Impact of Pesticide Toxicity in Aquatic Environment

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Abstract: The intensified agricultural crop production for growing high yield varieties requires the indiscriminate use of pesticides and fertilizers, which protect the crop from pests, thus helps in improving the quality and quantity of crops. The aquatic environment gets contaminated by the application of pesticides through several routes: runoff, spray drift, and leaching, which pose serious health risks to the aquatic ecosystem as well as to human beings. This exposure can directly affect all levels of biological organization, including primary producers, microorganisms, invertebrates, or fish. Thus, monitoring methods should be adopted for controlling the runoff events in the spraying method, such as suspended matter sampler for particle-associated pesticides that can be used for controlling the number of toxic substances in water bodies.

Keywords: aquatic; environment; toxic; water; pesticides.

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1. Introduction

Rapid industrialization and urbanization in the last few decades, with the concomitant growth in population, had taken a toll on the natural resources. Several anthropogenic activities like pollution by toxic substances through pesticides or heavy metals on regional, or global scale results in climate change. Large-scale mortality of living organisms’ most important wildlife such as sea mammals and expanding threat to human health, i.e., chronic respiratory diseases, cancer, damage to several major organs like the brain, lungs, kidneys are being witnessed in the recent years as a result anthropogenic perturbations [1]. Of all the anthropogenic sources of pollution, agricultural, industrial, and domestic activities are the major sources responsible for contaminating natural freshwater resources [2]. For example, about 300 billion kilograms of mixtures used in engineering and farming products reach the freshwater frameworks consistently. 10% of the universally open spillover is utilized, producing a surge of wastewater, which streams into groundwater, waterways, lakes, or the seas [3, 4].

With the increase in world population in recent years, there is a pressure on the existing agricultural system, and nowadays, the prime objective of most of the countries is to increase the food production to meet the demands of a growing population which are expected to grow nearly to 10 billion by the year 2050 [5,6]. The process of increasing cop production utilizes the application of higher quantities of agrochemicals such as herbicides, fungicides,
nematicides, and fertilizers. These agrochemicals are used for controlling the pest population and increasing the yield for the production of an ample amount of food for the global population, which is estimated at 6.8 billion in 2009, and it reached 7 billion in 2012 [7, 8]. In underdeveloped countries where 1.02 billion people are undernourished, which accounts for 15% and 1.3 billion people live on an inadequate diet, which accounts for 19% thus, there is a need for sufficient sustenance supply. However, freshwater and terrestrial ecosystems are highly polluted by a large number of toxic substances, most importantly by the application of pesticides and fertilizers by the agricultural sector [2], which becomes an important issue globally. Pesticides that are used for the eradication of harmful pests are today flattering an essential part of modern life. Ideally, these should only be toxic to the target organisms [7], but several pieces of evidence from the developing research shows that the industrial chemicals, pesticides, heavy metals, and several other toxic substances interfere with the normal functioning of a large number of species including human beings and aquatic organisms [8-10]. Pesticides are present at higher levels should be removed from drinking water for human safety. There is a need to maintain control on disposal of industrial waste or Agriculture waste in water bodies and to bio-monitor the trace elements in the water and other eatables [11,12].

2. Pesticides

Pesticides are a mixture of substances that are designed to control or slaughter or control the development of pests (undesirable organisms). These pests usually plant pathogens, nematodes, microorganisms, and insects that compete with human food and are responsible for transmitting diseases and destroying crops. Pesticides are usually categorized into biological or synthetic (Fig. 1). The biological pesticides are derived from natural sources, for example, plant extracts (azadirachtin from neem or pyrethrin from chrysanthemum plants), whereas synthetic pesticides are made through the industrial processes. Another category of pesticides are broad-spectrum (used to control a wide range of species) or narrow-spectrum (used to control a small group of species) and they are also categorized depending on the kind of pest they regulate, i.e., insecticides are used for controlling insects, herbicides for weeds and fungicides are used for controlling fungi.

2.1. Insecticides.

Most of the insecticides affect the nervous system at several target sites; they interfere with the membrane transport system of sodium, potassium, calcium, or chloride ions, which inhibits the selective enzymatic activities involved in the chemical transmission at nerve endings [13] (Table 1).
2.1.1. Organochlorines.

They are a class of insecticides that affect the nervous system as they are chemically unreactive stable compounds, which leads to long-lasting effects. DDT is the most studied pesticide among all insecticides, which inhibits the release of neurotransmitters. Endrine and lindane are other two organochlorine insecticides, in addition to DDT, which affects the nervous system [11].

2.1.2. Organophosphates.

In previous years many countries banned some of the organochlorines (DDT), which were replaced with organophosphorus insecticides like malathion and parathion [14]. This group of insecticides is also neurotoxic, i.e., they inhibit the enzyme acetylcholinesterase (AChE), and the signs and symptoms of intoxication are longer and persistent [15, 16].

2.1.3. Carbamates.

This category of insecticide also inhibits AChE by attaching to the reactive site of the enzyme [10]. It has short and reversible inhibition action of AChE.

2.1.4. Synthetic pyrethroids.

This is the newest category of insecticide, which shows two different acidic portions chrysanthemic or pyrethric acids resulting in type I and type II syndrome [13]. Both of these syndromes affect the sodium channels in the nerve membranes, which is responsible for causing the repetitive neuronal discharge; this mechanism is quite similar to the DDT action. Pyrethroid insecticides have several other sites of action. Some of them include inhibition of Ca^{2+}, Mg^{2+}-ATPase, which results in the interference with calcium removal from nerve endings, causing the release of neurotransmitters in the postsynaptic gap.

2.2. Herbicides.

Herbicides are classified into several categories based on their action. They are produced for killing the harmful plants (weeds) thus. They are associated with affecting various mechanisms that are involved in photosynthesis, respiration, growth, cell and nuclear division, or during the protein or lipid synthesis [13, 17].

2.1.1. Glyphosate.

The most commonly used herbicide for controlling weeds inhibits the single plant enzyme EPSPS (5-enolpyruvoylshikimate 3-phosphate synthase), which is the key enzyme for catalyzing the amino acid biosynthetic pathway, and the inhibition of this enzymes affects the protein synthesis mechanism [18, 19]. In addition to these, herbicides also inhibit many physicochemical and physiological pathways [20, 21]. The ecotoxicologists are highly concerned about the exposure of a non-target aquatic organism to the formulations of glyphosate because of the extensive use of glyphosate in the shallow water ecosystems, and it also possesses high water solubility [22].
2.2.2. Chlorophenoxy herbicides.

This category of herbicides mainly includes 2,4-D (2,4-dichlorophenoxyacetic acid), 2,4,5-T (2,4,5-trichlorophenoxyacetic acid), and MCPA (4-chloro-o-toloyxyacetic acid), which are known for mimicking the role of growth hormone, i.e., auxin in plants [13, 23, 24] and it is also responsible for several growth abnormalities at higher concentrations which mainly includes leaf or stem curling, inhibition of shoot and root growth [25] which ultimately results in necrosis and plant death.

2.3. Fungicides.

Fungicides are the group of an insecticide which disturb the energy supply in fungi and inhibits spore germination [26]. For example, dithiocarbamates (e.g., maneb and thiram) and the R-S-CCl₃ compounds (e.g., captan and dichlofluanid) have multisite action by inhibiting the enzymes which are involved in respiratory processes, whereas another group of fungicides, i.e., the phenylpyrroles, which includes fenpiclonil and iprodione inhibits the spore germination and causes several morphological alterations in the germ tubes of plants which means the elongation of germ-tube is inhibited [27, 28]. In addition to this, fungicides are also identified to constrain the electron transport chain in the respiration process [29].

