Chapter

Pesticides Occurrence in Water Sources and Decontamination Techniques

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Abstract

Pesticides are essential in crop protection as they keep the plants safe from insects, weeds, fungi, and other pests in order to increase crop production and feed billions of people throughout the world. There are more than 500 pesticide molecules currently in use all around the world. Their non-judicious use has noticeably contaminated the environment and caused negative effects on humans and other life forms. The rainfall or irrigation water takes away the pesticide residues to nearby surface water bodies through runoff or to the groundwater sources through leaching. The occurrence of pesticides in water resources could have multiple consequences. Exposure of pesticides through contaminated water becomes the cause of acute and chronic health problems in people of all ages. Pesticide residues have the potential to disrupt the ecosystem equilibrium in water bodies. Contaminated irrigation water can contaminate other crops as well as their environment. This chapter will discuss the major exposure routes of pesticides in water bodies mainly from agricultural sectors and their effect on the ecosystem. The chapter will also discuss decontamination techniques to eliminate pesticide contaminants from water bodies.

Keywords: pesticides, residues, water, leaching, runoff, decontamination, ecosystem

1. Introduction

The growth of the population of the world is increasing at an alarming rate, which draws the attention of researchers, scientists, environmentalists, and policymakers across the globe. According to a scientific report, the global human population is likely to increase up to 9 billion by 2050 [1]. To meet the food requirement of this growing population as well as to cover their modified consumption patterns, there is an ultimate requirement of intensification and diversification of agricultural sectors. The current food production of the globe needs to be increased by 60% by 2050 [2].

Thanks to the green revolution that instigated the use of various agrochemicals that effectively increased agricultural productivity by many folds. Besides traditional agrochemicals (fertilizers and pesticides), new ones such as hormones, antibiotics, vaccines, growth promoters, etc., also brought revolutionary changes in different food production sectors. Undoubtedly, the use of agrochemicals has directly or indirectly benefitted millions of people all over the globe by increasing food production, there are instances that the action has put questions toward the well-being of the environment. Among all the environmental compartments, water resources are especially affected to a greater extent as agricultural works mostly depend on water and use about 70 % of total water resources globally [3]. In crop production sectors, some of the most important crops such as rice and wheat generally consume a huge amount of water and the total amount of water used; most part is for irrigation. Production of 1 kg of wheat requires approximately 1 m^3 of water and 1 kg of rice requires 1.2 m^3 of water [4]. Rice, which is the staple food for most people living in Asia, consumes about 80% of freshwater resources for irrigation. Apart from crop production, a huge amount of water is also used indirectly in livestock sectors through the production of fodder crops and forage. These amounts of water are directly or indirectly recycled back to surface water as well as groundwater sources carrying the pollutants such as pesticides, fertilizers, salts, sediments, hormones, antibiotics, etc., from crop fields. Now agriculture has become a major source of freshwater pollution in rivers and lakes, the second major source for wetland pollution, and the third major source for estuaries and groundwater pollution [5].

2. Pesticides and their groups

A pesticide is a chemical substance or combination of different chemical substances used to eliminate pests to protect crops. Food and Agriculture Organization (FAO) defined a pesticide as “a substance intended for preventing, destroying, repelling or mitigating any pest in crops either before or after harvest to prevent deterioration during storage and transport.” Pesticides are designed to control pests of the standing crop in the crop fields as well as to protect the stored crops after harvest, thus finely ensuring food security. Pesticides are classified according to their chemical nature, their target, modes of action, period of activity, mode of formulation, activity spectrum, toxicity level, etc [6].

2.1 Mode of action

After application, pesticides either remain on the part of the plant to which those are applied or enter into the vascular system of the plant body and get transported to different organs. According to this principle, pesticides are categorized as systemic and non-systemic ones. In the case of systemic pesticides, the compound penetrates the plant body, gets into the vascular tissue system, and spreads to different parts of the plant showing its effects uniformly. In contrast to this, non-systemic pesticides do not effectively penetrate the plant tissue and remain at the applied area on the plant body.

2.2 Target of the pesticides

This classification of pesticides is the most common and familiar as the categorization is based on the effectiveness of the pesticide on different types of pests. For an instance, pesticides those act on insects are called insecticides, those acts on fungi are called fungicides, and those acts on herbs are called herbicides and so on. Likewise, there are rodenticides, molluscicides, nematicides, plant growth regulators, etc., used to protect plants.

2.3 Chemical composition of pesticide compounds

This type of classification of pesticides is done based on their chemical composition and the active ingredients they contain. This classification of pesticides is actually the most useful one as it helps in studying the occurrence of pesticides in the field, which implies their physical and chemical properties, helps to know their persistency in the environment etc. Based on their chemical nature, pesticides are categorized mainly into seven groups; those are organochlorines (OC), organophosphates (OP), carbamates, pyrethroids, amides, anilines, and azotic heterocyclic compounds. Of these seven classes, organochlorines are highly toxic pesticides. In their chemical structure, they contain five or more chlorine atoms. The chemical structure of this group of pesticides makes them highly persistent in the environment. However, the use of these pesticides is now banned in many countries due to certain problems such as their toxicity toward humans and persistency in ecosystems. Other groups of toxic pesticides are organophosphates and carbamates. Organophosphates have a chemical structure that makes them easily degraded in nature, and hence, these constitute a group of most commonly used pesticides in almost all countries. These pesticides are comparatively less toxic but effective pest controlling chemicals nowadays. However, their widespread use has now become a serious problem for ecosystems due to the occurrence of residues in different environmental compartments including water resources. The groups of pesticides—anilines, pyrethroids, amides, azotic heterocyclic compounds—constitute comparatively less toxic groups. Pyrethroid pesticides derive from a plant-based product and are made from flowers of Pyrethrum *(Chrysanthemum cinerariaefolium)*. These are used for their quick action against insect pests, easy biodegradability, and low toxicity toward mammals [7]. However, these pesticides are found to be toxic to aquatic organisms. Amide pesticides are also less persistent, and in many studies, they have been found to be completely degraded after 10 weeks of their field application. Though aniline pesticides are found to be very effective against insect pests, their toxicity toward mammals and aquatic animals made them banned in many European countries.

2.4 Mode of formulation

Pesticides constitute mainly of two parts—active ingredient (AI) and inert ingredient. The active ingredient is the pure form of the chemical, and this gives a pesticide its actual pesticidal property. However, for improving its activities, long-term storage, safe handling, and enhanced effectiveness, the active ingredients are usually mixed with some inert ingredients. This is called pesticide formulation, and it is of different types such as emulsifiable concentrates (EC), wettable powder (WP), soluble concentrate (SL), soluble powder (SP), suspension concentrate (SC), capsule suspensions (CS), water-dispersible granules (WG), granules (GR), dusts (Dp), etc [8].

2.5 Active spectrum

Pesticides that are active against a wide range of crop pests are included under broad-spectrum pesticides and those which act only on a selective group of pests are called selective pesticides.

2.6 Toxicity

Pesticides are categorized into five groups according to the potential risk they exert on humans and based on that pesticides are extremely hazardous, highly hazardous, moderately hazardous, slightly hazardous, products unlikely to present acute hazards in normal use [7].

Organochlorine insecticides were the first group of pesticides that were used successfully in eliminating crop pests. However, due to the reported toxicity toward humans and other mammals and persistency in different ecosystems, the use of organochlorines is now withdrawn. New groups of pesticides developed later, such as organophospahtes in 1960s, carbamates in 1970s, and pyrethroids in 1980s, herbicides in 1970s–1980s brought revolutionary changes in the field of crop pest regulation. Today pesticide production is a large industry with an annual turnover worth USD 35 billion. Currently, about 4.6 million tonnes of chemical pesticides are applied to crop plants, thereby put into the environment each year. In 2004, this amount included 47.5% of herbicides, 29.5% of insecticides, 17.5% of fungicides, and other group of pesticides account for 5.5% [9]. The overall usage of pesticides from 1990–2019 is depicted in **Figure 1**. The trend of use of different groups of pesticides is now changed. For example, the use of herbicides has been increased and the use of insecticides, fungicides, and bactericides has decreased largely in the last few decades [10].

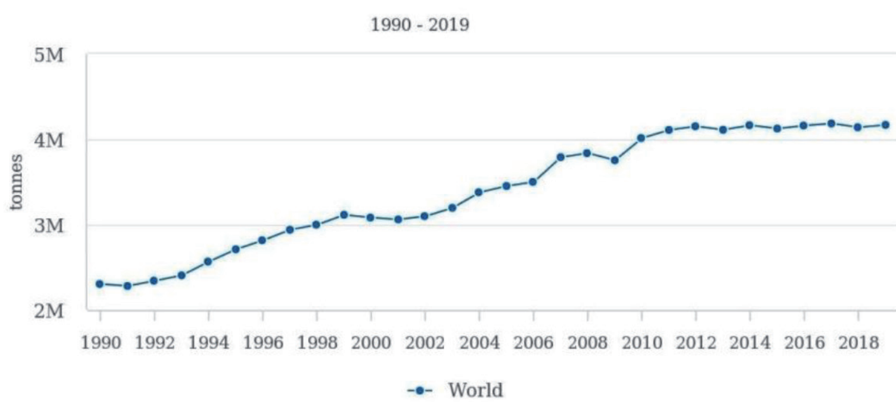

Figure 1.
Consumption of pesticides in world from 1990 to 2018. Source: Food and Agriculture Organization (FAO).

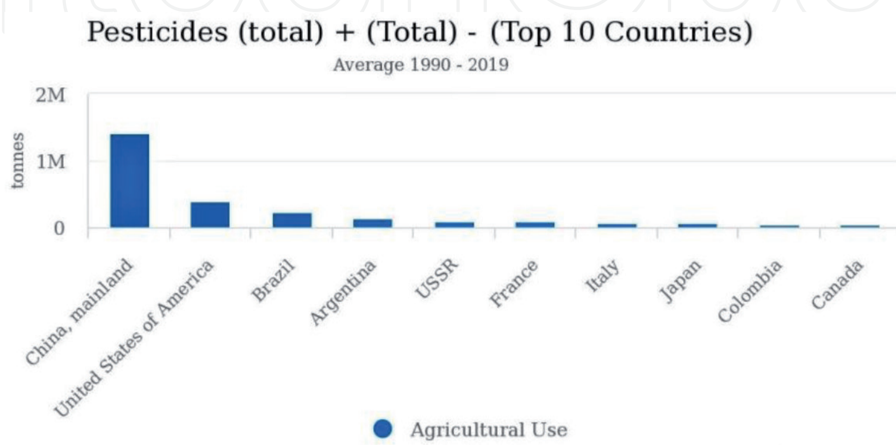

Figure 2.
Consumption of pesticides in different countries from 1990 to 2019. Source: Food and Agriculture Organization (FAO).

China tops the list of the highest amount of pesticide user in the world followed by the United States [11]. India ranks fourth in pesticide manufacturing and 12th in the list of highest pesticide-consuming countries (**Figure 2**) [12].

