

## Mechanistic action of pesticides on pests and their consequent effect on fishes and human health with remediation strategies

Anita Singh<sup>a</sup>, Monika Mahajan<sup>b</sup>, Richa Kothari<sup>c</sup>, Naveen Kumar Singh<sup>d</sup> and Rajeev Pratap Singh<sup>b,\*</sup>

<sup>a</sup> Department of Botany, Center for Advanced Studies, Institute of Science, Banaras Hindu University, Varanasi 221005, India

<sup>b</sup> Institute of Environment and Sustainable Development, Banaras Hindu University, Varanasi 221005, India

<sup>c</sup> Department of Environmental Sciences, Central University of Jammu, Rahya Suchani (Bagla) Samba, Jammu and Kashmir 181143, India

<sup>d</sup> Department of Chemistry, Environmental Science Discipline, Manipal University Jaipur, Dehmi Kalan, Jaipur, Rajasthan 303007, India

\*Corresponding author. E-mail: rajeevprataps@gmail.com

### ABSTRACT

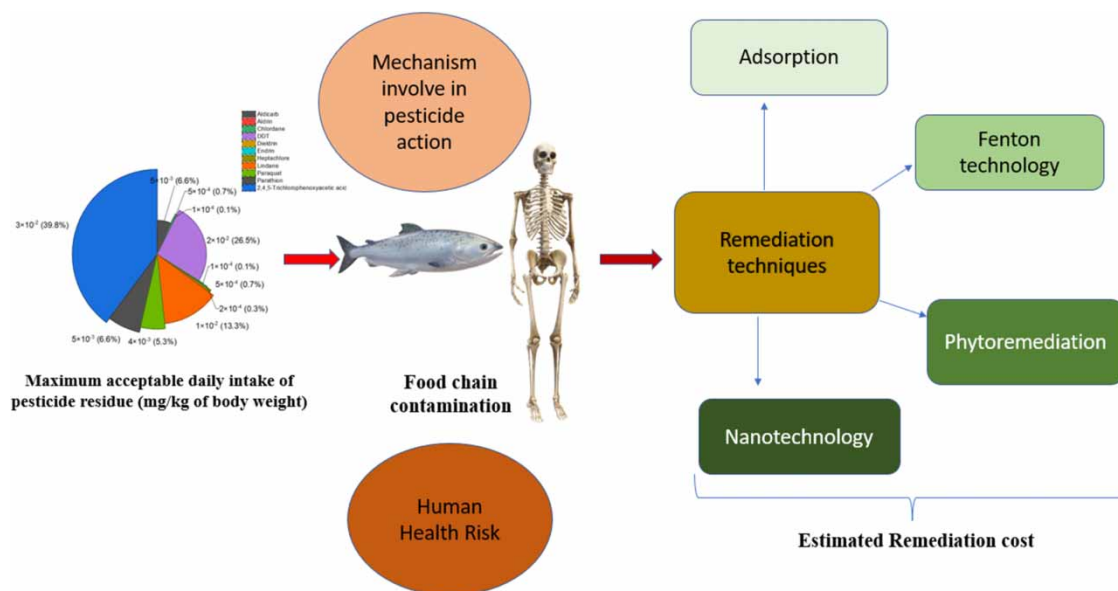
Population detonation and inflated demand for agricultural products have resulted in the rampant use of pesticides in recent years. These pesticides are used to reduce the number of pesticides by different mechanisms. They have been utilized in agriculture to expand agrarian profit, crop yield, quality, and storage life. The incessant and extensive use of resistant pesticides has contaminated the water bodies, fields, crops, and aquatic biota as well as posing a threat to human health. As a result, stringent regulations and limits are established to monitor the pesticide matrix. The current review focuses on pesticide contamination in the food chain, particularly from the aquatic bodies to fishes and humans. It also discusses strict regulations and limits including maximum residual limits for food items, acceptable daily intake, theoretical maximum daily intake, and estimated carcinogenicity/non-carcinogenicity for fishes and human health risks. In addition to conferring the negative effects of pesticides, this article discusses cost-effective remediation techniques such as phytoremediation, adsorption, the Fenton oxidation method, microalgal/high-rate algal ponds, and nanotechnology with the comparison of their remediation cost.

**Key words:** food chain, mechanism, pesticide, remediation, tropic level

### HIGHLIGHTS

- Pesticide action involves nervous breakdown and growth retardation.
- Maximum daily intake of pesticide residue is higher in fishes and the human being.
- Phytoremediation is the most sustainable and cost effective strategy.

## GRAPHICAL ABSTRACT



## 1. INTRODUCTION

Extensive use of pesticides for increasing food production simultaneously declined food quality. Even while farmers have a conventional grasp of agriculture, they are vulnerable because they lack a technical understanding of pesticides and their uses (WHO/FAO 2016). In the past decade, the global consumption of pesticides has elevated as a result of a demographic outburst and escalating urbanization (FAOSTAT 2019). Instead of agriculture, many pesticides such as insecticides, herbicides, and fungicides are generally used for household purposes in form of sprays, powders, and liquids for controlling mosquitoes, ticks, cockroaches, and bugs. Pesticides have numerous benefits, but the risk aligned with their use is also high. According to Mahmood *et al.* (2016) <1% pesticides reached the targeted organism to affect their nervous system, growth, and energy production system. The maximum amount of pesticides gets accumulated in the environment such as soil and water. As deposits of excessive pesticide and their metabolites residue in food and aquatic environment may be detrimental to fishes as well as for human health (Boobis *et al.* 2008; Zhou *et al.* 2015). Various reports indicate the risk associated with consuming pesticides with different modes of action; continuous exposure to pesticides causes depression and neurological deficits, diabetes, respiratory diseases such as rhinitis and, in extreme cases, cancer, fetal death, spontaneous abortion, and genetic diseases (Ntzani *et al.* 2013; Mojiri *et al.* 2020). In addition to ingestion, it is obvious that exposure to these pesticides, particularly for spray workers, has detrimental health impacts (Tsimbiri *et al.* 2015).

Residue analysis provides a criterion for assessing the quality of food in order to minimize potential threats to human health and determine the degree and duration of chemical contamination in the natural environment. Fifty nations comply with the maximum residual limits (MRLs) established by the Codex Alimentarius Commission (CAC) (Codex 2011), the European Union (EU) Commission (IIT Roorkee Report 2018), and the Gulf Cooperation Council (GCC). Twenty-three additional nations, including the Food Safety and Standard Authority of India (FSSAI), subscribe to their own MRLs (FSSAI 2011). Pesticides are categorized as either inorganic or organic based on the components that comprise their chemical composition. Synthetic pesticides such as cycloidian, organophosphate (OP), synthetic pyrethroids, organochlorine (OC), nicotinoid, triazole, and carbamate are extensively used in crop production (Grube *et al.* 2011).

Subsurface drainage, leaching, runoff, and spray drift are all potential entry points for pesticides into water bodies (Cosgrove *et al.* 2019). Due to the direct effects, interest in the process of eliminating pesticide residues from the environment is increasing. Several chemical, physical, and biological treatment methods, including adsorption, the advanced oxidation process, and membrane filtration, as well as phytoremediation, bioremediation, and the activated sludge process, have been utilized to effectively remove pesticides from aqueous solutions (Chakraborty *et al.* 2022; Richards *et al.* 2022). However, the vast majority of modern cleanup technologies are not only inflexible, but also costly, inefficient, and may even

generate secondary poisons (Shamsollahi & Partovinia 2019). Furthermore, it is also challenging to comprehend the global trends in pesticide concentrations in streams, fish, and human beings, as well as the removal methods of pesticides by a range of adsorbents. Therefore, the current review analyzes the level of pesticides in aquatic body and their associated organism at a global scale. The overview data will motivate the hydrobiologist, hydrogeologist, and sustainable development manager to fill the gap. A consortium of river conservation with sustainable practices and cost-effective pragmatic techniques will help in policy formulation to achieve the agenda targets of SDGs within a stipulated time period.

**2. MECHANISMS INVOLVED IN PESTICIDE ACTION**

Pesticides have been utilized since antiquity. Now, pesticides are widely used in every region of the globe. It is necessary to understand the mechanisms of pesticide action in order to identify the health risks of non-target organisms, hence facilitating the development of a more comprehensive remedial assessment. Here, three major pesticides will be discussed.

**2.1. Insecticides**

Insecticides are primarily active on three target sites in the nervous system: (1) the acetylcholine receptor, acetylcholinesterase, an enzyme that plays a crucial role in the transmission of nerve impulses (organophosphorus and carbamates) and (2) sodium ion channels crossing the nerve membrane which obstructs the synthesis of chitin as well as ecdysone agonists (Chandler *et al.* 2011). Additionally, pesticides are divided based on their manner of action (Jayaraj *et al.* 2016).

- (a) Nerve and muscle active site: mode of action of insecticide (Table 1).
- (b) Growth and development targets: mode of action (Figure 1).
- (c) Energy production targets.

(i) Electron transport inhibition

Electron transport hindrance could cause inhibition of energy supply to the targeted organism. For example, aliphatic type of OC insecticides are electron transport inhibitors.

(ii) Interruption of oxidative phosphorylation

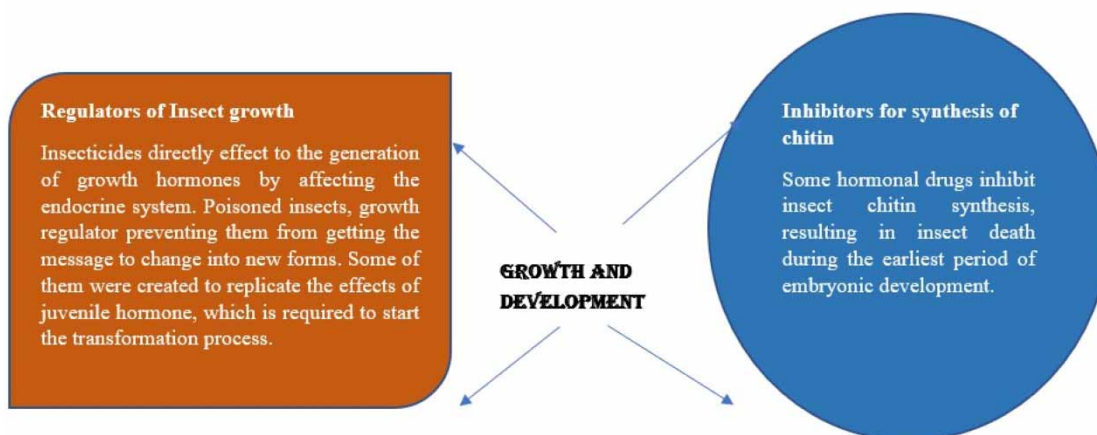
This is one of the most lethal types of mechanism, in which organotin miticides can block the mitochondrial electron transport chains on the other side pyrroles break electron transport and oxidative phosphorylation. This results in a reduction in ATP release and ultimately death of insects (Jayaraj *et al.* 2016; Thapa *et al.* 2017).

**2.2. Herbicides**

Herbicides are chemical agents used to eliminate or control weeds. They are utilized instead of the mechanical method of weed removal. Herbicides deprive plants of the benefits of metabolic pathways such as photosynthesis, plant hormone activity, regulation of cell division, synthesis of amino acids as an antidote, and monooxygenase inhibition by graminicides (De Roos *et al.* 2005; Pretty 2008; Thrall *et al.* 2011). Herbicides can be classified according to a variety of parameters, including the site of action, mode of action, chemical composition, length of use, translocation, and selectivity (Varshney *et al.* 2012; Torrens &

**Table 1** | Mode of action of insecticide: nerve and muscle active site

Mode of action of insecticides	Cholinesterase inhibition	Acetylcholine receptor stimulation	Chloride channel regulation	Sodium channel modulator
Explanation	Carbamate and organophosphate pesticides, which overstimulate the insect nervous system, demonstrated this type of suppression. The outcome of this is the insect's demise	Both spinosad mimics and neonicotinoid pesticides exhibited neurotransmitter acetylcholine activity. They bind to acetylcholine receptors, causing prolonged stimulation that ultimately results in the insect's death	Chloride channel activation can occur via three pathways: (1) suppression of gamma-aminobutyric acid (GABA) receptor (organochlorine insecticides); (2) agonists of the GABA chloride channel; (3) activation of chloride channels	This mode of action is demonstrated by pyrethrins and pyrethroids insecticides, which bind to sodium channels, resulting in the fixation of insects in the open state, which causes tremors and kills insects



**Figure 1** | Mode of action: growth and development targets.

Castellano 2014). Herbicides attach themselves to an herb's active site prior to killing it. They are able to affect many sites within plants and in the areas of action. Each herbicide has a unique method of action, which is described in Table 2.

### 2.3. Fungicides

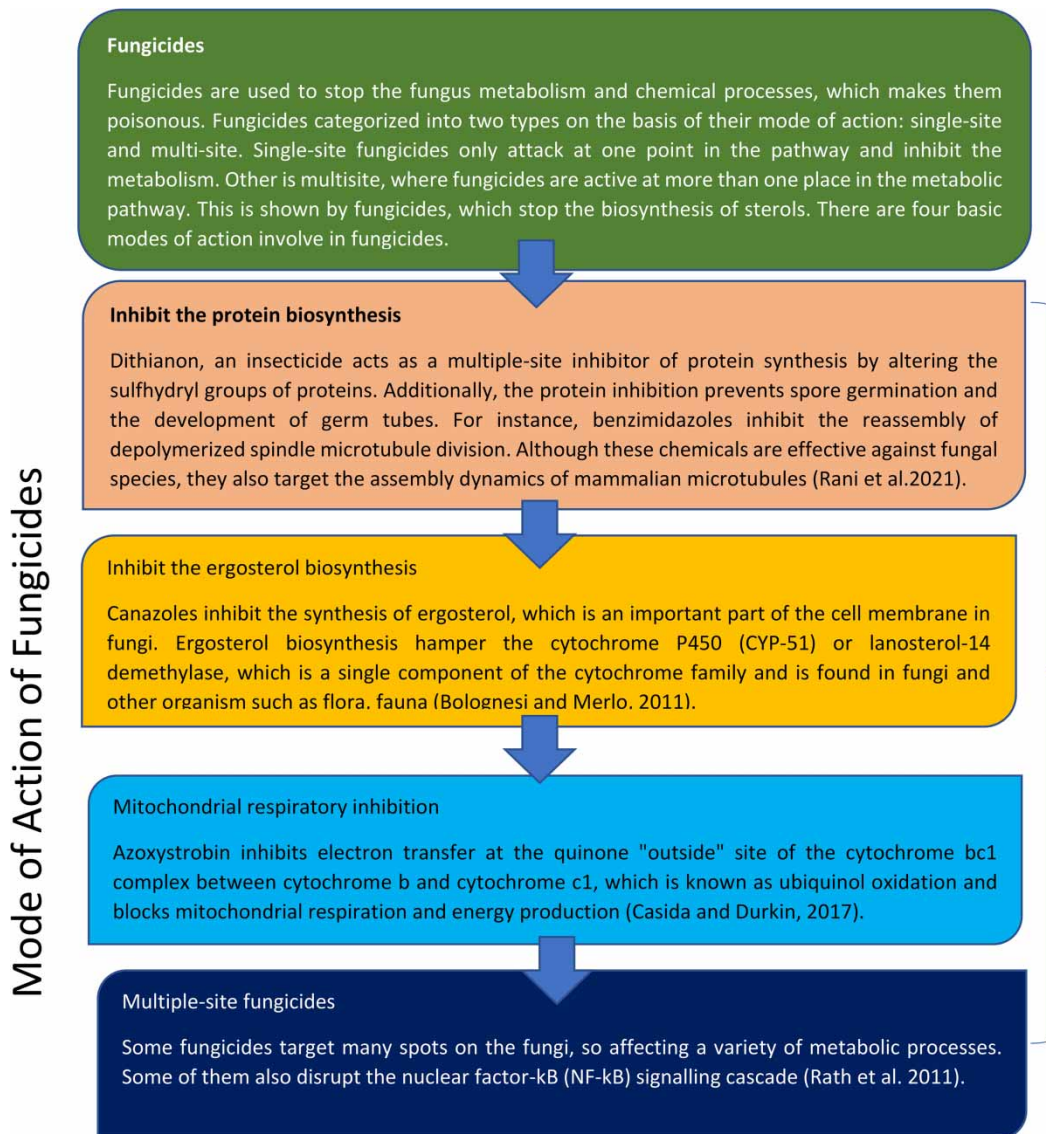
Mode of action of fungicide (Figure 2).

## 3. MRLS OF PERSISTENT ORGANIC PESTICIDES

Persistent pesticides harbor for a longer time on treated crops in the form of their residues, and they enter humans via the food chain (Bhushan *et al.* 2013; Yadav *et al.* 2015). The residues of persistent pesticides should not exceed their

**Table 2** | Mode of action of herbicides

Mode of action of herbicides	Brief explanation	References
1. Growth regulators	These herbicides can kill or suppress broad-leaf weeds; they primarily affect plant growth hormones, such as 2,4-dichlorophenoxyacetic acid, and their mechanism of action is based on their auxin-like capacity	Jablonkai (2011)
2. Seedling growth inhibitors	Thiocarbamates and acid amides herbicides serve as potent inhibitors for both root and shoot. They interrupt the growth of the plant, mainly at the growth point	Rani <i>et al.</i> (2021)
3. Photosynthesis inhibitors	These types of herbicides hinder photosynthesis by interfering with biomembranes through highly active chemicals. The death of plants is ultimately caused by an increase in highly reactive chemicals that break cell membranes. For instance, triazine herbicides, which were once employed to destroy broad-leaf weeds, are no longer effective	Sathiakumar <i>et al.</i> (2011)
4. Lipid biosynthesis inhibitors	There are some herbicides which block the production of lipids, which results in no biological membrane, fluazifop and sethoxydim are the example of these herbicides	Rani <i>et al.</i> (2021)
5. Amino acid biosynthesis inhibitor	These classes of herbicides can affect the biosynthesis of some amino acids. The active ingredient in Roundup herbicide is glyphosate [N-(phosphonomethyl)glycine], which inhibits the formation of aromatic amino acids such as tryptophan, phenylalanine, and tyrosine. In addition, numerous substances serve as potent inhibitors of glutamine synthase, the enzyme that catalyzes the integration of ammonia onto glutamate	Jablonkai (2011); Tarazona <i>et al.</i> (2017)
6. Inhibitors of pigment biosynthesis	Herbicides containing clomazone inhibit the formation of photosynthetic pigments, namely the biosynthesis of carotenoids. These pigments play a crucial role in protecting chlorophyll from light, and if carotenoids are not present in the plant, chlorophyll will be destroyed, preventing photosynthesis from occurring	Corniani <i>et al.</i> (2014)



**Figure 2** | Mode of action of fungicide.

recommended limits as this may pose a menace to human health. To avoid this threat, the concepts of MRLs (maximum residue limits), ADI (acceptable daily intake), and TMDI (theoretical maximum daily intake) have been introduced and developed to regulate residues of persistent pesticides in the food chain (Bhushan *et al.* 2013) (Table 3). The MRL is the maximum level of pesticide residues (expressed in mg/kg) in or on food or feed based on good agricultural practices (GAPs) and to ensure the lowest possible consumer exposure (Claeys *et al.* 2011). An ADI is the maximum daily dose of pesticides that may be consumed from all dietary sources without causing a chronic health risk. The TMDI is used to compare the maximum pesticide intake (Table 3) to the current MRLs for an individual as a result of a given dietary behavior. The TMDI can be calculated from the MRL values using the following equation (Marques & Silva 2021):

$$TMDI = MRL_i \times F_i$$

where  $MRL_i$  is the maximum residue limit for a given food commodity and  $F_i$  is the per capita food regional consumption of that food commodity.

**Table 3** | Diets considered for calculating theoretical maximum daily intake

Food commodities	For adult (60 kg) quantity (g/day)	For 1- to 3-year-old child (12.9 kg) quantity (g/day)
Cereal and millets	375	60
Rice	173	28
Wheat	139	22
Others	63	10
Pulses	75	30
Roots and tubers	200	50
Potato	116	29
Onion	62	15.5
Green leafy vegetable	100	50
Cabbage	36	18
Palak and others	64	32
Other vegetables	200	50
Tomato	44	11
Cauliflower	24	6
Brinjal	34	8.5
Fruit	100	100
Mango	14	14
Banana	56	56
Sugar	20	15

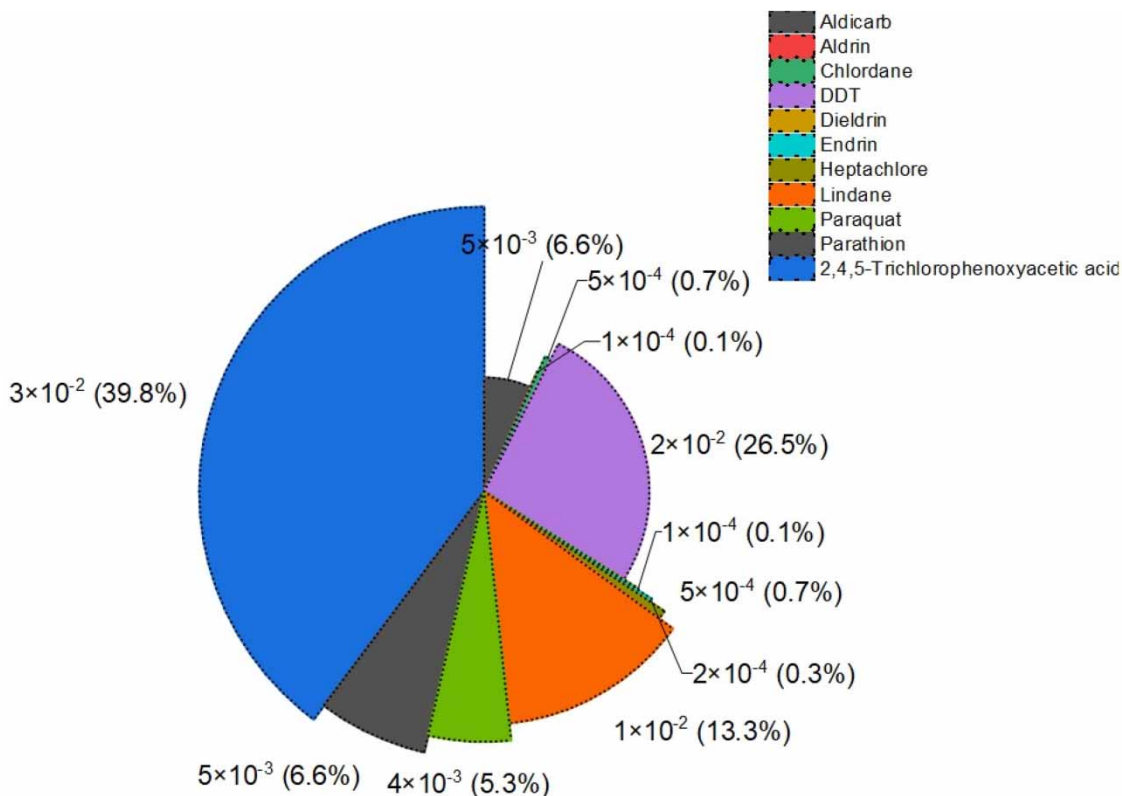
Source: Dietary Guidelines for Indian, NIN (2010); Bhushan *et al.* (2013).

However, FAO and WHO have recommended the acceptable rate for POPs in a few samples or matrices (FAO/WHO 2011). FAO and WHO together with efforts from Joint Meeting on Pesticide Residues (JMPR) and the CAC have developed the most broadly acknowledged and widely accepted safety limits for pesticides. The JMPR meeting conveyed the recommendation after reviewing residue based on analytical aspects of the pesticide, including data on their metabolism, environmental fate, usage patterns, and estimating the maximum residue levels that could result in the use of pesticides for GAPs (Fishel 2010; FAOWHO 2011).

Additionally, it is recommended that pesticide limits should not be less than the analytical LOQ (limits of quantification) possible in the certified laboratories under standard conditions. India also has a few agencies such as the CIBRC (Central Insecticides Board and Registration Committee) and the FSSAI that register and recommend MRLs of pesticides for several crops. The MRLs (Figure 3) should be recommended for all registered persistent pesticides for various crops. Some neem-based products, biopesticides, and chemical pesticides like sulfur do not have fixed MRL values. A total of 299 pesticides have been registered by CIBRC (Insecticides/Pesticides Registered under section 9(3) of the Insecticides Act, 1968 for use in the Country 2021).

#### 4. PESTICIDE CONTAMINATION IN GLOBAL RIVER WATER/SEDIMENT

Pesticide contamination in river water emerges as a significant concern. Millions of lives depend on the river for their livelihood such as Ganga, Brahmaputra, etc. The Brahmaputra is a river that flows across borders. In Bangladesh and India's eastern and northeastern states, the Brahmaputra River provides a steady flow of freshwater for agricultural, human, and industrial use (Sarker *et al.* 2021). A researcher (Chakraborty *et al.* 2019) collected surface water from various locations along the Brahmaputra River to analyze the presence of organochlorine pesticides (OCPs). This class of insecticides, they claim, is widely used in the areas surrounding the Brahmaputra River. OCPs are detected in the river at elevated intensities ranging from 0.002 to 0.245 g L<sup>-1</sup> (0.047–0.067 g L<sup>-1</sup>).  $\gamma$ -HCH demonstrated the highest level of coverage among hexachlorocyclohexanes (HCHs) that used lindane continuously ( $\gamma$ -HCH). dichlorodiphenyl trichloroethane (DDT) OCPs were also



**Figure 3** | Maximum acceptable daily intake of pesticide residue (mg/kg of body weight) (WHO 1997).

detected with high intensity as ND-0.225 g L<sup>-1</sup> (0.030–0.066 g L<sup>-1</sup>), with o,p'-DDT having the highest concentration and p,p'-dichlorodiphenyldichloroethane (DDD) having the second highest (Chakraborty *et al.* 2019).

Adversity is not boundary-specific or nation-specific, and pesticide contamination in rivers and sediments becomes a trans-boundary concern. Five pesticides were detected in the Kabul river of Pakistan, namely, triclosan, carbaryl, chlorpyrifos, carbofuran, and methomyl (Saad *et al.* 2007). Polluted river water pollutes the sediment also. Just like the Asian river, some major rivers of the world face analogous conditions of pesticide contamination levels. In a study, Ahmed *et al.* (2008) experimented on the Nile River, Rosetta Branch, Egypt. The study estimated the OCP (total DDTs, total HCHs, heptachlor, dieldrin, aldrin, endrin, endosulfan, and methoxychlor) that were found >0.01 µg/kg and was within safety limits. Ogbeide *et al.* (2015) reported high concentrations of β-BHC, γ-BHC, and α-BHC contamination in Owan River, Nigeria, with concentrations ranged between 0.82 and 2.14 µg/kg/dw (dry weight) and 0.04–2.34 µg/kg/ww (wet weight) in sediments. Reports have estimated 125–130 K metric tons of pesticide application in Nigeria each year. Specifically, it was used to promote yield, agricultural enhancement, and resist vector diseases (Asogwa & Dongo 2009). The presence of pesticide residue without their metabolites in the Nile River, Cairo, Egypt is self-explanatory about the active utilization of p,p'-DDT and aldrin in this region (Shalaby *et al.* 2018). The concentration of p,p'-DDT (40.3 ppb) in summer, 73.4 ppb in autumn, and aldrin (31.4 ppb) was reported in the autumn season in Nile river sediment, Egypt (Shalaby *et al.* 2018). Polluted river water may contaminate the sediment of the river Ganga, and eventually, it bioaccumulates in aquatic biota.

## 5. ECOTOXICOLOGICAL EFFECT OF PESTICIDES ON AQUATIC FAUNA

The toxicity of POPs on fishes is very prominent. The seriousness of the problem associated with pesticide exposure in fish was reported by several researchers (Hamilton *et al.* 2016; Saaristo *et al.* 2018). According to their study, pesticide exposure can reform fishes physiologically and behaviorally. It also alters their immunity system and predator avoidance sensitivity. An experiment was performed by Akter *et al.* (2020) to check the potential hazards of Envoy 50 SC on *Heteropneutes fossils*. The

result illustrates LC<sub>50</sub> of Envoy 50 SC abruptly altered the tissue structure of their vital organs such as kidney, gill, and liver. In blood cells, modification is reflected in peripheral nuclear erythrocytes, binucleated cells, tear-shaped cells, etc.

The Ganga nourishes more than 140 species of fish both native and exotic (Sarkar *et al.* 2012). The surface water ecosystem supports fisheries resources and contributes significant financial benefits to the riparian inhabitants and to the national economy. The Ganga is home to diverse and abundant fauna and endangered species, like dolphins (*Platanista gangetica*); otters (*Lutrogaleperspicillata*, *Lutralutra*), and *Aonyx cinereus*; gharial (*Gavialis gangeticus*); crocodiles (*Crocodylus palustris* and *Crocodylusporosus*); turtles (*Batagurkachuga*); and fishes (*Tor putitora* and *Tenualosailisha*) (Wildlife Institute of India 2018). The addition of organic and inorganic pollutants and the reduced volume of water in river Ganga have deteriorated fish diversity and health (Vaseem & Banerjee 2013). An extensive flow of pesticides and herbicides into Ganga water through various means accumulates in the fish, and it hampers the fish's reproductive system and its metabolism (Wildlife Institute of India 2018).

There are numerous studies reported other than in the Ganga basin on the effects of pesticide contamination on aquatic biota (Yahia & Elsharkawy 2014). According to Yamashita *et al.* (2000), p,p'-DDE was predominantly found in fish (7.6–67 ng/g wet weight) in the Nile River, Egypt. An experiment was conducted by Shalaby *et al.* (2018) and found OC, OP pesticides in the sample of *Clarias gariepinus*, *Oreochromis niloticus*, and *Tilapia zillii*. Fish samples were collected from the world's longest river Nile from Egypt. Pesticides such as heptachlor, dicofol, p,p'-DDT, diazinon, chlorpyrifos, endosulfan, and aldrin ranged between 1.7 and 46.0 ppb in *Oreochromis niloticus* sample (Shalaby *et al.* 2018). According to Varol & Sünbül (2017) experiment on the Euphrates river's aquatic biota in Turkey, a study reported four out of 34 fish muscle samples presence of p,p'-DDE ranged from 0.010 to 0.019 mg/kg. The maximum concentration of DDE isomers found in the gill sample of fishes was 0.032 mg/kg. In fish samples obtained from several sites along the Ganga, Aktar *et al.* (2009) have observed five pesticide residues, namely, dimethoate  $\Sigma$ -HCH, malathion  $\Sigma$ -DDT, and  $\Sigma$ -endosulfan. In the majority of the samples, the amounts of  $\Sigma$ -HCH and  $\Sigma$ -DDT were found to be above the MRL.

Previous studies showed massive bioaccumulation of HCH and DDT in fishes residing in the river Ganga, whereas aldrin and endosulfan were moderately less (Kumari *et al.* 2001a, 2001b; Samanta 2013). A comparative study was done on fishes residing in the river Ganga by Kumari *et al.* (2001a, 2001b), and according to their study, HCHs concentration (upto 7-folds) and endosulfan (upto 2-folds) were higher than the FAO (Food and Agriculture Organization) tolerance limit (Singh *et al.* 2008). The tolerance limit (mg kg<sup>-1</sup>) is HCH (0.25) and Endosulfan (0.2). According to Kumari *et al.* (2001a, 2001b), numerous OCPs found in the muscles of fishes such as DDT, HCH, aldrin, and endosulfan and their values are in the range of 13.6–1,665.9, 115.8–1,206.8, 3.1–86.1, and 2.9–74.5 ng g<sup>-1</sup>, respectively. Similar results are also reported by Singh *et al.* (2008). More than the tolerance limit of HCHs and DDTs were found in fish samples collected from river Ganga and its tributary Gomti. The consequences have been very disruptive to fish reproductive systems (Singh *et al.* 2008).

Pesticides have a negative impact on all aspects of aquatic ecosystem life, including microbes, invertebrates, plants, and fish (Liess & Ohe 2005; Castillo *et al.* 2006). These cause a risk to human health when entering the food chain. There are three main trophic levels (algae → aquatic invertebrates → fish) that cover the larger food chain in the aquatic ecosystem. The risk to aquatic species may be quantified via risk ratios, which are then classified into four risk categories: high, medium, low, and insignificant ecological risks, which correspond to RQ (risk quotient) values  $\geq 1$ , 0.1–1, 0.01–0.1, and  $< 0.01$ , respectively (Palma *et al.* 2014; Zhang *et al.* 2016). Contaminated fish consumption and direct intake of toxicants may pose a severe health risk to humans (Gerber *et al.* 2016).

## 6. ECOTOXICOLOGICAL EFFECT OF PESTICIDES ON HUMAN HEALTH

Toxicants like pesticides degrade the river water quality of Ganga and tremendously influence human health by direct intake of water or through chain contamination. Fishes and irrigated crops near polluted water are directly exposed to these hazardous contaminants. Ingestion of contaminated fish bioaccumulates and magnifies at every trophic level (Mitra *et al.* 2012; Sudhakar 2014). Consumption of tainted fish from Ganga water sometimes poses a non-carcinogenic health hazard to humans. Few agencies estimated this hazard risk with the establishment of the reference dose (USEPA 1992, 2017). The reference dose of a chemical is the single daily intake rate that does not appear to be toxic if consumed over a long period of a lifetime (USEPA 1991) (Table 4).



**Table 4** | Estimated non-carcinogenic health risk through consumption of pesticide tainted fishes of Ganga water (US EPA 2017)

Name of pesticide	Lifetime average daily dose (mg/kg/day) LADD	Reference dose (RfD)	Hazard quotient (HQ)
$\Sigma$ -HCH	$1.11 \times 10^{-2}$	$3.0 \times 10^{-4}$	36.93
$\Sigma$ -DDT	$1.76 \times 10^{-2}$	$5.0 \times 10^{-4}$	35.28
$\Sigma$ -Aldrin	$3.0 \times 10^{-4}$	$3.0 \times 10^{-5}$	10.0
$\Sigma$ -Endosulfan	$3.93 \times 10^{-3}$	$6.0 \times 10^{-3}$	$6.56 \times 10^{-1}$
Dimethoate	$6.69 \times 10^{-3}$	$2.2 \times 10^{-3}$	3.047
Malathion	$7.20 \times 10^{-3}$	$2 \times 10^{-2}$	$3.60 \times 10^{-1}$

Hazard quotient = LADD/RfD, LADD =  $(Cf \times IR)/BW$ ; LADD, Lifetime average daily dose; RfD, reference dose mg/kg/day; Cf, the concentration of contaminant in fish; IR, ingestion rate of 80 g/day; BW, average body weight taken as 60 kg.

The Hazard Quotient is calculated from the average concentration of an individual group of pesticides in fish. The maximum health risk reported from DDTs is preceded by HCHs whereas the Hazard Quotient for endosulfan group, dimethoate, and malathion was found below 1 (USEPA 2017). OCP contamination in humans may pose a significant impact on human and animal health including neurotoxic, tumorigenic, reproductive, immunological, developmental, and genotoxic effects (Yilmaz *et al.* 2020). Gerber *et al.* (2016) studied the effects of OCPs on three rivers of South Africa Olifants, Letaba, and Luvuvhu rivers and the bioaccumulation of pesticides on Tiger fish. The result revealed a high risk of cancer for the local inhabitants because of the consumption of contaminated fish. This result assessment demonstrated that the human health risk was as high as 2 in 10 risk factors.

Downstream of Ganga, the consumption of fish for the subsistence of inhabitants may pose severe health risks. USEPA (2017) established ADI values which take into account the maximum permissible daily intake of hazardous toxicants over a person's life span without substantial risk to the individual's health. The chlorinated persistent pesticide has been spotted in animal tissue, human blood, and adipose tissue via food chain contamination. An increment is observed in several cancer cases in and around the Ganga basin with a significant number of gall bladder cancer patients (Jain *et al.* 2013; Saini *et al.* 2015).

The risk estimate value of  $10^{-6}$  means the risk of one or more incidences of cancer in a million people. The risk levels lower than  $10^{-6}$  are accounted for as slight risk or come to an acceptable risk level of the USEPA range ( $10^{-6}$ – $10^{-4}$ ). A risk level of more than  $10^{-4}$  for pesticides indicates a high carcinogenic risk from the consumption of individual toxicants (USEPA 2017). A drastic rise in the number of cancer patients in the river basin could be the result of the composite effect of multiple chemicals and pesticides or the consumption of contaminated fish. This level of risk is calculated using maximum reported values of individual toxicant ranges lie between  $10^{-3}$  and  $10^{-2}$  (Dwivedi *et al.* 2018). The increase in the number of cancer cases could be partially attributed to the ill effects of pesticides and other pollutants.

## 7. PESTICIDE REMEDIATION TECHNIQUES

This section will discuss a few cost effective and highly efficient techniques. Pesticide removal techniques involve Fenton technology, adsorption, bioremediation, phytoremediation, and nanotechnology.

### 7.1. Fenton technology

Photo-Fenton process is considered one of the most effective ways of pesticide removal from water. The Photo-Fenton reaction is high-performing and can be carried out at room temperature and normal pressure. The Photo-Fenton process is crucial for the reduction of recalcitrant substances in polluted water. This process has some prerequisites which include the presence of (i)  $Fe^{2+}$  and (ii)  $H_2O_2$  (hydrogen peroxide) under ultraviolet radiation, which generates oxidative species such as hydroxyl radicals which react to pollutants like pesticides and at last cause complete mineralization. UV light is the most important part of photo-Fenton reactor design because UV light enhances the efficiency of the reactor by promoting  $Fe^{3+} \rightarrow Fe^{2+}$  and hydroxyl radicals.

A microwave electrodeless ultraviolet (MWEUV) lamp was used with the photo-Fenton process to mineralize pesticides in wastewater. It was evaluated in terms of average oxidation state, the oxidation state of carbon DOC, and inorganic anion concentration. According to Cheng *et al.* (2015), the complete degradation of Triazophos, Malathion, and Dimethoate, in

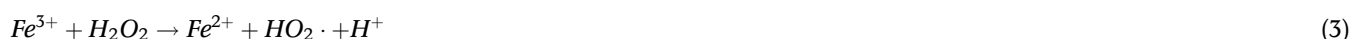
MWEUV/Fenton technique with initial pH 5, H<sub>2</sub>O<sub>2</sub> dosage of 100 mmol/L, and Fe<sup>2+</sup> dosage of 0.8 mmol/L in 240 min was achieved. The photo-Fenton is very effective but MWEUV expenses have increased its cost. So, to make it cost-effective instead of MWEUV, solar light coupled with extensive raceway pond reactors (RPRs) and parabolic collectors have been used (Carra *et al.* 2014). In this process, the reaction is enhanced through iron and hydrogen peroxide as oxidants. Iron is cyclically reduced and oxidized in a redox cycle (Carra *et al.* 2014):



Reduction takes place in the presence of UV–vis irradiance



Takes place in the dark



It implies irradiance absorption is essential.

We can also use Fenton technology in tertiary treatment before discharging the effluent in the river. After disinfecting the contaminated water Solar photo-Fenton is reported to have the potential to remove the acetamiprid and thiabendazole (Carra *et al.* 2014). Júnior *et al.* (2021) evaluated the combination of coagulation–flocculation–settling and photo-Fenton and found that it could help in the removal of ametrine, atrazine, imidacloprid, and tebuthiuron. Photo-Fenton with solar irradiance or black light treatment could reduce the target pesticides by 82–95%.

There are a few limitations of this technique which require a need to explore other alternatives. UV Photo-Fenton technique has a high cost and solar photo-Fenton does not work out at the time of high turbidity and elevated concentration of suspended solid (da Costa *et al.* 2017). So other methods such as phytoremediation were explored for pesticide remediation.

## 7.2. Adsorption technique

Adsorption comes under the physical method of removal. According to Netto *et al.* (2021), experiment concludes the hydro-char has rough small cavities and it expresses a favorable role in atrazine adsorption. Activated carbon (AC) has a significant potential for pesticide removal from wastewater. AC has a 164 mg/g removal capacity of carbofuran (Salman & Abid 2013). Some fungicides such as triazole can be removed up to 99% via the use of AC (Crini *et al.* 2017). Graphene-based compounds, biochar, bentonite clay, Zeolite, and Chitosan-based adsorbents are also convenient and technically efficient in the amelioration of pesticides (Mojiri *et al.* 2020). This is an economical technique; we can use it to check the mobility of pesticides in water. Before discharging effluent directly into Ganga, a permeable reactive barrier (PRB) will be introduced. PRB can be prepared with iron-turning waste. A study has been done by Abbas *et al.* (2021) on the evaluation of long-term PRB column performance with iron-turning waste of dieldrin for removal, lindane, and endrin. Pesticide-releasing industries could use such effective techniques to reduce pesticides up to a remarkable level before the outflux of effluent.

## 7.3. Microalgal/high-rate algal ponds' role in remediation

Microalgae and cyanobacteria create microbial groups that live symbiotically in a community-defined consortium when they establish associations with other aerobic or anaerobic microorganisms, such as bacteria. This consortium of algae and bacteria has the potential to work synergistically to break down organic and inorganic contaminants considerably more efficiently than any single microbe. According to Abdel-Razek *et al.* (2019), a consortium of microalgae can reduce malathion by up to 99% from wastewater. The consortium of algae *Scenedesmus quadricuda*, *Spirulina platensis*, and *Chlorella vulgaris*, was found to be most efficacious in removing pesticides (Abdel-Razek *et al.* 2019).

Bio-adsorption is a passive process (Ardal 2014). Pesticides and other organic pollutants, such as aromatic chemicals, may be adsorbed by microalgae. According to recent research (Mishaqa 2017), farmed algae eradicated 87–96% of different pesticides (simazine, dimethoate, atrazine, pendimethalin, propanil, metoalcholar, molinate, carbofuran, isoproturn, and pyriproxin) from the aqueous phase through bio-adsorption. All processes including electrostatic interaction, ion exchange, absorption, surface complexation, and precipitation are involved in the bio-adsorption process (Nie *et al.* 2020). According to Nie *et al.* (2020), pesticide removal is dependent on two factors: (i) optimal conditions for the biome's survival and activity;

(ii) the chemical structure of the pesticide and factors supporting the growth of microalgae such as pH, nutrient, light, contact time, availability of water, aeration, redox potential, surface bonding, and carbon substrate (Rath 2012).

Garcia *et al.*'s (2020) study affirms that a semi-closed, tubular horizontal photobioreactor (PBR) can reduce pesticides from agricultural runoff. According to their illustration high solar irradiation is the best condition for a PBR. It has reduced Cybutrine, terbutylazine, Malaoxon, and Fenthion Sulfoxide up to a certain extent. The Indo-Gangetic basin has ideal conditions to establish high-rate algal ponds and tubular horizontal PBRs such as high solar irradiation and temperature. The establishment of open microalgae system in high-rated algal ponds has low O&M cost and energy consumption. These are some initiatives that government should incorporate in the manifesto of 'Aviral and Nirmal Ganga' or the Ganga rejuvenation program.

#### 7.4. Phytoremediation

In recent days, numerous natural and cost-effective adsorbents have been working in conjugation for the removal of methyl parathion pesticides, such as waste jute fiber carbon (Senthilkumaar *et al.* 2010), *Rhizopus oryzae* biomass, and *Typha australis* leaf powder (N'diaye *et al.* 2018). Aquatic macrophytes are mostly used for the purpose of pesticide removal possibly because of requisite characteristics of phytoremediation such as (1) rapid growth; (2) easy spreading; (3) minimal cost; (4) facile harvesting; and (5) innocuous for the environment (Ammeri *et al.* 2021). Some non-edible plant roots and shoots are very emphatic in removing OCPs and pyrethroid pesticides such as *Eichornia crassipes*, *Pistia strateotes* (Riaz *et al.* 2017). Riaz *et al.* (2017) performed an experiment on *E. crassipes* and *P. strateotes* for the removal of OCPs and pyrethroid. During the experiment, the root of both aquatic macrophytes performed well in removal but *P. strateotes* (76%) removal efficiency was found much better than *Eichornia* in pyrethroid removal (Table 5). Numerous other aquatic plants also have the potential to reduce pesticide concentration such as water spinach (*Ipomoea aquatica*), duckweed (*Lemna minor*), Hydrilla (*Hydrilla verticillata*), and water ferns (*Azolla caroliniana*, *Azolla filiculoides*, and *Azolla pinnata*) (Anand *et al.* 2019).

Mangroves are the exclusive group of plants near the coastlines, and their explicit property encourages contaminant removal from river water and provides good space to nurture the mangrove ecosystem (Murdiyarso *et al.* 2015). A comparative study performed between mangrove and non-mangrove ecosystems concluded that mangrove forests could alleviate the contaminant level of such OCPs and pyrethroid than non-mangrove systems. Root exudates of mangroves have a wide range of compounds, such as organic acids, amino acids, and other secondary metabolites which play a crucial role in the interception or assimilation of these pollutants (Jia *et al.* 2016). Root exudates promote the absorption of DDT (Ivorra *et al.* 2021).

A study evaluated 88% pentachlorophenol removal through the combination of *Lemnagibba* and *Typha angustifolia* after the incubation of 9 days (Ammeri *et al.* 2021). Phytoremediation is a technologically efficient and sustainable way to remove contaminants from water and soil. However, this technique also has certain limitations and requirements like (1) selection of potential plant species for specific pesticide removal, (2) coexisting of other ions and organics, (3) effectiveness in particular soil and pH, and (4) disposal of biomass waste (Jeevanantham *et al.* 2019).

#### 7.5. Nanotechnology

Numerous kinds of nanomaterials, including nanoparticles, nanotubes, and nanocomposites have resulted from ample research in the field of amelioration (Zhang & Fang 2010). Several advantages of nanoparticles in the amputation of a pesticide are as follows: (1) easy fabrication steps, (2) subtle and quick results, and (3) high efficiency of removal. The specific optical characteristics of AuNPs (gold nanoparticles) enable the removal of aromatic compounds (Gu *et al.* 2016). Zero-valent iron nanoparticles (ZV-FeNPs) have been used for lindane degradation (Rawtani *et al.* 2018). The mechanism involved in the reduction of lindane via ZV-FeNPs is to eliminate dichloro and dehydrohalogenation. Chlorobenzene, dichlorobenzene, and benzene were found as the degradation products (San Roman *et al.* 2013). Nanoscale zero-valent iron (nZVI) could remove profenofos (94.51%) at pH 5.12 and 13.83 g L<sup>-1</sup> concentrated catalysts (Mansouriieh & Khosravi 2015) (Table 5).

The application of nanotechnology in wastewater treatment will efficiently reduce the pesticide more than other techniques (Table 5). The previous research (Sharma *et al.* 2016; Shen *et al.* 2017) and their impactful results urge pollution control boards to implement nanotechnology in wastewater treatment. It can effectively reduce agrochemicals from a variety of matrices.

**Table 5** | Remediation techniques involved in pesticide removal

Method	Pesticide specific	Efficiency	Advantage	Limitation	References
Activated charcoal	• Triazole	99%	(i) High porosity (ii) Large surface area	(i) Expensive process	Crini <i>et al.</i> (2017)
Photo-Fenton solar	• Ametrine • Tebuthiuron • Atrazine • Imidacloprid	80–90%	Cost-efficient	Not effective in highly turbidity	Júnior <i>et al.</i> (2021)
Microalgae	• Simazine • Atrazine • Pendimethalin • Molinate • Carbofuran • Propanil • Dimethoate • Isoproturon • Metolachlor • Pyriproxin	87–96%	(i) Cost-effective (ii) Reduced risk of secondary pollutant (iii) Environment friendly	Specific requirement (i) Salinity (ii) Nutrient (iii) Substrate (iv) Light (v) Water	Nie <i>et al.</i> (2020)
<i>Pistiastrateotes</i> <i>Eichornia</i> <i>Crassipes</i>	• Pyrethroid	76%	(i) Easy spread and harvesting (ii) Innocuous to environment (iii) Rapid growth	(i) Specific pH (ii) Hinder with coexisting ions and organics	Riaz <i>et al.</i> (2017)
<i>Lemnagibba</i> <i>Typha angustifolia</i>	• Pentachloro phenol	88%	Sustainable removal technique	Effectiveness depends on: (i) pesticide (ii) soil (iii) pH Disposal of biomass waste	Ammeri <i>et al.</i> (2021)
Nanoscale zero-valent iron (nZVI)	• Profenofos	94.51%	High efficiency	Requirement (i) pH (ii) concentration	Mansouriih & Khosravi (2015)
Zinc oxide nanoparticles (ZnONPs)	• Permethrin	99%	No specific temperature	Necessary for effectiveness (i) pH (ii) temp (iii) catalyst (iv) dosage	Rawtani <i>et al.</i> (2018)

## 8. REMEDIATION COST

The prime goal of divergent remediation attempts for the polluted sites is to reinstate the pristineness and flawlessness of the soil water system. A paradigm shift in technological advancement and vision has been incorporated into remedial actions for the cost-effective treatment of contaminated sites. Apropos this intent, bioremediation has been ascertained as an economical biological method to administer the contaminants, for instance in *in situ* bioremediation (US\$ 50–150), and phytoremediation cost for metal and metalloids is evaluated around US \$10–35 (Mahajan *et al.* 2021). They highlighted proximate feasible European and US markets for phytoremediation to 36–54 US\$, with a share of 1.2–1.4 billion US\$ for the expulsion of heavy metals from the soil. The global market for remediation was quantified at around US\$30–35 billion in 2001 and computation also shows positive feedback in the forthcoming future with the favor of 1.5 billion per annum (Singh *et al.* 2008), but on the other hand, physicochemical treatments like solidification, soil venting, solvent extraction and incineration show much costlier figures as US\$240–340, US\$ 20–220, US\$360–440, and US\$200–1,500, respectively. Notwithstanding, nanotechnology is an emerging field which has begun to compete for the aforesaid established technologies such as soil vapor extraction and thermal desorption for soil, but there is an exigency of comprehensive experimentation in that technology for analyzing intermediaries' pros and cons of the application. Now moving toward biological remediation, for CD remediation, the economic cost is assessed by different valuation approaches including 'willingness to pay, substitution cost, and hedonic price analysis'.

Hedonic price analysis delivers much promising value according to their premise which incorporates internal characteristics and external factor affecting. The hedonic price is approximately 14,600 and 14,850€h<sup>-1</sup>. However, there are diverse implicit factors like site conditions, climatic conditions, types of contaminants, and production costs for the remediation crop, and after all the suitability should be taken into consideration prior to the selection of a particular method and simulation–optimization tools for target contaminated sites must be employed in order to estimate the cost and moreover for multicriteria decision-making.

## 9. CONCLUSION

Pesticides have multiple uses, including increasing crop output, controlling vector-borne diseases, and eliminating dangerous pests. However, pesticides' negative consequences cannot be concealed. As they cause major harm to both aquatic and terrestrial environments, such as fish and humans, they degrade the quality of water and soil, which contaminates the food chain. Pesticides also have a negative impact on biodiversity, and continuous direct or indirect exposure to pesticides can pose grave health risks to humans. Numerous authorities, such as FAO, WHO, etc., have recommended MRL, ADI, and TMDI values for food and pesticide use in an effort to mitigate the dangers to human health. Various remediation strategies, such as adsorption, bioremediation, advanced oxidation, etc. have been described for the removal of pesticides from contaminated environments. The current review suggests some sustainable remediation techniques for reducing pesticide contamination levels. Review promotes the use of nano and Fenton technology in tertiary treatment methods in sewage treatment plants. However, in the context of cost–benefit analysis according to critical review, adsorption and phytoremediation are the most effective procedures since they are ecologically benign, cost-efficient, and produce less harmful byproducts. Environmental protection organizations, farmers, health officials, makers of pesticides, and governments should collaborate to lower the risk of pesticide poisoning.

### 9.1. Recommendation

To effectively manage pesticides, it is necessary to impose stringent rules and toxicity limits. Pesticides should be manufactured with more precision and accuracy, as well as a safer profile, to reduce their detrimental influence on the environment and individuals. This changing trend in policies will provide creditable results in near future in terms of eradicating pesticides' ill response.

### 9.2. Future perspective

The outcome of an extensive literature review on decadal change pesticide contamination in river Ganges and their major tributaries, we have noticed the vital gaps as per our present understanding that opens a wide spectrum of future research:

- evaluate the effect of Ganga contamination on human health;
- mechanism of pesticide health hazards caused in plants and humans;
- possible cost–effect and feasible alternative to improve productivity and toxic response on non-targeted organisms; and
- implementation of cost-effective pilot-scale projects for decreasing the pollution loads in rivers.

## ACKNOWLEDGEMENTS

The authors are thankful to the Dean and Head, DESD (Department of Environment and Sustainable Development) and Director, Institute of Environment and Sustainable Development, Banaras Hindu University, for providing needed facilities. R.P.S. is grateful to the authorities of Banaras Hindu University, Varanasi, for providing support under the Institute of Excellence (IOE) scheme under Dev Scheme No. 6031.

## DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

## CONFLICT OF INTEREST

The authors declare there is no conflict.

## REFERENCES

- Abbas, T., Wadhawan, T., Khan, A., McEvoy, J. & Khan, E. 2021 Iron turning waste: low cost and sustainable permeable reactive barrier media for remediating dieldrin, endrin, DDT and lindane in groundwater. *Environmental Pollution* **289**, 117825. <https://doi.org/10.1016/j.envpol.2021.117825>.
- Abdel-Razek, M. A., Abozeid, A. M., Eltholth, M. M., Abouelenien, F. A., El-Midany, S. A., Moustafa, N. Y. & Mohamed, R. A. 2019 Bioremediation of a pesticide and selected heavy metals in wastewater from various sources using a consortium of microalgae and cyanobacteria. *Slovenian Veterinary* **56** (Suppl 22), 61–73. <https://doi.org/10.26873/SVR-744-2019>.
- Ahmed, A., Barbary, E., Yehia, M. M., Mohamed, M. & Bouraie, E. 2008 Evaluation of organochlorine pesticides (OCPs) in surface water and bed sediment samples from the river Nile at Rosetta Branch, Egypt. *Journal of Applied Sciences Research* **4** (12), 1985–1993.
- Aktar, M. W., Paramasivam, M., Sengupta, D., Purkait, S., Ganguly, M. & Banerjee, S. 2009 Impact assessment of pesticide residues in fish of Ganga river around Kolkata in West Bengal. *Environmental Monitoring and Assessment* **157** (1), 97–104. <https://doi.org/10.1007/s10661-008-0518-9>.
- Akter, R., Pervin, M. A., Jahan, H., Rakhi, S. F., Reza, A. H. M. & Hossain, Z. 2020 Toxic effects of an organophosphate pesticide, envoy 50 SC on the histopathological, hematological, and brain acetylcholinesterase activities in stinging catfish (*Heteropneustes fossilis*). *The Journal of Basic and Applied Zoology* **81** (1), 1–14. <https://doi.org/10.1186/s41936-020-00184-w>.
- Ammeri, R. W., Di Rauso Simeone, G., Hassen, W., Ibrahim, C., Ammar, R. B. & Hassen, A. 2021 Bacterial consortium biotransformation of pentachlorophenol contaminated wastewater. *Archives of Microbiology*, 1–13. <https://doi.org/10.1007/s00203-021-02589-9>.
- Anand, S., Bharti, S. K., Kumar, S., Barman, S. C. & Kumar, N. 2019 Phytoremediation of heavy metals and pesticides present in water using aquatic macrophytes. *Phyto and Rhizo Remediation* **9**, 89–119.
- Ardal, E. 2014 *Phycoremediation of Pesticides Using Microalgae*.
- Asogwa, E. U. & Dongo, L. N. 2009 *Problems Associated with Pesticide Usage and Application in Nigerian Cocoa Production: A Review*.
- Bhushan, C., Bhardwaj, A. & Misra, S. S. 2013 *State of Pesticide Regulations in India*. Centre for Science and Environment, New Delhi, pp. 1–72.
- Boobis, A. R., Ossendorp, B. C., Banasiak, U., Hamey, P. Y., Sebestyen, I. & Moretto, A. 2008 Cumulative risk assessment of pesticide residues in food. *Toxicology Letters* **180** (2), 137–150. <https://doi.org/10.1016/j.toxlet.2008.06.004>.
- Carra, I., Santos-Juanes, L., Fernández, F. G. A., Malato, S. & Pérez, J. A. S. 2014 New approach to solar photo-Fenton operation. raceway ponds as tertiary treatment technology. *Journal of Hazardous Materials* **279**, 322–329. <https://doi.org/10.1016/j.jhazmat.2014.07.010>.
- Castillo, L. E., Martínez, E., Ruepert, C., Savage, C., Gilek, M., Pinnock, M. & Solis, E. 2006 Water quality and macroinvertebrate community response following pesticide applications in a banana plantation, Limon, Costa Rica. *Science of the Total Environment* **367** (1), 418–432. <https://doi.org/10.1016/j.scitotenv.2006.02.052>.
- Chakraborty, P., Mukhopadhyay, M., Sampath, S., Ramaswamy, B. R., Katsoyiannis, A., Cincinelli, A. & Snow, D. 2019 Organic micropollutants in the surface riverine sediment along the lower stretch of the transboundary river Ganga: Occurrences, sources and ecological risk assessment. *Environmental Pollution* **249**, 1071–1080. <https://doi.org/10.1016/j.envpol.2018.10.115>.
- Chakraborty, T. K., Ghosh, G. C., Hossain, M. R., Islam, M. S., Habib, A., Zaman, S., Bosu, H., Nice, M. S., Haldar, M. & Khan, A. S. 2022 Human health risk and receptor model-oriented sources of heavy metal pollution in commonly consume vegetable and fish species of high ganges river floodplain agro-ecological area, bangladesh. *Heliyon* **8** (10), e11172. <https://doi.org/10.1016/j.heliyon.2022.e11172>.
- Chandler, D., Bailey, A. S., Tatchell, G. M., Davidson, G., Greaves, J. & Grant, W. P. 2011 The development, regulation and use of biopesticides for integrated pest management. *Philosophical Transactions of the Royal Society B: Biological Sciences* **366** (1573), 1987–1998. <https://doi.org/10.1098/rstb.2010.0390>.
- Cheng, G., Lin, J., Lu, J., Zhao, X., Cai, Z. & Fu, J. 2015 Advanced treatment of pesticide-containing wastewater using Fenton reagent enhanced by microwave electrodeless ultraviolet. *BioMed Research International* 2015. <https://doi.org/10.1155/2015/205903>.
- Claeys, W. L., Schmit, J. F., Bragard, C., Maghuin-Rogister, G., Pussemier, L. & Schiffers, B. 2011 Exposure of several belgian consumer groups to pesticide residues through fresh fruit and vegetable consumption. *Food Control* **22** (3–4), 508–516. <https://doi.org/10.1016/j.foodcont.2010.09.037>.
- Codex 2011 International Food Standards. Food and Agriculture Organization of the United Nations, World Health Organization. Available at: <https://www.fao.org> Accessed: 15 December 2022.
- Corniani, N., Velini, E. D., Silva, F. M., Nanayakkara, N. D., Witschel, M. & Dayan, F. E. 2014 Novel bioassay for the discovery of inhibitors of the 2-C-Methyl-D-erythritol 4-phosphate (MEP) and terpenoid pathways leading to carotenoid biosynthesis. *PloS one* **9** (7), e103704. <https://doi.org/10.1371/journal.pone.0103704>.
- Cosgrove, S., Jefferson, B. & Jarvis, P. 2019 Pesticide removal from drinking water sources by adsorption: a review. *Environmental Technology Reviews* **8** (1), 1–24. <https://doi.org/10.1080/21622515.2019.1593514>.
- Crini, G., Saintemarie, A. E., Rocchi, S., Fourmentin, M., Jeanvoine, A., Millon, L. & Morin-Crini, N. 2017 Simultaneous removal of five triazole fungicides from synthetic solutions on activated carbons and cyclodextrin-based adsorbents. *Heliyon* **3** (8), e00380. <https://doi.org/10.1016/j.heliyon.2017.e00380>.
- da Costa Soares, I. C., Da Silva, D. R., do Nascimento, J. H. O., Garcia-Segura, S. & Martínez-Huitle, C. A. 2017 Functional group influences on the reactive azo dye decolorization performance by electrochemical oxidation and electro-Fenton technologies. *Environmental Science and Pollution Research* **24**, 24167–24176. <https://doi.org/10.1007/s11356-017-0041-z>.

- De Roos, A. J., Blair, A., Rusiecki, J. A., Hoppin, J. A., Svec, M., Dosemeci, M., Sandler, D. P. & Alavanja, M. C. 2005 Cancer incidence among glyphosate-exposed pesticide applicators in the Agricultural Health Study. *Environmental Health Perspectives* **113** (1), 49–54. <https://doi.org/10.1289/ehp.7340>.
- Dietary Guidelines for Indian 2010 National Institute of Nutrition (NIN), Indian Council of Medical Research. Available at: <https://www.nin.res.in> Accessed: 12 December 2022.
- Dwivedi, S., Mishra, S. & Tripathi, R. D. 2018 Ganga water pollution: a potential health threat to inhabitants of ganga basin. *Environment International* **117**, 327–338. <https://doi.org/10.1016/j.envint.2018.05.015>.
- FAOSTAT 2019 Data, Food and Agriculture Organization of the United Nations. Available from: [www.fao.org/faostat/en/data](http://www.fao.org/faostat/en/data). (accessed 17 October 2022).
- FAO/WHO FOOD STANDARDS PROGRAM 2011 *Codex Pesticides Residue in Food Online Database*. Available from: [www.fao.org](http://www.fao.org). (accessed 12 September 2022).
- Fishel, F. M. 2010 The EPA conventional reduced risk pesticide program. *EDIS* **2010** (1), 1–9.
- FSSAI, Food Safety and standards 2011 *Contaminants, Toxins and Residues Regulations*. Available from: [www.fssai.gov.in](http://www.fssai.gov.in). (accessed 30 November 2022).
- García-Galán, M. J., Monllor-Alcaraz, L. S., Postigo, C., Uggetti, E., de Alda, M. L., Díez-Montero, R. & García, J. 2020 Microalgae-based bioremediation of water contaminated by pesticides in peri-urban agricultural areas. *Environmental Pollution* **265**, 114579. <https://doi.org/10.1016/j.envpol.2020.114579>.
- Gerber, R., Smit, N. J., Van Vuren, J. H., Nakayama, S. M., Yohannes, Y. B., Ikenaka, Y. & Wepener, V. 2016 Bioaccumulation and human health risk assessment of DDT and other organochlorine pesticides in an apex aquatic predator from a premier conservation area. *Science of the Total Environment* **550**, 522–533. <https://doi.org/10.1016/j.scitotenv.2016.01.129>.
- Grube, A., Donaldson, D., Kiely, T. & Wu, L. 2011 *Pesticides Industry Sales and Usage*. US EPA, Washington, DC.
- Gu, H. X., Hu, K., Li, D. W. & Long, Y. T. 2016 SERS detection of polycyclic aromatic hydrocarbons using a bare gold nanoparticle coupled film system. *Analyst* **141** (14), 4359–4365.
- