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Effect of pesticide toxicity in aquatic environments: A recent review

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Abstract

Pesticides are widely used in modern agriculture to enhance the quantity and quality of yield in an effective and economical manner, leading to improved food security worldwide. Organochlorines, organophosphates, carbamates and pyrethroids are the four major groups of pesticides used. However, with increasing pesticide use, especially in developing countries, the risk of its toxicity caused by them is on the rise. Despite a low per hectare use of pesticides in India, their injudicious use has led to the presence of pesticide residues in both terrestrial and aquatic ecosystems. It has been observed that major riverine ecosystems like Ganges, Yamuna, Cauvery, Tapi and many others show the presence of pesticides in the water column as well as the river bed sediments. Pesticides tend to bioaccumulate in the food chain. Agricultural runoff into aquatic systems raises the risk of exposure of pesticides to non-target species, leading to adverse consequences on the ecosystem. In this review, an attempt has been made to critically review the usage of pesticides in India, their entry into riverine ecosystems and the impact of pesticides on freshwater microorganisms, invertebrates and vertebrates. The review of legislation in India to control pesticide usage shows that proper implementation of the laws is needed on an urgent basis.

Keywords: Pesticides, riverine ecosystems, pollution, Indian scenario, legislation

Introduction

Pesticides are chemicals of natural or synthetic origin which are used to control pests, weeds and pathogens in plants. It can include insecticides, fungicides, rodenticides, bactericides and larvicides. Annually, around 45% of the food produced worldwide is destroyed due to pests. Therefore, it is necessary to implement effective pest management using a wide range of pesticides. Widely used in modern agriculture, pesticides effectively increase the quality and quantity of yield at a relatively less economic cost ^[1].

Rapid economic development around the world at the end of the Second World War in both industrial and agricultural sectors have led to a progressive increase in the manufacture and utilization of pesticides. The use of pesticides along with fertilizers has played an important role in improving food security in the last 50 years ^[2]. The most commonly used method of classifying pesticides is based on their chemical composition and properties of active ingredients. Classification of pesticides, based on chemical composition, gives four main groups namely, organochlorines, organophosphates, carbamates and pyrethroids ^[3]. Organochlorine pesticides belong to the oldest group of pesticides synthesized and used. Most of them are broad-spectrum insecticides for the control of agricultural and domestic insects. They show a long-term persistence in the environment. The mechanism of action of organochlorines is to disrupt the nervous system leading to convulsions and paralysis in insects which ultimately causes death. Dichlorodiphenyltrichloroethane (DDT), lindane, endosulfan, aldrin, dieldrin and chlordane are some of the common examples of organochlorines ^[4]. Even if DDT has been banned in most developed countries long back, it is still being used in most tropical developing countries, including India for malaria vector control ^[5-6]. Organochlorines were widely used till the 1990s, followed later by increased use of organophosphates ^[7]. Organophosphates are also broad-spectrum pesticides which act as a stomach poison, contact poison and nervous poison. Some of the widely used organophosphorus insecticides include parathion, Malathion, diazinon and glyphosate ^[8-9]. Carbamates are similar to organophosphates in their structure and way of action, but their origin is different ^[10].

Some of the widely used insecticides under this group include carbaryl, carbofuran, propoxur and aminocarb^[8]. Synthetic pyrethroids and neonicotinoids are pesticides that are highly toxic to insects and fish but slightly toxic to mammals and birds. They are considered to be amongst the safest insecticides for use in food. Cypermethrin and permethrin are the most used synthetic pyrethroid pesticides^[11].

The widespread use of pesticides throughout the environment has led to pollution and has disastrously impacted the environment as well as human health. Pesticides can be carried to aquatic ecosystems through agricultural runoff, spray drift, atmospheric fallout, soil erosion, leaching, industrial and domestic sewage, careless disposal of empty containers, equipment washing and ground infiltration^[12-13]. Pollution of water bodies adversely affects aquatic organisms as well as makes it unfit for human consumption. In areas with water scarcity problems, this can lead to unmitigated disaster^[14-15]. Most of the pesticides used are a threat to living organisms, both terrestrial and aquatic, due to their high toxicity and ability to bioaccumulate^[14, 16].