3. Exposure routes of pesticides in water bodies through crop production

To cope with the growing world's population, crop production has also been increasing. Till 2015, cereal production has increased threefold, production of vegetables increased fourfold, production of tomatoes increased fivefold, and production of soybean increased eightfold as compared with 1970 [13]. This huge increase in crop production has been achieved through the expansion of crop lands, cultivation of high-yielding crop varieties, and most importantly through the use of pesticides. In India, cotton is at the top of the list consuming the highest amount of pesticides (45%) followed by rice (22%), vegetable (9%), plantation crops (7%), wheat (4%), and other crops (9%). Among the vegetables, cabbage consumes the highest amount of pesticides. On an overall basis, pesticide consumption is the highest in fruit and vegetable cropping. In developing countries such as India, about 600g/ha of pesticides are used, whereas the amount is 6000g/ha in developed nations. According to estimation, about 4.6 million tonnes of pesticides are being integrated into the environment each year through crop production of which 51.3% was consumed in Asia, 33.3% in the Americas, 11.8% in Africa, and 1.4% in Oceania in 2016.

Pesticides are usually directly applied on plant parts or plant parts are subject to pesticide pretreatment. However, only 1% of the applied pesticide reaches the target pest, and the rest amount gets incorporated into different environmental compartments exerting its harmful effects on biodiversity, and nontarget organisms. The aerial application of pesticides may pollute surrounding areas with macro-droplets or micro-droplets of pesticides. Several studies showed that pesticide spraying enhances the distribution of pesticides in areas far from the spraying site. For an instance, spraying of pesticides caused health-related issues in children living within 1000 m of a greenhouse [14].

Depending on the chemical composition of pesticides, they show different degrees of solubility, according to which they follow different pathways to reach the water bodies after their application to crop fields (**Figure 3**). The common pathway through which pesticides enter the surface water sources such as ponds, pools, ditches, lakes, streams, rivers, etc., is through irrigation or when immediate rainfall occurs after pesticide application. Small water bodies situated adjacent to agricultural fields are more prone to pesticide pollution as the pesticides applied to the crop fields directly washed away into those water sources. These water bodies receive considerably higher amounts of pesticide as compared with farther or larger water bodies [15]. In the case of groundwater systems, the common pathway for the entry of pesticides is through leaching. Also, other routes of exposure of pesticide molecules include soil erosion, direct disposal, or sedimentation, etc.

Some major pathways through which pesticides reach water sources are as follows.

3.1 Leaching

Leaching of pesticides is the vertically downward movement of pesticide molecules through the minute capillaries formed by soil particles or channels formed by roots and root hairs to the groundwater table and deeper aquifers. The pesticides with

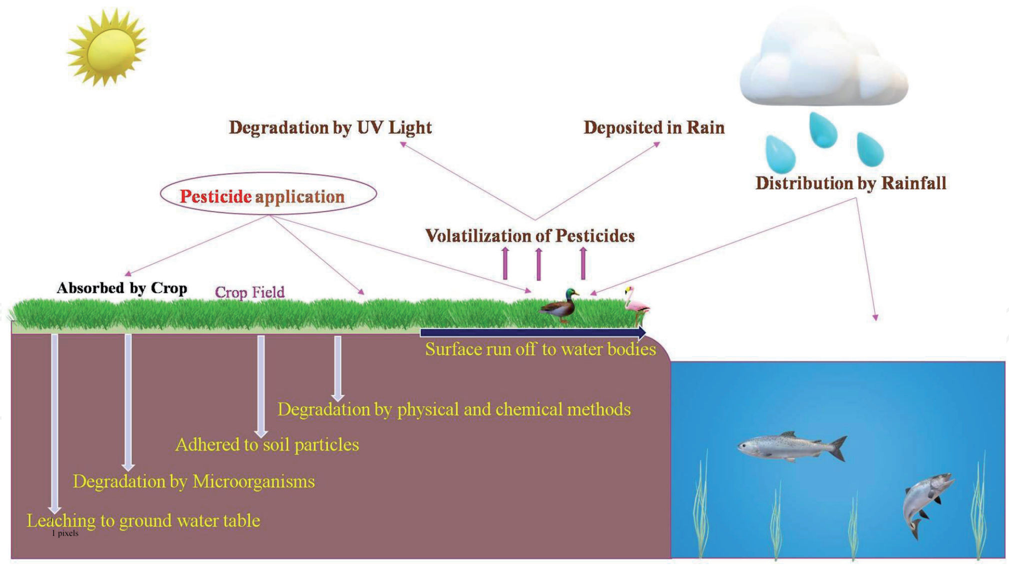

Figure 3.
Pathways of pesticide entry into different ecosystems.

a lower persistency value tend to degrade within less time posing a comparatively lesser threat to groundwater. There are two types of leaching observed, which may provide pathways for pesticide movement toward the groundwater [16].

- Preferential flow—leaching of pesticides in soil profile through the cracks and crevices, large voids, channels formed by already penetrated roots and root hairs, etc.

- Matrix flow—water moves through capillaries formed by small soil pores.

Among the pesticides used, atrazine, an herbicide, has a high potential to leach into the underground water table due to its high persistency. In contrast to this, cyanazine and methyl parathion show low leaching potential due to their shorter half-life, high rate of adsorption to soil particles, and low persistency. Herbicide, 2, 4-D, is a hydrophilic pesticide and easily gets broken down by the actions of microorganisms, hence less chance of accumulation in soil [17], thereby exerting a lesser chance of water contamination. Pesticide leaching to the groundwater may be enhanced by rainfall or through irrigation only when the concerned pesticide is fairly soluble in water. The pesticide may get dissolved in water or form suspension or emulsion. Water that is moving at a higher speed as in rivers or streams as compared with ponds or ditches is more likely to carry heavy pesticides and to a farther distance. Several factors affect the rate of leaching of pesticides such as physical and chemical characteristics of pesticides, the permeability of pesticides in soil, volatilization of pesticide molecules, crop-root uptake, methods and doses of pesticide application and types of weather conditions, variation in temperature and precipitation pattern [18].