| Pesticide category | Major classes | Purpose | Mode of action | Examples | References |
|--------------------|---------------|---------|----------------|----------|------------|
| Insecticides       | Organophosphates, Carbamates, Pyrethroids, Organochlorines, Neonicotinoids | Kill or repel insects | Neurotoxic, bioaccumulates, and biomagnifies | Malathion, methyl parathion, aldicarb, carbaryl, methomyl | [30] |
| Herbicides         | Phosphonates, Chlorophenoxy herbicides, Dipuridyl herbicides | Kill weeds or unwanted plants | Neurotoxin to specific stages of insect during development | Glyphosate, 2,4-D, mecoprop, Diquat, Paraquat | [31] |
| Fungicides         | Thiocarbamates, Triazoles, Strobilurins | Kills mounds and other fungi | Prevent fungal spore formation and stop plant diseases | Metarn sodium fluconazole, myclobutanil, triadimefon | [32] |

For agricultural purposes, the pesticide use is enhanced in recent years for increasing the crop yield to meet the needs of the growing human population [33, 34] whereas their use harms the environment and also affects non-targeted organisms along with the targeted pests [26] which are a matter of major concern for decades [35] as it negatively affects several links in the food web. Both the soil and aquatic ecosystem are affected negatively by the pesticide pollution as they move from one ecosystem to another because of their specialized properties such as half-life, solubility, mobility, and degradation (Table 2). The pesticide enters the aquatic ecosystem through runoff, vapourization to the atmosphere, agricultural returns, groundwater intrusions, or by adsorption or through plant uptake [36-38], which adversely affects the health of aquatic organisms. Most of the pesticides in urban and agricultural settings are negatively affecting the deaths of several aquatic organisms, such as birds, fish, and zooplankton [39].

The following given factors are considered to determine the ecological impacts of pesticides in water:
### Table 2. Factors affecting pesticide toxicity in aquatic systems.

| Factor     | Description                                                                                                                                                                                                 | References |
|------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------|
| Toxicity:  | Both in the situation of mammals and non-mammals, the toxicity is expressed in the form of Lethal Dose (LD), which is the concentration of the toxic substance (pesticide) responsible for killing the half test organisms in a certain period of time. The lower the value of LD50, the greater will be the toxicity; values of 0-10 are extremely toxic. Using a risk-based assessment, the drinking water and food guidelines are determined. Generally, Risk = Exposure (amount and/or duration) × Toxicity. Toxic response is observed in two forms: **Acute**: death **Chronic**: in this effect, death does not occur during the test period, but certain observable characteristics such as tumors, reproductive failure, and growth inhibition are noticed in the test organism. | [40, 41] [42] [43] |
| Persistence: | It is measured in the form of half-life, which is the time required for the diffused concentration to decrease by 50%, and its persistence is determined by the degradational processes, whether it be biotic (biodegradation and metabolism) or abiotic (hydrolysis, photolysis, and oxidation) (Calamari and Barg, 1993). | [44] |
| Degradates: | The process of degradation leads to the formation of degradates, which may have lesser, equal, or greater toxicity when compared to the parent compound, for example, which DDT degrades it results in DDD and DDE. | [45] |
| Fate (Environmental): | The environmental behavior of the pesticide is mostly affected by the chemical’s natural affinity (Calamari and Barg, 1993) for any of the four compartments: solid matter, liquid, gaseous form, and biota. | [46] |

### 3. Pesticides in the Aquatic Ecosystem

To grow high yielding crop varieties farmers, tend to use pesticides to protect the crop from pests as these crops are highly susceptible to the pests and diseases, which may lead to a 40% loss in crop production; thus, these pesticides as used to improve the quality as well as quantity of crop by protecting them from pests [47-51]. Among all the toxic substances that run off into the aquatic ecosystem, pesticides are of major concern as they are known to cause serious threats to the biological organisms, including human beings. Through several different routes such as spillage, industrial effluent, surface runoff, or through pesticide-treated soils, these toxic substances enter into the water sources [52-54]. The toxic effects caused by exposure to these toxic substances can be categorized according to the exposure period, which may be short or long-term, and exposure type, which can be lethal or sub-lethal. The period of short-term exposure does not exceed 96 hours, while long-term exposure is considered to be more than 96 hours (Table 3).