Around 3.5 million tonnes of pesticides are used worldwide, half of which are insecticides^[17]. Approximately 64% of world agricultural land is at risk of pesticide pollution and 31% is at high risk. South Africa, China, India, Australia and Argentina as high-concern regions because they have high pesticide pollution risk^[18]. Pesticide use is increasing very rapidly in developing countries, especially in Southeast Asia^[19]. Environmental pollution caused by pesticides poses a serious environmental risk, especially in Asia, Africa, Latin America, the Middle East and Eastern Europe^[20].

In addition to the inherent risks posed by pesticides, their indiscriminate and unsafe use is a significant concern in rural areas. It has been seen that farmers do not follow the proper safety protocols during the application of pesticides in the field. This is true even with respect to farmers who have long-term experience in the use of pesticides. It has been observed through various research studies that even though the farmers are well aware of safety measures to be followed, these are adopted infrequently by them in the field^[21-22]. Such indiscriminate use exacerbates the unintended exposure of non-target organisms to pesticides in the environment. Hence judicious use of pesticides is important with respect to the health of the farmer and the protection of the environment.

Studies conducted in 2018 showed that pesticides chlorpyrifos, diazinon and quinalphos were more frequent in water and sediment samples in North-West Bangladesh. Chlorpyrifos showed the highest concentration of organophosphate pesticides in water, however, diazinon was found highest in sediment samples^[23].

Pesticide pollution in aquatic ecosystems: An Indian scenario

In India, pesticides in riverine systems have become a major source of concern. Many of the fertile agricultural lands in India are on the banks of rivers. Hence the risk of agricultural runoff polluting the rivers is very high^[24]. A review of the existing literature indicates that hexachlorocyclohexane (HCH), DDT and endosulfan have been the major pollutants in water column and biota while HCH, DDT, aldrin and dieldrin have been dominant in the sediment phase^[7].

Major riverine systems like the Ganges, including tributaries like the river Yamuna have been found to be heavily polluted^[25-26]. Pesticides like DDT, endosulfan, endrin, aldrin, dieldrin, and heptachlor have been detected in potable water

samples from river Yamuna^[27]. Studies on river Gomti, another tributary of river Ganga, showed the presence of lindane, endrin, heptachlor epoxides and DDT in the bed sediments, indicating accumulation of the sediments of the river bed^[28]. This pattern of pesticide pollution has been repeatedly observed in studies conducted on other rivers in India like the Ghaggar river in Haryana, Cauvery river in Karnataka and Hindon river in Uttar Pradesh^[12, 24]. Analysis of pollution in the perennial Tamiraparani river basin in southern India showed the presence of DDT, HCH and 15 other organochlorine pesticide residues exceeding the acceptable limits^[29-30]. Contamination of water and sediment samples with organochlorine pesticides residues in surface water and sediments from the Tamiraparani river basin can be explained by the agricultural and municipal outfalls in this region^[31]. Surface water and sediment samples from the Tapi River showed the presence of endosulfan, chlorpyrifos, and methyl parathion. In fish samples, levels of endosulfan, chlorpyrifos, and methyl parathion detected were 101.28, 0.392, and 3.49 ng/g, respectively. These results revealed that highly toxic pesticides are still being used in the surrounding area, and there is an urgent need for enforcement of rules to control the production and application of such pesticides^[32]. A case study in the Hooghly River basin in West Bengal, India reported the predominant presence of insecticides over herbicides and fungicides in the river water samples. Organochlorine pesticides were dominant in nearby agricultural areas of this river and most river samples exceeded European drinking water limits for pesticides^[33]. When water samples along the 230-km stretch of the river Ghaggar in Haryana were analyzed for the presence of organochlorine insecticide residues, HCH and DDT were traceable in all the water samples. The concentrations of HCH and DDT were found to be above the permissible limits prescribed by the European Commission Directive for drinking purposes^[12].

