Pesticide Degradations, Residues and Environmental Concerns

Abdullah Al-Mamun

1 Introduction

Pesticide ingredients started to use versatilely after the second world war with the introduction of DDT (dichlorodiphenyltrichloroethane), BHC (benzene hexachloride), aldrin, dieldrin, endrin, and 2,4-D (2,4-dichlorophenoxyacetic acid) [1]. Now a day, approximately 1.0–2.5 × 10^6 tons per year of pesticides and their components are applied over the large fields of agricultural and urban premises to enhance the production of food and to limit the growth of pests [2, 3]. It is widely presumed that pesticides are toxic to targeted organisms and are harmless to non-targeted species. But this assumption does not hold true in most of the cases. Therefore, the applications of pesticide become a severe environmental concern. The ways of spreading contaminants by pesticides are not only from its application to food crops, but also from the unintentional release during transport and manufacturing, as well as from the accumulation of degraded by-products in crops and environment (i.e. soil, water, sediments) [4].

Although pesticides are useful in regulating pests, their unregulated and inappropriate applications cause adverse effects to human and ecosystem. These cause severe health hazards due to rapid fat solubility and bioaccumulation in non-targeted organisms [5]. Their adverse impacts depend on the degree of sensitivity of organisms to a specific chemical. The recurrent application of pesticides accumulates its concentration not only in soil, water, and sediment, but also in the food chain. The spread of pesticides by diffusion and dispersion has also posed the occupational health risk to the exposed inhabitants.

Despite the prohibition of some environmentally persistent (least biodegradable) pesticides (e.g., organochlorines), their uses are increasing in many countries.

A. Al-Mamun (✉)
Department of Civil and Architectural Engineering, Sultan Qaboos University, Muscat, Oman
e-mail: aalmamun@squ.edu.om

M.S. Khan, M.S. Rahman (eds.), *Pesticide Residue in Foods*,
DOI 10.1007/978-3-319-52683-6_5

Therefore, the benefits of pesticides use should be measured by considering the impacts of their persistence in the environment. Although the processes of degradation can eliminate pesticides to certain extents, it is accumulating toxic degraded compounds in the environment. Despite the extensive statistical data of pesticide degradations from regulatory agencies and testing organizations, it is still ambiguous to define the exact routes of pesticide degradation under a specific ground circumstances. Therefore, in this chapter we discuss the scientific contexts to pinpoint the pesticide degradation processes in the environment and their ultimate fate with the effects these pose to human and ecosystem.

2 Degradation Mechanisms of Pesticides in Environment

A pesticide is certified to apply only when it seems to be a non-persistent (i.e., degradation half-life should be few days to weeks) in the environment. After application, the majority of pesticides are adsorbed by targeted and non-targeted plants and species. The remaining fraction is degraded to by-products that are transported to other compartments of the environment [6]. Most of the pesticide degradation processes end with the formation of new toxic chemicals (residues) that have a chronic effect on the immediate inhabitants and ecosystems. All over the world, residues of many pesticides are identified in environmental samples from $ng{\cdot}L^{-1}$ to $mg{\cdot}L^{-1}$ concentrations. Recurrent investigations on the ground and processed drinking water in many parts of the world detect 15–20 types of pesticide degraded compounds in their highest permissible concentration (>0.1 $mg.L^{-1}$) [7, 8]. These unpleasant observations of the widespread pesticide persistence showed that approximately 50% of detected substances have long been prohibited to use, and 10–20% of the detected substances are the degraded compounds. These detected contaminants are not limited only in groundwater, but also in surface water, soil and sediments [9]. Recently, some pesticides and degraded compounds have been detected in high altitude regions, indicating their sufficient transport and persistence over hundreds of kilometers in the atmosphere [10]. Therefore, it is an urgent need to monitor the degradation of pesticides and their ultimate fate in order to control and clean them from the natural environment. This monitoring can improve the protection of the natural food and water sources.

The amount of pesticides to be transported from applied soil to other environmental compartments is determined by their chemical characteristics (volatility, solubility, and adsorption capacity), soil properties (porosity, clay content, and organic content), hydraulic loading, and crop management practices [11]. Degradation/transformation is the process of eliminating excess pesticides in the environment. It is a chemical or a bio-chemical process by which pesticides are transformed and broken down into less harmful chemicals that are bio-compatible to the environment [12–14]. But most of the pesticide degradation processes end with the formation of new toxic chemicals (residues) that have a chronic effect on the immediate inhabitants and ecosystems [11, 15]. Some of the degraded residues along with the non-degraded pesticides are most concerning chemicals in the environment as they are recurring back to human beings through bio-accumulation and bio-magnification.

The degradation of pesticides involves both biotic and abiotic processes. The biotic degradation is mediated by microorganisms or plants. The abiotic degradation, e.g., chemical and photochemical, is mediated by environmental agents, such as electromagnetic radiation, the presence of radical forming agents, temperature, acid and alkaline conditions. The governing degradation process for a specific pesticide is determined by its structural affinity to specific process, and the environmental conditions it is exposed (Fig. 1). For instance, redox gradients in soils, sediments, or aquifers often determine which biotic and/or abiotic degradations can occur. Similarly, photochemical transformations are restricted to compartments exposed to sunlight—e.g., the topmost meter(s) of lake or river water, the surface of plants, or submillimeter layers of soil. The atmospheric photo transformations strongly affect the chemical nature and transport potential of pesticides [16].

Pesticide degradation is not expected before the pest is controlled. Their degradation in the environment has been affected by a couple of soil parameters including pH [17, 18], temperature [13, 19–21], and moisture content [22]. The degradation processes are broadly categorized as microbial degradation (biodegradation), chemical degradation and photo-degradation [11, 23, 24].

2.1 Bio-degradation/Microbial Degradation

Microbial degradation is the dominant mechanism of pesticide degradation in soils [25]. It is a coincidence process during microbial metabolism. Soil microorganisms such as bacteria, actinomycetes, fungi, algae and protozoa use pesticides as a source of carbon and energy, or ingest them with other sources of food and energy. Approximately 100 million individual bacteria populations and 0.01 million fungi colonies live in 1 g of fertile soil with about 5 to 7 thousand of different species. These abundant diverged microorganisms in the soil make itself as an effective and eco-friendly bio-reactor to degrade toxic chemical wastes [26–29]. Such an enzyme bio-catalytic reaction ends with a variety of structural and toxicological modification into the parent pesticides [30, 31].

The exact pathways for bio-degradation of pesticides inside the microbial cells are still ambiguous. Numerous investigations in the recent decade have revealed that microorganisms use a specific genetic material (DNA bounded protein) to encrypt the necessary reactions to deal with a specific metabolic compound. Some other investigations have suggested that a specific group of microbes is responsible for specific substrate degradation [32, 33]. The dissolved pesticides in the soil solution transport across the cell membrane of the specific microbial colonies to be metabolized. Some other microbial extra-cellular enzymes predigest pesticides out of the cell that are poorly transported across the cell membrane. Once the pesticides enter into the microbial cell, it is metabolized via internal enzymes. The rate of biodegradation for

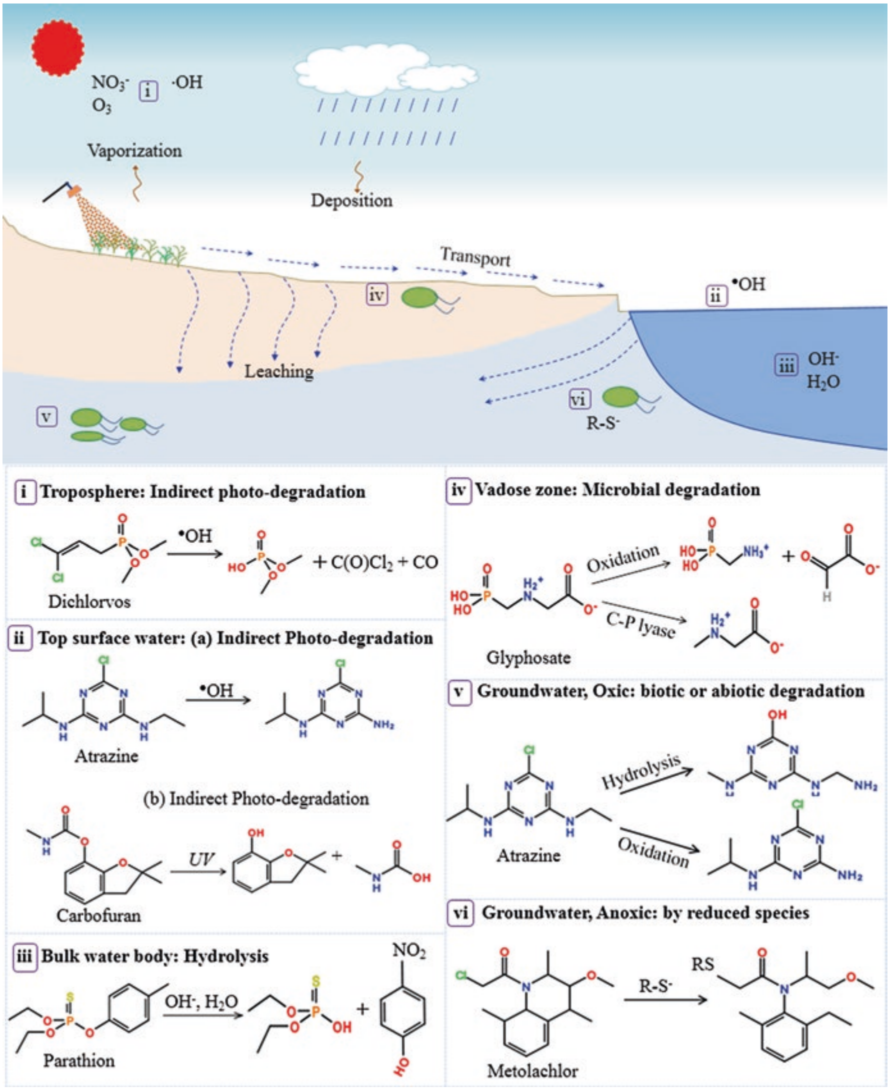


Fig. 1 Examples of pesticide degradation in the environment. (*Upper*) Examples of compartments and reaction partners in environment responsible for pesticide degradation. (*Lower*) Examples of relevant reactions in each compartment for some representative pesticides

a specific pesticide depends on the presence of necessary enzymes and the favorable environmental conditions to stimulate the bio-chemical reactions. Sufficient concentration of microbes, their diversity, and contact period between extra-cellular enzymes and pesticides are necessary for an efficient degradation process.

A number of mathematical models have been anticipated to represent the kinetics of the bio-degradation. Most of the models confirm either the first or the second order kinetics. However, in case of first-order kinetics, the rate of degradation is a function of temperature, pH, and limiting nutrients; while in case of second-order kinetics, the rate is a function of the available concentration of pesticides along with the size of bacteria populations [6, 34, 35]. The rate of biodegradation is also affected by some ground circumstances such as:

- Soil conditions (optimum pH, temperature, aeration level, moisture content, and organic content). The higher rate of biodegradation will be achieved at a high temperature, and moist soils with neutral pH.
- Crop alternating practice and frequency of the pesticide application (changing the groups of pesticides can maximize the potential for microbial degradation as well as pest resistance).

Some pesticide degradation, mainly hydrolysis, proceeds through both biotic and abiotic routes. But the higher rate of hydrolytic degradation is detected in the case of enzyme catalytic reactions. For instance, the abiotic dechlorination of atrazine to hydroxyl-atrazine in earlier days was observed as a slower process than the biotic (bacterial) degradation of atrazine with atrazine dechlorinating enzymes in recent studies. The recent investigations found the biodegradation following a second-order rate constant of 10^5 M^{-1} s^{-1} [36] (Fig. 1v). The statistical survey of atrazine dechlorination on topsoil and surface water revealed the abundance of genes that were encoded the atrazine dechlorination enzymes. Therefore, it is most likely the biodegradation of atrazine dominants in the environment. In case of biotic degradations, that have never been occurred abiotically, the rate of degradation is fairly depended on the activity of encoded enzymes. For example, glyphosate (herbicide) contains a C-P bond that is stable in strong electromagnetic radiation, acid or base, and other environmental conditions. The microbes that can break the C-P bond or metabolize it are widely spread in the environment (Fig. 1iv). The enzyme that catalyzed the C-P lysis reaction is encrypted by a 14-gene operon [37]. The pesticide compounds that do not have proper reactive groups are commonly degraded by chemical process. The rate of those chemical reactions depend on high pH and low-redox environments, as well as the in-situ formation of abiotic catalysts (e.g., poly-sulfides, surface-bound Fe(II), and MnO_2). These kinds of chemical transformation are sometimes mediated by microorganisms, which enhance the formation of abiotic catalysts.

2.2 Chemical Degradation

Chemical degradation is an abiotic process caused by the presence of environmental reactants and radicals (oxidizer, reducer, hydroxyl and hydrogen ions). The most usual chemical reactions that are involving in chemical degradations are hydrolysis, redox, and ionization. All of these common chemical degradation processes are affecting by the pH of the media [26, 38].

Hydrolysis Hydrolysis is the chemical reaction in which the functional groups of a pesticide compound is replaced by a hydroxyl radical or ion. As the hydrolytic reaction occurs only at the presence of OH^-, the rate of such reactions is mostly affecting by the pH of the pesticide containing media [38]. Such reactions modify the chemical structure of the complex pesticide compounds to make it simpler one. Depending on the substitution of specific groups, degraded products are usually less toxic than the parent chemicals. The predicted hydrolytic reactions for several pesticide compounds are listed in Fig. 1. Few investigations on abiotic hydrolysis of pesticides identified several functional groups that are more prone to replace by OH^- are organophosphates (Fig. 1iii), amides, carbamates, carboxylic acid esters, epoxides, carbonates, lactones, sulfonic acid esters, some halides (methyl bromide, propargyl), and many more [6, 39].

Some hydrolysis degradation has only been observed under a specific condition. An example of such degradations are clay-catalyzed triazine hydrolysis (Fig. 1v) [40], chloroacetanilide [41] and nitroaromatics transformation [38] in sulfidic environments (Fig. 1vi), or glyphosate oxidation by MnO_2 [42]. Hydrolysis has also been observed in groundwater or lake hypolimnions, which have longer hydraulic retention times (order of years) and lower biomass concentration due to almost complete removal of organic carbon by assimilation.

Redox (Oxidation-Reduction) Reaction Redox reaction consists of transferring electrons from the reduced ingredients to oxidized products. Some common pesticides show redox-degradation in the natural environments includes mercury, toxaphene, and DDT. The rate of redox reaction depends on the redox potential of the couple (oxidation/reduction), the number of electrons transfer, temperature, pH, and composition of metal ions present in the electrolytic media (soil and water). For instance, the reduction half-life of the organophosphorus insecticide (parathion) is on the order of minutes in a strong reducing environment [43]. The redox potential is the dominating factor to produce the oxidation state and final structure of the degraded product of pesticides in the environment. Not only the chemical degradation, but also the biodegradation is strongly influenced by the redox potential of the reaction. In this case microbes act as electron donors and/or acceptors, such as, oxidation of halogenated pesticides by methanotrophs, anoxic biodegradation with nitrate, reduction of halogenated compounds, and sequential aerobic/anaerobic degradation of halogenated organics.

Ionization The degradation of pesticides that are characterized either as organic acid or base is mostly determined by the concentration of H^+ in water within the environmental media. Similarly, the pesticides that are partitioning between liquid-gas and liquid-solid will be dominated by the acid-base interactions between the aqueous phase of chemicals and the liquid or gas concentration within the environmental media. The pesticides that are characterized as weak organic acids or bases do not have a significant influence in changing the pH of the environmental system. Therefore, the pH of the environmental media can be regulated whether the pesticide to be present as neutral or ionic forms [44]. The capacity of adsorption, dissolution, bioaccumulation, bio-persistent, and toxicity of a hydrophilic (extensively ionized) pesticides can be completely different from the pesticides that are characterized as weak acids or bases. For instance, the solubility of an ionic pesticide is likely be higher than that of the neutral species. Therefore, the ionized species could stay in water and has a low chance to be absorbed by the sediments. The ionized species can also change the pH of the environmental system. The approximate pH of the most aquatic systems ranged between 4 and 9, with extreme values lower than 2 and greater than 11.

2.3 Photo Degradation

Photo degradation is a process of breaking the chemical bonds in pesticide molecules by electromagnetic radiation (photon energy) coming from sunlight. It is possible on the surface of vegetation, topsoil (a sub millimeter), water (up to the depth of sunlight penetration), and in the atmosphere. Pesticides that are applied to the surface of vegetation and soil are more prone to photo degradation than pesticides that are incorporated into soil [11]. Photo degradation is taken place by the direct absorption of photon energy or by the radicles produced from other molecules that absorb photon energy. The second one is known as indirect photo degradation.

Direct photolysis has already been represented by first-order kinetics. The reaction rate of such kinetics is determined by the radiation energy needed to break the bonds and the intensity of available light. Light absorption bands for the molecules showed a little bit overlap for different pesticides in case of direct photolysis processes. However, such overlap is not affecting the degradation of pesticides except for trifluralin [45].

There are various photo-chemically active light absorbing agents are detected in surface water for indirect photolysis. Of them, dissolved organic matter (DOM), nitrate, and nitrite ions are important. DOM is the precursor of molecular oxygen, superoxide radical, and other radicals. Nitrate and nitrite ions produce hydroxyl radicals under irradiation. Therefore, the degradation rate of indirect photolysis depends on the concentrations of all relevant reactive species [46]. Such kinds of degradation is categorised by second-order kinetics.

All kinds of pesticide are subject to photolysis to some extents. Factors affecting pesticide photolysis are intensity of sunlight, time of exposure, the properties of the sites, the method of application, and the properties of pesticides. Chloroaromatics, aldehydes and ketones, etc., are more prone to photo degradation [47].

3 Fate of Pesticides in Environmental Media

Transport and leaching of pesticide pollutes surrounding air and water bodies, while adsorption by soil particles increases the chance of degradation and the risks of persistence in the environment (more than 1–6 months). Ecological toxicity and public health hazards are the two parameters to determine the effects of pesticide in the environment. Ecological toxicity is a cumulative measure of the negative impacts of pesticide through the entry into the food chain. The negative impacts are approximately measured by considering: (a) the reduced growth of zooplankton and phytoplankton in surface water; (b) the accumulation of carcinogens and neurotoxins that create reproductive and viability disorder in the offspring of the fish, amphibians, insects, invertebrates, and mammals; (c) the declining growth of beneficial organisms like pollinators; (d) the growth of drug-resistance to the disease causing pests and vectors (e.g., malaria, dengue and Chagas disease); and (e) the changes in biogeochemical cycles that interfere the growth and reproduction of aquatic and terrestrial macro and microorganisms. The public health hazards of pesticides are measured mostly by the acute toxicity caused to the immediately exposed populations or to the indirectly exposed populations through the contaminated air, water and food [48].

The risk of pesticides to contaminate surrounding environmental compartments (air, water and soil) is governed by the factors, such as the characteristics of the soil (porosity, bulk density, surface area, clay content, organic content, buffering capacity, and sorption capacity, etc.) and pesticide (volatility, solubility, stability, sensitivity to light, chemical structure, aliphatic and aromatic content, and chlorite content, etc.) [11, 49], method of application (dosage and form, e.g., granular, solution, suspension, powder or mixed with organic solvent), climatic conditions of the site (rainfall intensity, temperature, sunlight, humidity, etc.), and crop management practices [6]. The higher porosity of soil favors the leaching of pesticide from soil to waterbodies [25, 50]. Soil achieves higher sorption capacity with the higher contents of clay and organic [51]. The higher sorption capacity increases the risk of adhering pesticides with soil particles. This adhering of pesticides favors biodegradation by soil microbes [11]. The volatile pesticide can easily change its phase from liquid to gas which basically favors its movement through the air. The chemical structure and the aliphatic-aromatic contents of pesticide, as well as, the buffering capacity of soil determine the water solubility of pesticide compounds. Chemical structure also determines the rate of degradation of pesticide. The larger the molecular size with the higher contents of aliphatic and aromatic, the slower will be the rate degradation in the environment [52, 53].

During transformation processes, certain types of pesticides turn to harmless end-products for targeted and non-targeted organisms, and the ecosystem. However, some other types of pesticides transform into toxic end-products that are more dangerous than the parent chemicals. Some transformation processes reached to end with the change of chemical structure, which will alter the mode of transport of pesticide degraded-compounds in the environmental media [53]. The persistent xenobiotics, such as, metabolic end-products and non-degraded pesticides accumulate in the different components of the ecosystem, come to be a part of the soil humus, or come across the food chain leading to bio-magnification. Figure 2 shows the ultimate fate of non-degraded pesticides, degraded compounds and metabolic end-products into the different compartments of the ecosystem.

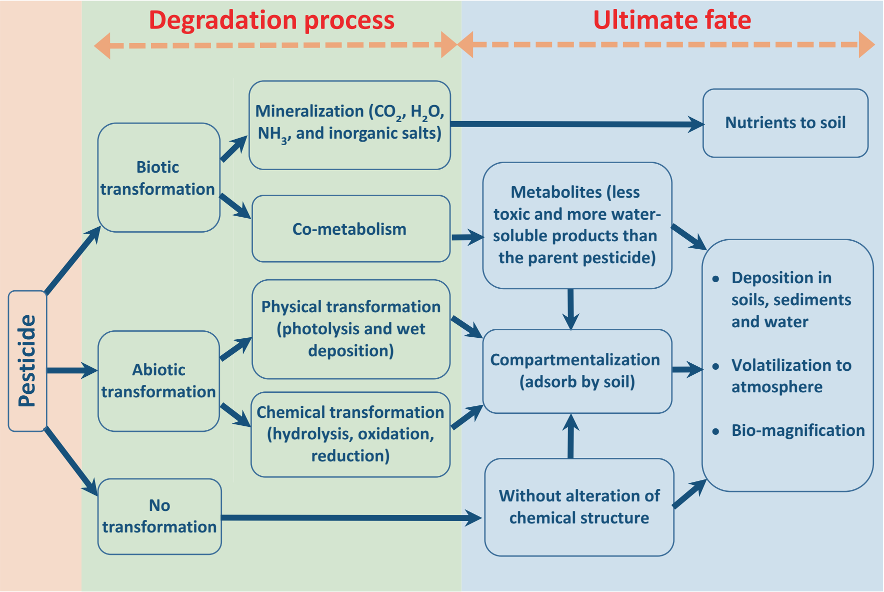


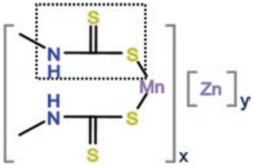
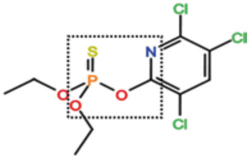
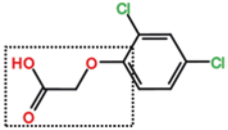
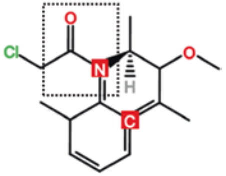
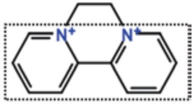
Fig. 2 Fate of pesticides and their degraded compounds in the environment

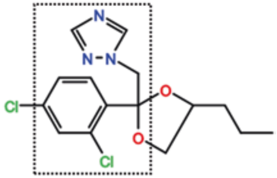
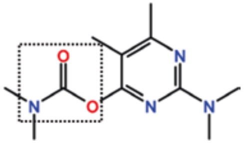
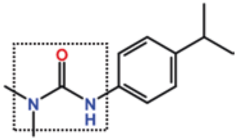
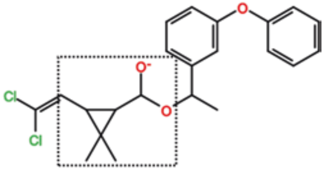
The ultimate fate of pesticides in the nature is mostly interrelated to the soil sorption capacity that determines not only their mode of transport, but also their availability to microbes [49]. The behavior of pesticides, their effective transformation (biotic and abiotic), and the risk of xenobiotics generation or persistence in the environment are subjective to the degradation kinetics and soil dynamics [54, 55]. The soils' dynamics that influence the rate of biodegradation are the moisture content and temperature, the physicochemical aspects, and the presence of other nitrogen and carbon sources, etc. This dynamic behavior of soil can entirely modify the microbial community and therefore, introduce a new microbial activity [49]. Table 1 summarizes the major pesticides' degradation routes with detected degraded compounds in the environment.

4 Reduction/Degradation of Pesticide Residue During Food Preparation

Generally the fresh and raw food ingredients need to be processed before table consumption. The processing techniques alter the fresh ingredients to value added products. Most of the food processing techniques help to reduce or completely eliminate the concentration of pesticide residues or insecticides on the surface or inside the food commodity. The common unit operations used to process the raw food commodities are washing, disinfecting, peeling, bleaching, parboiling and cooking.

Table 1 Top 10 pesticide classes, their major degradation pathways and persistence of the degraded compounds

Pesticide class	Utilization category	% in global utilization	Active representative group and structural formula	Possible environmental degradation routes	Persistence in environmental compartments (soil, water, sediments)
Dithiocarbamates (DTC)	Fungicides	7.1		Acid-catalysed hydrolysis; formation of potential NDMA[a] precursors [56]	Infrequently observed
Organophosphates	Insecticides	6.7		Microbial transformation (oxidation and hydrolysis)	Glyphosate and AMPA[a] frequently detected in groundwater [57–59]; chlorpyrifos, diazinon, disulfuton detected in rainwater and remote lake waters [60, 61]
Phenoxy alkanoic acids	Herbicides	4.7		Microbial transformation (oxidative dealkylation and aromatic ring cleavage)	Parent compounds frequently detected in groundwater [57, 58, 62]
Amides	Herbicides	4.2		Microbial transformation (hydrolysis and glutathione coupling)	Chloroacetanilides and their transformation products oxanilic (OXA) and ethanesulfonic acid (ESA) frequently detected in groundwater [57]; metolachlor and alachlor detected in remote lake waters [60, 61]
Bipyridyls	Herbicides	3.2		Only very slowly bio-transformed due to strong sorption to soil matrix	Rarely observed; mainly sorbed to sediments and soils

Triazines	Herbicides	2.3		Microbial transformation (oxidative dealkylation and hydrolysis)	Parent compounds and hydroxyl and dealkylated transformation products frequently detected in groundwater (significantly beyond phase-out period); atrazine and DEA[a] detected in remote lake waters [60, 61]
Triazoles, diazoles	Fungicides	2.0		Slow microbial transformation (oxidation); photo transformation of specific representatives	Flutriafol detected in remote lake waters [61]
Carbamates	Insecticides/ herbicides	2.0		Ready microbial or base-catalyzed transformation (hydrolysis of ester bond); photo transformation of specific representatives	Rarely observed
Urea derivatives	Herbicides	1.7		Microbial transformation (oxidative dealkylation and hydrolysis)	Parent compounds frequently detected in groundwater [57, 58]
Pyrethroids	Insecticides	1.3		Microbial transformation (hydrolysis, oxidation); photo transformation (direct and indirect)	Rarely observed; mainly sorbed to sediments and soils

Values are based on amounts used relative to total global pesticide consumption in 2009/2010 [2]

[a] *AMPA* aminomethylphosphonic acid, *DEA* desethylatrazine; *NDMA* N-nitrosodimethylamin

Table 2 Examples of the effects of food processing techniques on pesticide residue dissipation

Processing	Food ingredients	Pesticide	Residue dissipation	Reasons	Reference
Washing (30 s)	Bitter grounds	Endosulfan	59%	Micro particles of pesticide on the surface of food ingredients are easily washed by stirring of water	[63, 64]
Washing (twice)	Soybeans	Dichlorvos	80–90%		[64]
Washing	Golden apple	Phosalone	30–50%	Reduction due to dissolution of pesticide in water or solution. Removal efficiency of washing depends on location of residue, age of residue, water solubility and temperature	[65]
Washing (Vinegar)	Tomatoes	HCB p,p-DDT Dimethoate	51% 34% 91%		[66, 67]
Washing (10% NaCl solution)		HCB p,p-DDT Dimethoate	43% 27% 91%		
Tap water washing		HCB p,p-DDT Dimethoate	9.6% 9.2% 19%		
Peeling	Bitter gourds Mango	Endosulfan Fenthion Dimethoate	84% 100% 100%	Peeling off fruit skin removed all residues, which are accumulated on pericarp	[63]
Parboiling	Rough rice	Malathion	99.99%	Inactivation or degradation of pesticide at high temperature	[68]
Cooking (10 min open cooking, 10 min steam cooking)	Bitter gourds	Endosulfan	63–68%	Increase volatilization and hydrolysis or other chemical degradation at high temperature, thus reduce residue level	[63]

Each operation collectively reduces the concentration of the pesticides present in food commodities. All most all the loose surface residues and polar chemicals are eliminated by washing. A significant portion of non-persistent chemicals are hydrolysed and bleached out by hot water washing. Non-polar chemicals (chlorinated hydrocarbons) are grimly detained in the waxy layers of the fruits and vegetables. Peeling of fruits and vegetables completely removes the pesticide residues accumulated in waxy layers, however this process reduces the beneficial phytochemicals in fruits and vegetables. Table 2 summarizes the common food processing techniques along with their degree of residue removal from processed foods.

5 Conclusions

Pesticides are extensively applied to achieve higher agriculture production. However, less attention has been paid to their potential harmful impacts on environment and ecosystem. Majority of the pesticides are persistent organic pollutants.

They are vastly stable in the environment and accumulative in ecological objects (e.g., organisms and food chains). Some of them have rapid toxicity to humans and animals; others have chronic effects on reproductive, immune and endocrine systems. Pesticides and their derivatives are also carcinogenic and transported through the environmental compartments over a longer distances from the points of application.

There are many physical and bio-chemical processes influence the transportation and degradation of pesticides. Pesticides and their residues are altered and eliminated by the food processing techniques before ingestion. All those processes collectively determine the ultimate fate of the pesticides in the environment. The ultimate fate is also affected by the site characteristics (e.g., soil porosity, sorption, organic contents, etc.), environmental conditions (e.g., temperature, pH, presence of oxygen or electron acceptors, and nutrients), crop management systems, and chemical handling practices. That's why; the understanding of fate can ensure the safe and effective application of pesticides into the environment.

Future knowledge in this field should address to improve the ability of predicting the long-term fate of pesticides, understand their degradation at threshold concentrations and in low-nutrient environments (e.g., groundwater, lake hypolimnions, and seawater). The development of such knowledge will need innovative way of characterizing the degradation procedures by using advanced analytical tools (e.g., compound-specific isotope analysis, enantiomer analysis, and mass spectrometry) to identify the degraded products. Also, the developments of bioinformatics to understand the functions of proteins by DNA sequences are expected to apply.

References

1. C.A. Damalas, Understanding benefits and risks of pesticide use. Sci. Res. Essay **4**(10), 945–949 (2009)
2. Food and Agriculture Organization of the United Nations (FAO), FAOSTAT (2012), faostat.fao.org
3. A. Grube, D. Donaldson, T. Kiely, L. Wu, in *Pesticides Industry Sales and Usage*, ed. by US EPA, Office of Chemical Safety and Pollution Prevention (US EPA Publications warehouse, Washington, DC, 2011).
4. EPA, What is a pesticide? http://www.epa.gov/opp00001/about/. Accessed 16 July 2012
5. A. Agrawal, R.S. Pandey, B. Sharma, Water pollution with special reference to pesticide contamination in India. J. Water Res. Protect. **2**, 432–448 (2010)
6. K. Fenner, S. Canonica, L.P. Wackett, M. Elsner, Evaluating pesticide degradation in the environment: blind spots and emerging opportunities. Science **341**(6147), 752–758 (2013)
7. H. Bartel et al., *Wasserwirtschaft in Deutschland. Teil 1, Grundlagen* (Umweltbundesamt (UBA), Dessau-Rosslau, 2010)
8. R.J. Gilliom et al., in *The Quality of Our Nation's Waters—Pesticides in the Nation's Streams and Ground Water, 1992–2001*, ed. by U. S. Department of the Interior, U.S. Geological Survey (USGS Publications warehouse, Reston, 2006).
9. S. Huntscha, H. Singer, S. Canonica, R.P. Schwarzenbach, K. Fenner, Environ. Sci. Technol. **42**, 5507–5513 (2008)
10. P.B. Kurt-Karakus, C. Teixeira, J. Small, D. Muir, T.F. Bidleman, Environ. Toxicol. Chem. **30**, 1539–1548 (2011)

11. M. Gavrilescu, Review – fate of pesticides in the environment and its bioremediation. Eng. Life Sci. **5**(6), 497–526 (2005)
12. R.C. Kuhard, A.K. Johri, A. Singh, O.P. Ward, in *Soil Biology*, Applied bioremediation and phytoremediation, ed. by A. A. Singh, O. P. Ward. Bioremediation of pesticide contaminated soils, vol l (Springer, Heidelberg, 2004), pp. 35–54
13. W. Chen, A. Mulchandani, M.A. Deshusses, Environmental biotechnology: challenges and opportunities for chemical engineers. AICHE J. **51**, 690–695 (2005)
14. O.P. Ward, A. Singh, in *Soil Biology*, Applied bioremediation and phytoremediation, ed. by A. Singh, O. P. Ward. Soil bioremediation and phytoremediation – an overview, vol 1 (Springer, Berlin/Heidelberg, 2004), pp. 1–12
15. Z. Aksu, Application of biosorption for the removal of organic pollutants: a review. Process Biochem. **40**, 997–1026 (2005)
16. R. Atkinson et al., Transformations of pesticides in the atmosphere: a state of the art. Water A S P **115**(1–4), 219–243 (1999)
17. J.J. Kells, C.E. Riek, R.L. Belvins, W.M. Muir, Atrazine dissipation as affected by surface pH and tillage. Weed Sci. **1980**(28), 101–104 (1980)
18. A. Moreale, R. van Bladel, Behavior of 2,4-D in Belgian soils. J. Environ. Qual. **1980**(9), 627–633 (1980)
19. S.M. Zhang, D.S. Liu, Z.S. Wang, X.F. Ma, A kinetic model describing the effect of temperature on the loss rate of pesticides in soil. Ecol. Model. **70**, 115–126 (1993)
20. R.-V. Roman, M. Gavrilescu, *Transfer Phenomena in Bioprocesses* (Dosoftei Press, Iasi, 1997)
21. Y.R. Li. A GIS-aided integrated modeling system for simulating agricultural nonpoint source pollution, Master Thesis, University of Regina, (2001)
22. L.T. Ou, D.H. Gancaiz, W.B. Wheeler, P.S.C. Rao, J.M. Davidson, Influence of soil temperature and soil moisture on degradation and metabolism of carbofuran in soils. J. Environ. Qual. **11**, 293–298 (1982)
23. J. Foght, T. April, K. Biggar, J. Aisabie, Bioremediation of DDT-contaminated soils: a review. Bioremediation J. **5**, 225–246 (2001)
24. V. Becaert, M. Beaulien, J. Gagnon, R. Vielemur, L. Deschenes, R. Samson, Development of a microbial consortium from a contami- nated soil that degrades pentachlorophenol and wood-preserving oil. Bioremediation J. **5**, 183–192 (2001)
25. M. Waldman, Y. Shevah, Biodegradation and leaching of pollutants: monitoring aspects. Pure Appl. Chem. **65**, 1595–1603 (1993)
26. F. Whitford, J. Wolt, H. Nelson, M. Barrett, S. Brichford, R. Turco, *Pesticides and Water Quality Principles, Policies and Programs* (Purdue University Cooperative Extension Service, West Lafayette, 1995)
27. J.B. Walsh, A feasibility study of bioremediation in a highly organic soil, Master of Science Thesis, Worcester Polytechnic Institute, 1999
28. A. Singh, P.O. Ward, in *Soil Biology*, Biodegradation and bioremediation, ed. by A. Singh, P. O. Ward. Biotechnology and bioremediation – an overview, vol 2 (Springer, Berlin/Heidelberg, 2004), pp. 1–18
29. E. Diaz, Bacterial degradation of aromatic pollutants: a paradigm of metabolic versatility. Intern. Microbiol. **7**, 173–180 (2004)
30. Boettcher G, Nyer EK, *In Situ Treatment Technology*, ed. by E. Nyer, et al. In situ bioremediation (CRC Press, Boca Raton, 2001)
31. S. Suthersan, *Natural and Enhanced Remediation Systems* (CRC Press, Boca Raton, 2001)
32. J.D. van Hamme, in *Soil Biology*, Biodegradation and bioremediation, ed. by A. Singh, O. P. Ward. Bioavailability and biodegradation of organic pollutants – a microbial perspective, vol 2 (Springer, Berlin/Heidelberg, 2004), pp. 37–56
33. M. Dua, A. Singh, N. Sethunathan, A. Johri, Biotechnology and bioremediation: successes and limitations. Appl. Microbiol. Biotechnol. **59**, 142–152 (2002)
34. G.M. Klecka, in *Environmental Exposure from Chemicals*, ed. by W. B. Neely, G. E. Blau. Biodegradation (CRC Press, Boca Raton, 1985)

35. L.P. Wackett, C.D. Hershberger, *Biocatalysis and Biodegradation: Microbial Transformation of Organic Compounds* (ASM Press, Washington DC, 2001)
36. L. Wackett, M. Sadowsky, B. Martinez, N. Shapir, Biodegradation of atrazine and related s-triazine compounds: from enzymes to field studies. Appl. Microbiol. Biotechnol. **58**(1), 39–45 (2002)
37. B. Jochimsen, S. Lolle, F.R. McSorley, M. Nabi, J. Stougaard, D.L. Zechel, B. Hove-Jensen, Five phosphonate operon gene products as components of a multi-subunit complex of the carbon-phosphorus lyase pathway. Proc. Natl. Acad. Sci. **108**(28), 11393–11398 (2011)
38. T. Zeng, Y.P. Chin, W.A. Arnold, Potential for abiotic reduction of pesticides in prairie pothole porewaters. Environ. Sci. Technol. **46**(6), 3177–3187 (2012)
39. W.B. Neely, in *Environmental Exposure from Chemicals*, ed. by W. B. Neely, G. E. Blau. Hydrolysis (CRC Press, Boca Raton, 1985)
40. J.C. Xu, J.W. Stucki, J. Wu, J.E. Kostka, G.K. Sims, Fate of atrazine and alachlor in redox-treated ferruginous smectite. Environ. Toxicol. Chem. **20**(12), 2717–2724 (2001)
41. A.R. Loch, K.A. Lippa, D.L. Carlson, Y.P. Chin, S.J. Traina, A.L. Roberts, Nucleophilic aliphatic substitution reactions of propachlor, alachlor, and metolachlor with bisulfide (HS-) and polysulfides (Sn2-). Environ. Sci. Technol. **36**(19), 4065–4073 (2002)
42. K.A. Barrett, M.B. McBride, Oxidative degradation of glyphosate and aminomethylphosphonate by manganese oxide. Environ. Sci. Technol. **39**(23), 9223–9228 (2005)
43. S.J. Larson, P.D. Capel, M.S. Majewski, in *Pesticides in Surface Waters – Distribution, Trends, and Governing Factors*, ed. by R. J. Gilliom. Series of Pesticides in the hydrologic system, vol 3 (Ann Arbor Press, Chelsea, 1997).
44. W.B. Mills, D.B. Porcella, M.J. Ungs, S.A. Gherini, K.V. Summers, L. Mok, et al., *Water Quality Assessments: A Screening Procedure for Toxic and Conventional Pollutants, Parts 1, 2, and 3, EPA-600/f6-82-004a, b, c* (US EPA, Washington DC, 1985)
45. H.D. Burrows, L.M. Canle, J.A. Santaballa, S. Steenken, Reaction pathways and mechanisms of photodegradation of pesticides. J. Photochem. Photobiol. B Biol. **67**(2), 71 (2002). doi:10.1016/S1011-1344(02)00277-4
46. J. Hoigné, W. Stumm, ed. Reaction rates of processes in natural waters, in *Aquatic Chemical Kinetics: Reaction Rates of Processes in Natural Waters* (Wiley, New York, 1990). ISBN 978-0-471-51029-1
47. T. Mill, W. Mabey, in *Environmental Exposure form Chemicals*, ed. by W. B. Neely, G. E. Blau. Photochemical transformations (CRC Press, Boca Raton, 1985)
48. H.L. Ortiz, S.E. Sánchez, G.E. Dantán, G.L. Castrejón. Pesticide biodegradation: mechanisms, genetics and strategies to enhance the process, in *Biodegradation – Life of Science*, ed. by Dr. R. Chamy (InTech, 2013). doi: 10.5772/56098
49. P. Besse-Hoggan, T. Alekseeva, M. Sancelme, A. Delort, C. Forano, Atrazine biodegradation modulated by clays and clay/humic acid complexes. Environ. Pollut. **157**(10), 2837–2844 (2009)
50. A. Tiktak, J.D. Piiieros Garcet, D.S. de Nie, M. Vanclooster, A. Jones, Assessment of pesticide leaching at the pan-European level using a spatially distribution model. Proceedings of the Diffuse Pollution and Basin Management Conf., Dublin, Aquatic Ecology and Dangerous Substances Section, 17–22 Aug 2003
51. S. Kleineidam, H. Rugner, P. Grathwohl, Desorption kinetics of phenanthrene in aquifer material lacks hysteresis. Environ. Sci. Technol. **38**, 4169–4175 (2004)
52. R.G. Nash, E.H. Woolson, *Persistence of Chlorinated Hydrocarbon Insecticides in Soils* (American Association for the Advancement of Science, 1967)
53. E.A. Kerle, J.J. Jenkins, P.A. Vogue, *Understanding pesticide persistence and mobility for groundwater and surface water protection,* Report EM 8561 (Oregon State University Extension Service, Corvallis, 1996
54. B.K. Singh, A. Walker, Microbial degradation of organophosphorus compounds. FEMS Microbiol. Rev. **30**(3), 428–471 (2006)

55. F. Worrall, M. Fernandez-Perez, A. Johnson, F. Flores-Cesperedes, E. Gonzalez-Pradas, Limitations on the role of incorporated organic matter in reducing pesticide leaching. J. Contam. Hydrol. **49**, 241–262 (2001)
56. L.P. Padhye, J.H. Kim, C.H. Huang, Oxidation of dithiocarbamates to yield N-nitrosamines by water disinfection oxidants. Water Res. **47**(2), 725–736 (2013)
57. R.J. Gilliom, J.E. Barbash, C.G. Crawford, P.A. Hamilton, J.D. Martin, N. Nakagaki, L.H. Nowell, J.C. Scott, P.E. Stackelberg, G.P. Thelin, D.M. Wolock, *Pesticides in the Nation's Streams and Ground Water, 1992–2001* (U.S. Geological Survey Circular 1291, 2006), 172 p
58. H. Bartel, U. Irmer, *Water Resource Management in Germany* (Umweltbundesamt (UBA), Dessau-Rosslau, 2010)
59. S. Kilchmann, M. Reinhardt, M. Schürch, D. Traber, *Ergebnisse der Grundwasserbeobachtung Schweiz (NAQUA). Zustand und Entwicklung 2004–2006* (Bundesamt für Umwelt (BAFU), Bern, 2009)
60. P.B. Kurt-Karakus, C. Teixeira, J. Small, D. Muir, T.F. Bidleman, Current-use pesticides in Ontario Inland Lakes, precipitation, air and zooplankton samples. Environ. Toxicol. Chem. **30**, 1539–1548 (2011)
61. D.C.G. Muir, C. Teixeira, F. Wania, Empirical and modeling evidence of regional atmospheric transport of current-use pesticides. Environ. Toxicol. Chem. **23**, 2421–2432 (2004)
62. F. Malaguerra, H.-J. Albrechtsen, L. Thorling, P.J. Binning, Pesticides in water supply wells in Zealand, Denmark: a statistical analysis. Sci. Total Environ. **414**, 433–444 (2012)
63. G. Nath, S. Agnihotri, Removal of endosulfan from bitter gourds by home processings. Pesticides **18**(8), 13–15 (1984)
64. M. Miyahara, Y. Saito, Effects of the processing steps in tofu production on pesticide residues. J. Agric. Food Chem. **42**(2), 369–373 (1994)
65. A.E. Marei, M.M. Khattab, A.H. Mansee, M.M. Youssef, M.R. Montasser, Analysis and dissipation of deltamethrin in stored wheat and milled fractions. Alex. J. Agric. Res. **16**(2), 275–291 (1995)
66. A.A.K. Abou-Arab, Effects of processing and storage of dairy products on lindane residues and metabolites. Food Chem. **64**, 467–473 (1999a)
67. A.A.K. Abou-Arab, Behavior of pesticides in tomatoes during commercial and home preparation. Food Chem. **65**, 509–514 (1999b)
68. V.V. Krishnamurthy, U.S. Sreeramulu, Studies on rice bran and rice bran oil. VI. Pesticides accumulation in the rice bran. Madras Agric. J. **69**(12), 820–821 (1982)