochemicals that remain in soil will depend on the relative importance of factors such as adsorption, degradation, volatilization, leaching, runoff and biological uptake. Some pesticides are highly susceptible to degradation while others persist in soil for months or even years, due to chemical stability, repeated usage, limited microbial degradation, or high affinity to soil particles. Residue ageing is caused by the progressive decrease in the extractability of a pesticide molecule as it diffuses into the soil organic matter, micropores, clay minerals or carbon-rich amendments. Although pesticides are not used in organic farming, their impact on soil systems is still evident in organically managed agricultural soils due to their historical use [34].

5.2 Bound Residues and Non-Extractable Residues

Bound residues are residues that are very tightly bound to soil organic matter, clay minerals or mineral surfaces and cannot be removed with conventional analytical methods. These non-extractable residues can affect the toxicity and mobility of the compound in the short-term, but can also become a long-term reservoir and release contaminants over time because of varying environmental conditions. The ability of soil amendments to do so may vary depending on their organic carbon content, surface chemistry and decomposition state [35]. Moreover, the long-term persistence and bioavailability of pesticides can be affected by the pore filling, surface complexation, hydrophobic interactions, and electrostatic attraction between modified biochar and pesticide [25].

5.3 Leaching and Vertical Movement Through Soil Profiles

Leaching may happen if agrochemicals migrate down the soil profile with water that percolates through the soil. Chemicals that are weakly absorbed, water-soluble, and can stay in the soil long are more likely to be found in deeper soil and in groundwater. Soils with a high sand content are more susceptible to leaching, and soils with a high clay content and organic matter may be more strongly bound. The occurrence of pesticides in the environment is strongly correlated with transport processes, hence it is very important to be able to understand the pesticide's leaching behavior for remediation and management planning [36].

5.4 Runoff and Transport to Surface Water Bodies

Alternatively, pesticides or pesticide residues can be carried horizontally via surface runoff, particularly following a rainfall or irrigation immediately after applying pesticides. Dissolved residues can be transported by the runoff water and strongly adsorbed residues can be carried by eroded soil particles. In so doing this process can cause ponds, streams, rivers and drainage channels in agricultural fields to be polluted. Hence, degradation processes of soil and water are also relevant as pesticide contamination is not limited to the place of application and can extend to the neighbouring environmental compartments [24].

5.5 Uptake by Plants and Entry into the Food Chain

Some agrochemical residues are still soluble in soil solutions and can be taken up by the roots of plants. Residues can be bioaccumulated in roots, stems, leaves, fruits or grains depending on their solubility, the plant species and the metabolic transformation. This allows pesticides to enter the food chain from the soil.

5.6 Ecological Risks to Soil Microorganisms, Earthworms, and Beneficial Fauna

Soil organisms such as earthworms, arthropods and soil organisms in general may be affected by agrochemical residues. Pesticides can help decrease the diversity of microbes effect enzyme activity, impact nitrogen and carbon cycling and decrease soil ecological resistance. The effect of agrochemicals on soil microbiota is particularly significant since soil microbial communities govern organic matter decomposition, availability of nutrients and natural degradation of contaminants [37]. Remediation technologies focus on minimizing these ecological risks by improving pesticide degradation, immobilization or removal from the soil [38].

5.7 Human-Health Implications Through Contaminated Crops and Water

Residuals of agrochemicals can enter humans via contamination of crops, drinking water, surface water and via the food chain. Long-term exposures to mixtures of pesticides can be harmful due to chronic toxicity, endocrine disruption, neurotoxicity, and other adverse health impacts, depending on the specific pesticide and concentration of exposure. Agrochemical residues may remain in the soil, move from soil to water and water to plants, and may be transformed along soil water plant systems, therefore proper monitoring and managing are needed. Biochar amendment, microbial degradation, phytoremediation, and better pesticide-use management are all essential sustainable remediation techniques that can help to minimize environmental and human-health hazards [24,36].

6. Analytical Methods for Residue Detection and Quantification

6.1 Soil Sampling, Storage, and Preparation

Representative soil sampling is an important first step in accurate residue analysis since pesticide distribution within the agricultural field is not always uniform, depending on how the pesticide is applied, the soil texture, irrigation, runoff, crop cover, and degradation rate. Samples are typically taken from the surface layer or from various depths for vertical sampling. Soil samples collected need to be air dried or freeze dried, sieved, homogenized and stored carefully to avoid degradation or contamination prior to analysis. In the context of pesticide residues monitoring, standardized sampling and preparation procedure is emphasized in all global monitoring studies, as it would allow the comparison of pesticide residues between agricultural soils and regions [5,39].

6.2 Extraction Techniques

In order to move the pesticide residues from the soil matrix to a solvent phase that is suitable for instrumental analysis, extraction is needed. Some conventional extraction techniques are: Solvent extraction, Soxhlet extraction, Ultrasonic-assisted extraction, Solid-phase extraction, and Accelerated solvent extraction. With its rapid, relatively simple, inexpensive and applicability to multi-residue pesticide analysis, however, Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) based extraction has gained popularity. The extraction efficiency for soil residue monitoring is affected by pesticide polarity, organic matter in the soil, the amount of clay, soil moisture and the strength of the pesticide's binding to the soil. The simultaneous monitoring of 311 pesticide residues in agricultural soils of loamy sand type shows the effectiveness of the QuEChERS methodology associated with advanced analytical chromatographic methods for wide spectrum analysis of pesticide residues [40].

6.3 Clean-Up Methods for Reducing Matrix Interference

Humic substances, pigments, lipids, minerals and other co-extracted compounds may be present in soil extracts which can result in interference with the detection of pesticides. Thus, clean-up procedures are required to increase the sensitivity, minimize matrix effects and prevent damage to analytical equipment. Primary secondary amine, graphitized carbon black, C18 sorbents, florisil, silica gel, and dispersive solid-phase extraction materials are the common materials used for clean-up. Special attention is needed in soils that have high levels of organic matter because strong adsorption could make it difficult to quantify pesticides and co-extracted organic compounds. Soil matrix properties influence the adsorption and degradation of pesticides and therefore require optimization of analytical procedures done on the soil matrix [23].

6.4 Instrumental Techniques

HPLC, GC, GC-MS, LC-MS/MS and UHPLC-MS/MS are commonly used instrumental methods for residue detection of agrochemicals, with GC used for thermally stable and volatile pesticides, and LC-MS/MS used for more polar, thermolabile, and modern classes of pesticides. Multi-residue studies are particularly beneficial for combined GC-MS/MS and LC-MS/MS platforms as pesticide mixtures consist of compounds with a wide range of chemical characteristics. This instrumental approach is crucial as pesticide usage in the world has led to the increase of the complexity of environmental residue profiles and the need for a reliable monitoring for soil contamination [41].

6.5 Method Validation and Quality Assurance

To ensure the reliability and repeatability of residue data, validated analytical methods are needed. Recovery, precision, accuracy, linearity, limit of detection (LOD), limit of quantification (LOQ), selectivity, repeatability, reproducibility and matrix effect are important validation parameters. The other parts of quality assurance include blanks, spiked samples, calibration standards, internal standards and certified reference materials and replicate analysis. In the field of regulatory monitoring and ecological risk assessment, method validation becomes even more significant as residues of pesticides are present at trace levels in complex soil matrices [40]. The current main analytical techniques and sustainable management approaches for agrochemical residue monitoring and risk reduction are presented in Table 4.

Table 4. Analytical methods and sustainable management strategies for agrochemical residue monitoring and risk reduction

Component	Key method or strategy	Purpose	Reference
Soil sampling and preparation	Surface and depth-wise sampling, drying, sieving, homogenization, cold storage	Ensures representative and reliable residue analysis	[42]
Extraction	QuEChERS, solvent extraction, ultrasonic extraction, SPE, accelerated solvent extraction	Transfers residues from soil matrix to analytical solvent	[40]
Clean-up	Dispersive SPE, C18, PSA, graphitized carbon black, silica-based materials	Reduces matrix interference and improves sensitivity	[42]
Instrumental analysis	GC-MS, GC-MS/MS, LC-MS/MS, UHPLC-MS/MS, HPLC	Detects and quantifies parent compounds and metabolites	[18]
Method validation	Recovery, precision, accuracy, LOD, LOQ, linearity, matrix effect	Confirms reliability of residue data	[43]
Bioremediation	Microbial degradation, vermiremediation, bioaugmentation	Reduces pesticide load and improves soil biological quality	[33]
Organic amendments and biochar	Compost, crop residues, rice straw biochar, modified biochar	Immobilizes residues, reduces mobility, and may support degradation	[32]
Sustainable management	Integrated pest management, precision spraying, reduced chemical input	Prevents excessive residue accumulation	[41]

6.6 Multi-Residue Analysis of Pesticide Mixtures

The residues in agricultural soils are frequently mixtures of pesticides, not single pesticides. Therefore multi-residue analysis is necessary to gain insight into contamination in the real field. Previous studies conducted in European agricultural soil have revealed that pesticide residues can be present as complex mixtures, from current use as well as past use [39]. Pesticide residue mixtures, transformation products, and the overall ecological effects of pesticide mixtures should be evaluated in sustainable pest management, in addition to the detection of specific pesticides [44].

6.7 Challenges in Detecting Metabolites and Bound Residues

The detection of metabolites and bound residues is still a significant analytical problem. In some cases, transformation products can be more polar, mobile or toxic than the parent compounds and non-extractable residues can be strongly sorbed by organic matter or clay minerals. These residues can be missed in normal extraction but can pose long term environmental risks. Hence, advanced extraction and high-resolution mass spectrometry, long-term monitoring and sustainable remediation assessment should be combined in future residue analysis to gain a better understanding of pesticide pollution in agricultural soils [42,45].