3.1.1 Soil organic matter

The organic matter content of the soil is the most important soil property that affects pesticide breakdown by microorganisms. Organic matter present in the soil helps in better adsorption of pesticide molecules by providing a larger surface area. The presence of organic matter also helps the soil to hold more amount of water, thereby increasing the chance of degradation by microorganisms. This ultimately decreases the rate of leaching of pesticides to the groundwater table.

3.1.2 Soil texture

Soil is composed mainly of sand, silt, and clay. This composition affects the movement of water through the soil. The coarse-textured soil will have more sand particles and large pores, allowing water to move rapidly carrying pesticides to the water table. Clay-textured soils will have more clay and hence will have less pore size that provides low permeability. This slows the downward movement of pesticides and increased the rate of degradation of pesticides on the soil surface.

3.1.3 Soil structure

In the soil where particles are loosely packed, pesticides tend to leach faster in the soil. Compact soil holds water back and prevents the free flowing of water through it. the soil in which openings and channels are formed, for an instance, burrows formed by earthworms or crevices due to freezing and thawing allow downward movement of water that may contain pesticides. Plant roots penetrate the soil, thus creating channels that allow water to carry pesticides downward toward the water table.

3.1.4 Soil water content

The amount of water present in the soil determines the leaching of pesticides into the groundwater sources. Pesticides that are more soluble will have a greater chance of leaching to the water table when the soil is fully saturated. However, in the case of dry soil when water is added, the water molecules just fill the pores in the soil surface, decreasing the chances of carrying the pesticide residues down through the soil profile via water.

3.1.5 Depth of groundwater

The water table is usually separated from the soil surface through a number of soil layers. The soil layers above the water table determine the pesticide adsorption and degradation. The more the depth of the water table, the more the groundwater is protected decreasing the probability of contamination. The water table is more prone to pesticide contamination when it is present nearer to the soil surface.

3.1.6 Type of bedrock

Bedrock is the bottommost layer present beneath soil or rock fragments. The types of bedrock determine the leaching of water that may carry pesticides. For example, in the case of limestone bedrocks, the downward water channels are comparatively larger, thereby allowing water to leach quickly. Limestone is highly soluble in water and hence dissolves in water creating underground passages that let water move out of the area rapidly, carrying pesticides to farther distances.

3.1.7 Slope

The topography of an area affects the rate of movement of water flow across the earth's surface. The areas with steep slopes allow fast surface runoff but reduce the chances for water to leach to the groundwater table. In contrast in valleys and flat areas, a runoff will be slow, but leaching to underground will be comparatively faster.

3.2 Runoff

Surface runoff is the movement of water molecules on the earth's surface in case of the availability of excess water on the soil surface that accumulates from different sources. It occurs when the amount of surface water reaches such a quantity that the soil fails to infiltrate or absorb that. It happens when there is irrigation, rainfall, or when the snow melts that add more water to soil surface that eventually flows down toward ponds, pools, ditches, canals, streams, rivers, or lakes. During runoff, the pesticide molecules present in the crop field soils tend to be carried away that get stored in the lentic water systems. Pesticides stored in the standing water systems get a longer period for leaching into the groundwater sources. Several factors such as environmental conditions, pesticide composition, soil characteristics, etc., affect the transfer of pesticides through runoff water.

3.2.1 Soil moisture content

The water content of the soil in an area will determine the amount of runoff that will occur from the site. Soil that is already saturated with water faces more risk of surface runoff. In the case of dry soils, the addition of water will lead to filling of the pores of soil decreasing the chances of runoff.

3.2.2 Soil texture

Soils that contain clay are more compact and hence more prone to runoff losses, whereas loose sandy soils possess less chance of surface runoff.

3.2.3 Weather or irrigation

Climatic conditions such as the temperature of the atmosphere, precipitation, etc., determine largely the rate of surface runoff. Pesticides applied in the crop fields when subjected to immediate rainfall lead to washing off of the applied pesticide molecules. The wasted pesticides along with surface runoff may reach the nearby water bodies. Also, pesticides that are applied where the soil is already saturated with previous rainfall or irrigation may be subjected to runoff if light rainfall or additional irrigation follows. At times when the temperature is very low, i.e., in the case of frozen soils, applied pesticides face the problem of runoff. Therefore, it is usually recommended not to apply pesticides in frozen soils and the pesticide application should not be followed by heavy rainfall or irrigation.

3.2.4 Slope

The slope is an important deciding factor for the runoff of pesticides with water. The type of landscapes where the ground has a slope will facilitate the runoff of pesticides.

3.2.5 Pesticide characteristics

The physical and chemical properties of a pesticide are the deciding factors for the surface runoff of those molecules. Pesticides that are hydrophilic or more soluble in water will get the opportunity for easy runoff. The hydrophobic pesticides get adhered to the soil particles and hence get less chance for surface runoff.

3.2.6 Pesticide persistence

Some pesticide molecules are easily degraded by the action of microorganisms and hence will not be available for surface runoff.

3.3 Soil erosion

Soil is composed of different constituents such as sand, silt, clay, minerals, organic matters, etc. These components of soil facilitate the adsorption of pesticide molecules to soil particles. The adsorption of pesticides determines their persistency in soil ecosystems. Pesticides that are hydrophobic tend to be get adsorbed to soil particles when applied in the crop fields [19]. These pesticides strongly bind in the soil and lose the chance of surface runoff. However, when the weather conditions become dry, that leads to soil erosion leading to the transfer of pesticides from crop fields to other regions and may reach the nearby aquatic systems. Some examples of pesticides that are displaced only when the soil particles are eroded are organochlorines, paraquat, and arsenical pesticides. These pesticides strongly bind to the soil particles and contaminate the water bodies only when erosion occurs in that area.

3.4 Irrigation

Pesticide movement on or within the soil surface is greatly determined by the process of irrigation, which is a common practice in crop production systems. Irrigation facilitates the movement of pesticides on the soil surface as runoff or leaching to the ground water table. When the rate of irrigation exceeds the rate of infiltration, soil promotes runoff that will carry pesticides away to nearby water bodies. Irrigation made the water molecules available on the soil surface, which interferes with the physical and chemical properties of pesticides and thereby facilitates their movement.

4. Pesticide residues in water bodies

Pesticide use in both developed and developing countries has no doubt enhanced food production and ensured food security, the inappropriate and poorly regulated practices of pesticide handling and application have led to contamination of water bodies. There are several scientific reports those indicate that only 0.1% of the applied pesticides in the field reach the target organisms, and a huge amount is lost into different environmental compartments [20]. Pesticides are chemical substances with harmful chemical properties such as toxicity and persistency. They remain as such in various ecosystems for a long time and are hence called persistent organic pollutants (POPs). “Persistency may be defined as the tendency of a chemical compound to conserve its molecular integrity and chemical, physical, and functional characteristics for a certain time after being released into the soil.” Pesticides are grouped into two categories—hydrophobic and hydrophilic based on which the extent of persistency of a pesticide is determined. The persistency of pesticides in the environment depends on several factors such as the type of soil, method of pesticide application, the capacity of soil to adsorb pesticides, organic matter content of the soil, etc. Hydrophobic pesticides are persistent and hence have the properties of bioaccumulation in the environment, e.g., organochlorines (DDT, endosulfan, endrin, heptachlor, lindane). Some pesticides being persistent persist in the soil and in that course of time may experience a variety of fates. Some amount of the pesticides will be taken up by the plants, and some amount will be degraded by the native microorganisms present in that area. The remaining amount of the pesticide active ingredients or their transformed products will be carried away by water at the time of rainfall or irrigation to different sources of water. Pesticides that will percolate vertically downward in the soil horizon finally reach the groundwater table and those that will move in surface water runoff reach nearby water bodies. Some amount of insoluble chemicals that get tightly bound to soil particles on the topsoil layer are subjected to erosion and ultimately reach surface waters. Pesticide residues that remain in the soil are sometimes subjected to volatilization, in the atmosphere that get accumulated in the rain and during rainfall, finally reach different water bodies. However, water source contamination through this pathway is insignificant. Some pesticides such as herbicides, carbamates, fungicides, and some organophosphates are hydrophilic, hence transported through runoff to surface water bodies and may be leached to groundwater sources.

The occurrence of pesticide residues in the ground as well as surface water sources is a widespread issue globally [21]. Some pesticides detected in major water bodies in different countries are presented in **Table 1**. Pesticide molecules are often found more frequently in surface water sources as compared with groundwater tables [33]. The reason is that the pesticides tend to slowly filter down the soil horizon and reach the deep aquifers, whereas the precipitations and frequent irrigations enhance the chances of pesticide transfer to surface water sources. It is hard to decontaminate the water in the groundwater table and the deep aquifers once pesticide residues contaminate the sources.

Surface water source contamination by pesticides is now common case in developing countries such as India. Not only the surface and groundwater sources but also the direct drinking water sources are found to be contaminated with some pesticide residues in almost all countries around the globe. In several reports where drinking water samples were collected from hand pumps or tube wells from one state of India, about 58% of the samples were found contaminated with various pesticide residues, mainly organochlorines above United States Environmental Protection Agency standards [34]. In China, drinking water samples were found contaminated with 42 different organochlorine pesticides at a concentration ranging from 0.001 to 2.65 μg/l [35–37]. Twenty-three OC pesticide residues were detected at a concentration of 0.01–0.34 μg/l in water samples from India [23]. Water samples from Turkey had 18 different types of OCs at a concentration of 0.007–0.159 μg/l [38]. OCs at a concentration of 0.01–0.03 μg/l were found in water samples from South Africa [39]. Fourteen OCs with a concentration of 0.003–0.09 μg/l were found from Mexico water samples [40]. Twelve OCs were found in water samples of the Philippines at a concentration of 0.02–0.74 μg/l [41]. In some studies of water samples from the United States [42] and Ireland [43], two different OCs were found at a concentration of 0.0004–0.22 μg/l. The occurrence of OC pesticides in water sources of the above-said countries may be due to the previous application of pesticides as insecticides in crop fields. For an instance, in China, a pesticide, dicofol, was applied in cotton fields that later became the cause of DDT contamination of water sources [44]. In the United States also organochlorine pesticides were widely applied in cotton farms that later became

Country	Water sources studied	Detected pesticides	Concentration of pesticides	Reference
Japan	Chikuma river, shinano river	Bromobutide	3 ng/l	[22]
		Isoprothiolane	8200 ng/l	
India	Yamuna river	Hexachloro-cyclohexane	12.76–593.49 ng/l	[23]
		DDT	66.17–722.94 ng/l	
Nigeria	Lagos Lagoon	Chlordane	0006–0.950 μg/l	[24]
		Heptachlor	0.067 μg/l	
		Methoxychlor	0.123 μg/l	
		Hexachloro-benzene	0.015–0.774 μg/l	
		Endosulfan	0.015–0.996 μg/l	
		Dtrichloro-ethane	0.012–0.910 μg/l	
		Dieldrin	0.015–0.996 μg/l	
		Aldrin	0.080–0.790 μg/l	
Bangladesh	Surface water samples from paddy and vegetable fields	Diazinon	0.9 μg/l	[25]
		Carbofuran	105.2–198.7 μg/l	
		Malathion	105.2 μg/l	
		Carbaryl	14.1–18.1 μg/l	
Southern Iran	Lake Tashk	DDT	0.028 ppb	[26]
		DDE	0.075 ppb	
		Lindane	0.082 ppb	
		Endosulfan	0.068 ppb	
Nepal	Ansikhola watershed	Endosulfan	50 μg/l	[27]
		Iprobenfos	3980 μg/l	
		Monochrotofos	118 μg/l	
		Mevinphos	103 μg/l	
		Acephate	43 μg/l	
		Butamifos	3980 μg/l	
Bangladesh	Fish ponds, Tube wells	Malathion	42.58–922.8 μg/l	[28]
		Diazinon	31.5 μg/l	
Ecuador	Guayas river basin	Cadusafos	0.081 μg/l	[29]
		Butachlor	2.006 μg/l	
		Pendimethalin	0.557 μg/l	
India	Chilika lake	Chlorpyrifos	0.019–2.73 μg/l	[30]
		Dichlorvos	0.647 μg/l	
China	Taihu lake	Carbendazim	508 ng/l	[31]
		Imidacloprid	438 ng/l	
Malaysia	Tengi river	Imidacloprid	57.7 ng/l	[32]
		Tebuconazole	512.1 ng/l	
		Propiconazole	4493.1 ng/l	
		Difenoconazole	1620.3 ng/l	
		Buprofezin	729.1 ng/l	

Table 1.
Pesticides detected in major water bodies in different countries.

a major cause of water pollution [45]. Many agricultural practices sometimes enhance the distribution of pesticides in nearby water sources from crop fields. For example, rice cropping requires flooding of the fields for a long duration, which increases the chances of transfer of pesticide residues from a contaminated site to non-contaminated sites as well as to water sources. In India, the huge application of organochlorine insecticides in crop fields has become the major source of surface soil contamination [46] and water pollution [47, 48] nowadays. Organochlorine pesticides remain for a longer period in the environment and cycle through various routes such as volatilization, runoff, or leaching [49]. As a result of which organochlorine pesticide residues get transported to water sources via environmental components. Organochlorine pesticides have high K_{ow} values and hence persist in soil for a longer duration as they get adsorbed to clay or organic matter present in soil and gradually released into water [50–52]. Sometimes organochlorine pesticides get evaporated from crop field soils into the surrounding atmosphere, get deposited in the rain, and eventually distributed in different water sources during rainfall events [53–55].

Organophosphorus pesticide residue detection in drinking water sources all around the world is noted in several published studies. This may be due to intensive OP application for crop protection. In China, OP pesticides are used at a higher amount that is about 1.5–4-fold higher as compared with other parts of the world [56]. OP pesticides were detected from water sources of Spain [57], Brazil [58], Canada [59], and United States [42] at concentration ranges of 1.01–21.95 μg/l, 0.21–0.57 μg/l, 0.01–2.56 μg/l, 0.001–0.06 μg/l and 0.06–0.22 μg/l, respectively. Compared with organochlorines, organophosphorus pesticides are less frequently detected in water sources due to their susceptibility to water hydrolysis at alkaline pH [60], photochemical degradation [61], and degradation by microbes in water bodies [62].

Carbamate pesticides such as carbofuran, carbaryl, methiocarb, fenobucarb, propoxur were found in water samples in Brazil, Spain, Vietnam, Burkina Faso. Carbofuran, carbaryl, methiocarb, fenobucarb, propoxur were detected at a concentration range of 0.06–2.95 μg/l, 0.17 μg/l, 1.35 μg/l, 0.04–0.074 μg/l, and 0.029–0.023 μg/l, respectively. The occurrence of carbamate pesticides in water bodies may be due to their use in agricultural sectors [63, 64], leaching in the soil profile [65], wash-off from plant surfaces during rainfall [66]. However, detection of a low amount of carbamate residues in water bodies may be due to its susceptibility to water hydrolysis [67], degradation by exposure to UV light [68], and degradation through the action of microbes [69].

Pyrethroids, neonicotinoids, and other pesticides were found in water samples all around the world at a concentration of 0.001–0.041 μg/l [22, 70, 71]. Drinking water samples from Burkina Faso [71], Brazil [58], Spain [57], and China [72] were found to have imidacloprid pesticide with a concentration of 0.01, 1.28, 3.99, and 8.33 μg/l, respectively. The low detected concentration of these pesticides may be due to their sensitivity to photo-degradation [73], and the concentration may be due to their usage in agricultural sectors [74].

Approximately 31 different parent herbicide residues were detected in more than 768 water samples collected from 18 countries around the world. Herbicide residues were detected in water samples from Portugal [75], Brazil [58, 76], Spain [57], Vietnam [77, 78], United States [79], Canada [59], China [80], Germany [81] at concentrations of 0.002–027 μg/l, 0.01–4.90 μg/l, 1.16–32.32 μg/l, 0.0001–0.47 μg/l, 0.03–1.8 μg/l, 0.0001–0.051 μg/l, 0.001–0.021 μg/l, 1.22–79.02 μg/l, respectively.

Herbicide glyphosate is highly water-soluble (10.5 g/l) and has a high dissociation constant and low partitioning coefficient, therefore considered as a nontoxic pesticide to humans; however, it is highly toxic to aquatic organisms. Due to widespread use, glyphosate residues have been found in many water sources, including drinking water, and also detected at a concentration of 1.42 μg/l in the groundwater table [82].

Different fungicides have been detected in water samples from different countries. Water samples collected from different places in Japan showed fungicide residues at concentration ranges of 0.013–0473 μg/l [22]. Fungicides are also detected at a concentration of 4.82–101.03 μg/l in Spain [57], 0.001–0.39 μg/l in Brazil [58], 0.0011–0.077 μg/l in China [83]. Fungicides are found in water samples due to their use in agricultural practices such as to control soil-borne plant diseases, seed dressings, foliar sprays, etc.

5. Consequences

Though the application of pesticides provides a range of benefits such as enhancing the quality of food and increasing the quantity of food production by reducing pest-related issues of crop plants; however, the inappropriate use of pesticides has also led to potential negative effects on the environment, mainly water sources. The adverse effects of the pesticides remain in the environment for a long time as the pesticide molecules also remain persistent for a long period. Surface water bodies such as ponds, pools, ditches, streams, lakes, estuaries, and groundwater remain vulnerable to pesticide pollution. Even when the amount of pesticide residues that enter the water bodies is very less, subjected to biomagnifications, and the residues get deposited at a noticeable amount. Pesticides in water bodies have the chance to enter the body of aquatic organisms and then get transferred to others in the food chain. Man occupies the highest trophic position in a food chain, and also man has access to a number of other food chains, hence tends to acquire the highest amount of pesticide residues than other organisms by a process of biomagnification. The accumulated pesticides in the human body interfere with physiological processes, and the consequences are decreased immunity, hormonal balance disruption, reproductive system abnormalities [84], and more importantly carcinogenic effects [49], the occurrence of breast cancers [85], prostate cancers [86], abnormalities in the endocrine system [87], the occurrence of Parkinson's disease [88], and imbalance in cardiovascular system [84]. Pesticides such as organochlorines when reach non-target insects disrupt their nervous systems leading to paralysis and ultimate death. Organochlorine residues in water bodies promote endocrine system disorders in aquatic organisms such as fishes. Hence these toxic pesticides are now banned in many nations worldwide. Organophosphate pesticides inhibit the function of the enzyme-acetylcholine esterase that hydrolyzes acetyl choline [89]. Farmers and field workers sometimes when exposed to pesticides while handling or applying face pesticide poisoning, and this adds to the negative impacts of pesticides with respect to public health problems [90]. Each year about 3 million cases are registered as pesticide poisoning of which the death of 250–370,000 people is reported [91]. This may be due to handling, spraying, and storage of pesticides without improper protection measures. Not only human beings but also plants, birds, and aquatic organisms get affected when exposed to pesticide-contaminated water. Contaminated aquatic organisms such as fishes or shell fishes transfer pesticide residues in their body to humans. Hence humans may acquire pesticide residues through two major pathways—ingestion of food and water. World Health Organization (WHO) and many other health and environmental agencies established the maximum allowable quantities of about 33 pesticides for daily ingestion under the term "acceptable daily intake (ADI)."

6. Decontamination techniques

Though the use of pesticides since nineteenth century has brought revolutionary advancements in crop production sectors, the inappropriate usage has now put questions to the sustainability of the environment. The pesticide active ingredients, as well as their transformation products in different ecosystem compartments , and more importantly in drinking water sources, have now drawn the attention of environmentalists to work in the field of removal of pesticides. Pesticides are usually organic compounds, hence put through various physical, chemical, and microbial degradation processes. Microorganisms mineralize the pesticides into final small molecules such as CO2 and water. Sometimes microbes transform the pesticides into a new modified compound by changing their chemical structure, which is called co-metabolism. Photochemical degradation or photolysis is a process where the pesticide molecules are broken down in the presence of ultraviolet rays. Chemical degradation of pesticides occurs via oxidation-reduction reactions as well as by hydrolysis in air and water.

Naturally, pesticides are removed from the environment through the exposure of UV light, sedimentation, adsorption-desorption, and microbial action, but to a smaller extent. On a large scale, the removal of pesticides from the environment may involve both physical and biological processes. The typical physical methods for removal of pesticides in treatment plants include ozonation [92], fluid extraction [93], solid-phase extraction [94], photocatalytic degradation [95, 96], adsorption [97], filtration [98], and sedimentation. These methods of pesticide decontamination of water usually have high operational costs and also may create the chances of the development of secondary pollutants such as sludge. So, now there are requirements of alternative pesticide removal processes, which will be long term and feasible. One of the most promising and clean technologies for decontamination of water is Advanced Oxidation Processes (AOPs). It is now the most accepted technique for water purification as it is thermodynamically feasible and has broad-spectrum applicability. The mechanism of the process involves the production of highly reactive hydroxyl radicals within the system. Highly reactive hydroxyl radicals are formed by different processes such as by using oxidants, catalysts, or UV rays. These in situ generated hydroxyl radicals carry out the oxidation of a wide range of chemical contaminants including pesticides and their transformation products and lead to their complete mineralization to CO2, water, and inorganic elements [99, 100]. In more complex systems, AOPs are recommended as a pretreatment process that converts the pesticides into a more biodegradable form followed by a biological treatment process that converts the pesticides into CO2, water, inorganic minerals, and biomass.

Adsorption of pesticides on activated carbon materials in its different forms such as granular activated carbon [101], powdered activated carbon [102], carbon cloth [103], carbon fibers [103], black carbon [104], activated carbon composites [105], etc., has now become a cheaper and renewable method of pesticide removal from waste water. Researchers are now trying to synthesize activated carbon from cheaper sources such as agricultural wastes such as coconut fibers, sal wood, coconut shells, horseshoe crab shell, corn stillage, oil palm fronds, wood, date stones, and biochar, etc., for effective removal of pesticides.