### Table 3. Classification of the effect of animals exposed to chemicals [55].

| Sr. no | Exposure classification | Classification based on effects | Description |
|--------|-------------------------|---------------------------------|-------------|
| 1.     | Exposure time            | Short-term                      | ≤ 96 h (mortality is measured as endpoint) |
| 2.     |                          | Long-term                       | cellular/molecular/biochemical/physiological level measure as endpoint |
| 3.     | Exposure type            | Lethal                          | ≥ 96 h (mortality is measured as endpoint) |
| 4.     | Sub lethal               |                                 | cellular/molecular/biochemical/physiological level measure as endpoint |

From agricultural fields pesticides generally runoff to reservoirs or drainage systems through rain or by irrigation process [56]. Aquatic organisms are exposed to pesticides primarily by three ways: (i) through the skin: as aquatic organisms are in contact with water thus, through dermal pores, pesticides cause harmful effects, (ii) through breathing: as they respire through gills thus the aquatic organisms directly uptake pesticide through breathing and (iii) orally: aquatic organisms usually get exposed to pesticides by feeding in pesticide-contaminated prey (which is also known as secondary poisoning for example: if fish feeds on...
pesticide exposed insects then they may get killed if a large amount of toxic compound is consumed by the insects) or by drinking contaminated water.

The aquatic ecosystem consists of various groups of organisms such as invertebrates, plants, microorganisms, fish, or amphibians. Pesticides can affect these organisms directly or indirectly; the direct effect includes physiological changes within an organism [57-59]. For example, the exposure of pesticides to water flea results in their mortality, which can be considered as the direct effect of pesticides, and it may lead to the drastic increase in the biomass of algae because of release from the grazing pressure considered as an indirect effect. Globally, herbicide, mainly glyphosate is used for controlling both the terrestrial and aquatic weeds, and in recent years its use has been tremendously increased, and thus, it is also known to negatively affect the non-target organisms in the aquatic environment [60]. Originally its mode if an action was designed to affect the plants [61] only, but in recent year’s several reports have been coming into the picture representing the adverse impact of non-target organisms [17, 62-64], which can be lethal or sub-lethal. The indicators for the exposed organisms at the physical level include a measure of survival, growth, morphological/behavioral changes. The reproductive performance can often be used for the assessment of sub-lethal response, which also includes sexual maturity, time taken to release the first brood, time taken for egg growth, fertility, and modifications in the characteristics of reproduction. In addition to this, several biochemical parameters can also be used to determine the toxicity in exposed animals, which may include disruption in metabolic pathways, steroid metabolism, lipid peroxidation, AChE activity, and activity of cytochrome P450 enzymes and levels of blood glucose.

In many studies, two direct measures of growth (body weight and length) have been used for the assessment of sub-lethal effects on arthropods. Simple dry weight is determined by drying organisms, which is sampled at an average temperature of 60º C for 48 hours [65-67]. Fishes interact closely with the physical, biological, and chemical marine ecosystem; thus, they are an important part of the aquatic ecosystem. They are an important food source for other animals such as sea birds and other marine mammals; thus, they are an integral part of the marine food web. Several studies have reported the decline of the fish population to the toxic effect of pesticides [68, 69] as several reports have been mentioned representing the decline in the fish population [12, 70-80].

4. Conclusions

This review paper deals with the effects of rapid growth in the human population on the aquatic ecosystem, which may be noticed in the form of climate change, nutrient enrichment of aquatic bodies, and pollution by the different types of toxic substances, including pesticides in both regional and global scale. These man-made disturbances within the environment are responsible for adversely affecting the normal functioning of living organisms, which includes developmental abnormalities from invertebrates to higher organisms that are mammals. It is being noticed that in past years the use of pesticides is increasing, and it affects non-target organisms at different biological scales.

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Conflicts of Interest

The authors declare no conflict of interest.

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