7. Risk Assessment, Remediation, and Sustainable Management Strategies

7.1 Ecological and Human-Health Risk Assessment of Soil Residues

The risk assessment of agrochemical residues in agricultural soils includes determining the concentration of the residues, their persistence and mobility, toxicity, exposure routes, and potential impacts on soil organisms, crops, water resources and human health. Residue data are frequently used to compare the concentration detected with toxicological thresholds, acceptable daily intake values, environmental quality standards and crop-safety limits. The LC-MS/MS and modified QuEChERS methods have been used in studies of fungicide residues in grapes and soil, both to quantify the residues and to estimate the dietary and environmental concern due to the residues [43].

7.2 Regulatory Limits, Maximum Residue Levels, and Soil-Quality Guidelines

Typically, maximum residues in food and allowable pesticide residue in water, as well as soil-quality guidelines are included in a regulatory evaluation. The soil specific limits are, however, less developed than the crop residue limits, and interpretation is difficult. Thus, monitoring residues should encompass parent pesticides and relevant metabolites, particularly if the pesticide is persistent or mobile. The adsorption desorption behavior is significant for the interpretation of regulations as strongly adsorbed residues stay in soil while weakly adsorbed residues can enter into the crops, groundwater, or surface water [22].

7.3 Bioremediation and Microbial Degradation Enhancement

Bioremediation involves technology that uses microorganisms, earthworms, enzymes or organic amendments to increase the rate of degradation of pesticides in the soil in a sustainable manner. Recently earthworm-assisted processes have been investigated for the reduction of chlorpyrifos (CP)-contaminated soils and can be used to contribute to the reduction in soil contaminants while also enhancing soil fertility indicators [33]. Bioaugmentation, biostimulation, compost amendment, moisture regime, aeration and organic matter can all be used to enhance microbial degradation.

7.4 Phytoremediation and Plant-Assisted Removal

Phytoremediation involves the uptake, immobilization, biotransformation, or degradation by rhizospheral activity of pesticide residues. Exudates from plant roots can promote microbial activity to aid in pesticide degradation. Phytoremediation is typically more time consuming than chemical remediation, but can be low cost, environmentally friendly, and effective for large, agricultural areas. It could be particularly beneficial in situations where low to moderate levels of residue and maintaining soil fertility are important.

7.5 Biochar, Compost, and Organic Amendments for Adsorption and Immobilization

Fertilizer amendment in the form of compost, manure, crop residues and biochar can improve the adsorption and immobilization of pesticides and protect them from mobility. They are effective depending on the composition of organic matter, its pH, surface area, porosity and functional groups. The composition of soil organic matter and pH significantly influence the retention of pesticides like carbaryl, carbofuran and metolachlor, indicating that the selection of pesticides must be based on both the chemistry of the pesticide and the soil's properties [26].

7.6 Integrated Pest Management and Precision Agrochemical Application

Residue reduction is a process that needs to be prevented in addition to being remediated. Excessive agrochemical inputs can be reduced by using integrated pest management, crop rotation, biological control methods, resistant cultivars, soil testing, precision spraying, controlled release formulations, and need-based pesticide application. Such practices reduce residues and keep productivity of crops.

7.7 Future Direction Toward Sustainable Soil-Residue Management

Advanced monitoring, risk-based regulation, bioremediation, use of organic amendments, and precision agriculture should be integrated as part of future residue management. The sustainable strategies should aim to decrease the use of pesticides, promote degradation, minimize the leaching potential and protect soil biodiversity, food safety and human health.

8. CONCLUSION

Despite their potential risks, agrochemicals are still considered to be a necessary part of modern agriculture, as they help to manage pests, weeds, diseases, and crop productivity. But their regular and high level application has led to significant issues about soil contamination, persistence of residues, ecological imbalance and food chain transfer. This review shows how interrelated processes like adsorption, degradation, transformation, mobility and residue accumulation control the environmental fate of agrochemicals in agricultural soil. The physicochemical properties such as solubility, polarity, hydrophobicity, partition coefficient, molecular structure, and half-life are important factors in determining the fate of agrochemicals in soil, their metabolism in soil, and their ability to leach to groundwater, surface water and plant uptake. The adsorption processes are among the most important that control pesticide mobility and bioavailability, and degradation processes control the persistence and toxicity of pesticide residues in soil systems. Four main processes can be used to minimize the persistence of agrochemicals, namely microbial degradation, chemical transformation, photodegradation and amendment assisted remediation. Meanwhile, bound and non-extractable residues are to be handled with care as they may be long-term sources of contamination. Multi-residue approaches are essential for the accurate detection and risk assessment and can be validated by advanced analytical methods. Residue monitoring, bioremediation, phytoremediation, organic amendments, biochar application, precision agriculture and integrated pest management should therefore be integrated in sustainable management. In general, the protection of the agro-ecosystem of agricultural soils calls for agrochemical use in balance, proper control and environmentally responsible remediation procedures.

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