In the last few decades, membrane technologies such as reverse osmosis and nanofiltration are found to remove pesticides from waste water efficiently. Nanofiltration is the most suitable technology for removing pesticides while reserving the inorganic nutrients in the water. The principle behind the process is the charged surface of the membrane that effectively removes pesticide molecules from treated water [106].

Reverse osmosis (RO) is a process that eliminates impurities from drinking water including pesticides residues. Here water is passed through a membrane having a pore size of 0.0001 micron under high pressure. Only 5–10% of the ions can pass through the membrane [107], and those are included under acceptable levels as per World Health Organization (WHO). RO systems are helpful in the removal of pesticide residues; however, the cost varies depending on the capacity of the plants, level of utilization, level of salinity, presence of other contaminants, and distance from the source of water. Removal of pesticides from water by the process of reverse osmosis through the use of membranes such as aromatic polyamines, cross-linked polyethylenimine membranes, e.g., NS-100, PA300 [107], cross-linked m-phenylenediamine membrane (FT-30) [108], etc., was successfully applied later.

Biotic degradation or biodegradation is defined as the breakdown of complex pesticide molecules into smaller products. The rate at which pesticides biodegrade varies widely. Some pesticides such as DDT and dieldrin are recalcitrant. Pesticides such as organophosphates, which are biodegradable, are nowadays given more preference over recalcitrant ones such as organochlorines. The biodegradation process involves both aerobic and anaerobic methods. Also, biodegradation is divided into three categories based on the location where bioremediation is done, i.e., ex situ and in situ. In in situ treatment, bioremediation is carried out at the contaminated site itself, and it is usually the aerobic process. Some of the in situ bioremediation techniques that can be instigated to eliminate pesticides are attenuation, bioaugmentation, biostimulation, bioventing, and biosparging. In ex situ treatment, the contaminated water is removed from the polluted site, transported to other sites where the pesticides in the water are biodegraded. During biodegradation, microbes use pesticides as co-substrates in their metabolic reactions, mineralizing them and thus eliminating them from the environment. The key microbial enzymes that carried out the process are hydrolases, peroxidases, oxygenases, etc. The process of biodegradation involves three steps. In the first step, through the processes such as oxidation, reduction, and hydrolysis, the pesticides are converted into more water-soluble forms. The transformed products are converted into sugars and amino acids, which are again

Pesticides	Microorganisms	Reference
Glyphosate	*Fusarium*	[111]
Chloropyrifos	*Ochrobactrum sp. JAS2*	[112]
Cypermethrin	*Bacillus subtilis*	[113]
Deltamethrin	*Streptomyces rimosus*	[114]
Fentopropathrin	*Rhodopseudomonas palustris*	[115]
Phorate	*Brevibacterium frigoritolerans* *Bacillus aerophilus* *Pseudomonas fulva*	[116]
Acetachlor	*Tolypocladium geodes* *Cordyceps*	[117]
Tebuconazole	*Serratia mercescens*	[118]
DDT	*Fomitopsis pinicola* *Ralstonia pickettii*	[119]

Table 2.
Microorganisms capable of degrading several pesticides.

more water-soluble and less toxic in the second step and finally converted into CO2, salts, minerals, and water in the final step. The availability of pesticides for microbes depends on their solubility, pH of water, temperature, microbial diversity, etc. The microorganisms that can carry out the degradation of pesticides are bacteria, fungi. In some cases, it is easier when a group of microorganisms called microbial consortium is used as compared with the pure culture. Among fungi, molds, yeast, and filamentous fungi are more useful for the biodegradation of pesticides [109]. Fungi are better degraders of pesticides than bacteria due to characteristics such as specific bioactivity, growth morphology, and high resistance even at high concentrations of pesticides [110] (**Table 2**).

7. Conclusion

Clean water is an important part of human life and plays a major role in the sustainability of life on earth. Access to clean water is a fundamental human right and vital to sustaining a healthy life. However, the occurrence of pesticide residues in different water sources including drinking water has now become a universal problem. Nowadays, the increasing demand for food has resulted in intensive agricultural practices that resulted in contamination of water sources with pesticide residues; degrade the water quality in both developed and developing nations. Freshwater is a scarce and vulnerable resource that can be easily contaminated and whose original quality is hard and expensive to be restored. Water pollution through pesticides is posing deleterious effects on many types of organisms, including useful microorganisms, insects, birds, fishes, and humans.

Briefly, it can be said that agriculture has no beneficial effects on water resources. As agriculture is a primary requirement for human society, it cannot be disregarded. So only we can minimize or regulate the activities in agricultural sectors to keep down the extent of water pollution. Although pesticides are considered as easy, cheap, quick methods for eliminating pests and weeds from crop fields, pesticide users should be recommended to completely eliminate chemical pesticides and replace that with bio-pesticides that will minimize the risks of environmental hazards. Also, there are reports that showed that cheaper pesticides sustain in the environment for a long time as they are resistant to natural degradation processes. In some developed countries, the use of such pesticides is banned already but due to their low cost, these are still in use in many developing nations. Integrated pest management (IPM) is another clean way for the management of insects and pests where the growth of healthy crops is emphasized that will discourage pest attack. The areas where pesticide occurrence in water bodies became more common should undergo constant observations. The water bodies where residues have been detected should be subjected to various treatment processes for decontamination and the potable water sources should undergo advanced decontamination processes. Finally to reduce the pesticide load in water sources as well as in other ecosystem compartments is the duty for all of us to do our part through the use of non-chemical pest control methods.

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Conflict of interest

The authors declare that they have no known competing interests or personal relationships that could have appeared to influence the work reported in this paper.

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