The Government of India has notified recommended MRL's (Maximum Residual Limits) under the Food Safety and Standards (Contaminants, Toxins and Residues Regulations, 2011. The MRL's for different pesticides are listed in this compendium and strict action is taken against the food manufacturers if the MRL's are exceeded^[34]

Table 1: Permissible limits of major pesticides in drinking water^[35]

| Pesticides | ISI Limit (µg/L) |
|-------------------|------------------|
| DDT | 42 |
| Aldrin | 17 |
| Lindane | 56 |
| Organic phosphate | 100 |
| Carbamate | 100 |
| Heptachlor | 18 |
| Dieldrin | 17 |

Effect on aquatic ecosystems

Individual pesticides are harmful to the ecosystem, but combining pesticides together results in enhanced toxicity. Knowledge about interactions of specific pesticides belonging to these groups in aquatic organisms is lacking. Therefore, it is often not straightforward to predict whether toxicity for a given combination of compounds will be enhanced or not^[36]. The extent of bioaccumulation of different pesticides in fish is influenced by the polarity and water solubility of the pesticides. There is an inverse correlation between water solubility of pesticide chemicals and bioaccumulation of that

chemical in fish. The extent of bioaccumulation decreases as the solubility of the pesticide in water increases. Hence water solubility is an important parameter in decreasing the dynamics of pesticides in aquatic environments [37]. The rate of elimination or desorption of pesticides appears to be species-specific. The level of pesticides in given species is determined by the rate of absorption and rate of elimination reactions [38]. There have been considerable efforts to determine and document the distribution of pesticide residues in the aquatic ecosystem. Many toxic effects associated with organochlorine insecticides and organophosphate metabolites have been discovered through a comprehensive residue analysis program [39]. Undesirable loss of ecosystems in the form of pathology and mortality of aquatic animals can be caused due to pesticides that enter aquatic ecosystems. This causes a decline of aquatic microorganisms, invertebrates like prawns, frogs, turtles, muscles and vertebrates like fish, water birds, etc. These aquatic animals are part of natural food chains. Hence other animals dependent on these aquatic organisms for food also get affected by the harmful chemicals present in the pesticides [70].

Effect on microorganisms

Pesticides can affect the microorganisms in aquatic ecosystems like estuaries and rivers through spills, agricultural runoff, and drift. Pesticide toxicity can impair the structure as well as the function of microbial communities. Pesticides can be metabolized by microorganisms or bioaccumulated in the ecosystem. Mechanisms of toxicity of pesticides in microorganisms vary depending on the type of chemical and the microbial species exposed to it [41]. The use of free pesticides adversely affected the abundance of soil microorganisms like *Pseudomonas*, *Bacillus*, *Pseudarthrobacter*, *Streptomyces*, *Penicillium*, and *Talaromyces* from 1.4 to 56.0 times for different types of pesticides [42]. Overuse of pesticides affects the abundance of nitrifying bacteria *Nitrospira* strain '*Nitrospira inopinata*' in paddy soils [43]. The application of organophosphate pesticides chlorpyrifos, phosalone, dimethoate and a pyrethroid insecticide, λ -cyhalothrin at commercial doses led to a decrease in soil microbial respiration. Among these, chlorpyrifos showed the highest toxicity as well as the highest persistence [44].

1. Effect on aquatic invertebrates

Bioassays performed by exposing *Daphnia magna* and *Parachromis dovii* to contaminated water collected from the field confirmed that *D. magna* is sensitive to pesticide contamination [71]. Shrimp aquaculture is one of the valuable sources of seafood that can be affected by accidental or environmental exposure to neonicotinoid insecticides like imidacloprid. Neonicotinoids act on the central nervous system of insects. A study conducted on adult black tiger shrimp (*Penaeus monodon*) evaluated the activity of stress enzymes in the abdomen, head, gill, and hepatopancreas for the acute and chronic effects of imidacloprid. This showed elevation in the activity of these biomarkers, and the enzymatic activity was positively correlated to the accumulation of imidacloprid in the tissue. The effects varied in a different tissue in dose-dependent and time-dependent manner. An elevated response in each of the mentioned biomarkers during routine monitoring depict that imidacloprid acts as an environmental chemical stressor for adult black tiger shrimp (*Penaeus monodon*) [46]. The cytotoxic effects of

a pyrethroid insecticide, flumethrin and a neonicotinoid, acetamiprid, were studied on primary cell cultures of the mantle, gill, gonad, and digestive gland tissues of *Unio* sp. This study showed that, as compared to acetamiprid, flumethrin was more cytotoxic to all tested cells [47]. The risk Quotient of most organophosphate pesticides was found to be higher for daphnia than for fish and algae [23].

Effect on aquatic vertebrates

Several studies have been undertaken in India to assess the impact of commonly used pesticides on aquatic vertebrates. Among the organophosphate pesticides, Chlorpyrifos is commonly used in agriculture [48]. Bifenthrin is not only used in agriculture but also in public health control programs, including mosquito control [49]. A study conducted to understand the genotoxic effect of a mixture of two pesticides, bifenthrin and chlorpyrifos, on the major Indian carp, *Labeo rohita*, at a sub-lethal concentration of 33% LC50, reported an increase in a time dependent DNA damage up to 56 days of exposure to sublethal dose and after that a slight decrease was observed in next fourteen days [50]. Chlorfenapyr is a pyrrole-based halogenated insecticide which is applied on agricultural crops for the insects and mites control [50]. Acetamiprid is extensively used in agriculture for pest management in numerous countries [20]. Dimethoate is a broad-spectrum organophosphate pesticide which is used against a wide range of insects and mites [52]. When the comparative effects of chlorfenapyr, dimethoate and acetamiprid on *Cirrhinus mrigala* under chronic exposure were studied, the results showed a significant difference in blood profile as well as disturbed thyroid profile. It was also observed that liver biomarker enzymes showed elevated levels in the serum of the fishes treated with pesticides. Significant alterations in the histological analysis of gills and liver were reported in all the treated groups. The toxicity trend of these three pesticides was ranked as chlorfenapyr > acetamiprid > dimethoate. This study concluded that indiscriminate use of such pesticides poses a serious threat to non-target organisms, ecosystems and human health [53]. Malathion is another organophosphate pesticide that has wide application in controlling a range of pests in agriculture. This pesticide is not only resistant to biodegradation, but it is also highly toxic. Once entered into the human body, it could remain for two generations [54]. The administration of a mild dose of malathion on *Channa punctatus* fish (Bloch) was evaluated after different time intervals, which showed that increased malathion exposure periods cause a progressive decrease in morphometric indices, various biochemical parameters and enzyme levels, especially of antioxidant systems [55]. Cypermethrin is a fourth-generation halogenated synthetic pyrethroid, which is widely applied in agriculture as well as household pest management. Cypermethrin was reported in surface waters in Hisar, India [56]. *Catla catla*, when chronically exposed to sub-lethal concentrations of cypermethrin, showed a significant increase in the activity of stress enzymes in the kidney after 15 days, followed by a decrease up to 45 days. Lipid peroxidation remained increased throughout the exposure duration. Histopathological analysis showed proliferated haematopoietic tissue as well as degeneration of tubules and glomerulus. Ultrastructure study presented cytoplasmic vacuolation, fragmented rough endoplasmic reticulum, lysosomal proliferation, degeneration of mitochondria and epithelial lining of renal tubules. Hence it was suggested that long-term exposure to cypermethrin could cause various

pathological alterations in the renal system, which might interfere with normal renal excretory mechanisms ^[57]. In a study that assessed the effect of cypermethrin on the reproductive behaviour of brown trout (*Salmo trutta* L.) in a large stream water aquarium, young trout exposed to a higher concentration of cypermethrin showed disturbed reproductive behaviour. Observations like fewer courting events, spending less time near the nesting females, lower volumes of strippable milt and significantly low level of 11-ketotestosterone were reported ^[58]. Single, as well as combined toxic effects of pesticides thiamethoxam and chlorpyrifos, beta-cypermethrin, tetraconazole, and azoxystrobin were assessed in a study on the rare minnow (*Gobiocypris rarus*). Results showed that beta-cypermethrin, chlorpyrifos, and azoxystrobin had the highest toxicities to *G. rarus*. Larval stages of rare minnow were found to be more sensitive to these pesticides than embryos. Pesticide mixtures showed synergistic toxicity to fish ^[59].

Amphibians are vulnerable to pesticide pollution due to their specific habitat requirements ^[60]. Bioaccumulation of DDT was assessed in Müller's clawed frog *Xenopus muelleri* collected from the lower Phongolo River floodplain in South Africa, which revealed that its concentration had significantly increased over time during the study period ^[61]. The diversity of pollutants also directly affects the breeding in adult water birds as well as causes developmental defects in embryos. The effects on embryos include mortality, reduced hatchability, failure of chicks to thrive, and other teratological effects like skeletal abnormalities, impaired differentiation of the reproductive system and nervous systems through mechanisms of hormonal mimicking of estrogens. The range of chemical effects on adult birds covers acute mortality, sublethal stress, reduced fertility, suppression of egg formation, eggshell thinning, and impaired incubation and chick rearing behaviors ^[62].

Legislation in India to tackle pesticide pollution

The Government of India has taken significant measures in order to protect environmental resources. The first law to be passed was the Wildlife Protection Act, 1972 by the National Committee on Environmental Planning and Coordination ^[63]. Since then, three more acts have been enacted at the central government level with respect to water pollution, the Water (Prevention and Control of Pollution) Act, 1974, the Water (Prevention and Control of Pollution) Cess Act, 1977 and the Environment (Protection) Act (1986). The Water Act 1974 resulted in the establishment of the Pollution Control Boards at the central and state level. Sections 20, 21 and 23 of the Water (Prevention and Control of Pollution) Act 1974 gives jurisdiction to the local authorities to act in cases of water pollution. The Water Cess Act 1977 allows the Pollution Control Board to charge the water users with a water cess. This would allow the Pollution Control Boards to support their activities financially. This Act was last amended in 2003. The Environment Protection Act 1986 is an all-encompassing legislation providing a single regulatory body in the country for the protection of the environment. It also aims to plug any loopholes in the earlier legislation. This law prohibits the pollution of any water body and mandates the approval from local SPCB (State Pollution Control Boards) for any potentially polluting activity. This law was last amended in 1991 ^[64-66].

The Directorate of Plant Protection, Quarantine and Storage under the Ministry of Agriculture and Farmers Welfare (DPPQS) have passed the Insecticides Act 1968 and

Insecticides Rules 1971. These regulate the import, registration process, manufacture, sale, transport, distribution and use of insecticides (pesticides) with a view to preventing risk to human beings or animals and for all connected matters, throughout India. All pesticides sold in India have to mandatorily undergo the approval process with the Central Insecticides Board & Registration Committee (CIB & RC). Thus, all the pesticides sold in India are listed on the "Schedule" of the Insecticides Act 1968. It is mandatory for the manufacturers to clearly label the nature of the pesticide, its use, composition, active ingredient, target pest(s), recommended dosage, caution signs and safety precautions. The Act states that a pesticide labelled for agriculture cannot be used in households. The CIB & RC also undertakes a periodical review of the pesticides and their usage. If recent research indicates that the pesticide can cause serious environmental and public health concerns, it can be banned even after registration. Thus, technically all insecticides (pesticides) in India are those substances that are listed on the "Schedule" of the Insecticides Act, 1968. The Registration Certificate mandates that a label be put on the packaging, which clearly indicates the nature of the insecticide (Agricultural or Household use), composition, the active ingredient, target pest(s), recommended dosage, caution sign and safety precautions. Therefore, a pesticide labelled for agriculture should not be used in a household ^[67-68]. Recently, the Union Cabinet, India has approved The Pesticide Management Bill 2020 (PMB2020) in February 2020, which will replace the Insecticides Act, 1968 ^[69]. It seeks to regulate the manufacture, import, sale, storage, distribution, use, and disposal of pesticides, in order to ensure the availability of safe pesticides and minimise the risk to humans, animals, and environment. Currently, it has been referred to the Standing Committee on Agriculture for examination.

Conclusion

The review of the existing literature on pesticide pollution reveals that it is widespread in freshwater ecosystems in India. As aquatic organisms have a tendency to bioaccumulate these pesticides along the food chain, it is imperative to have strict implementation of existing policies and development of mitigation strategies in India.

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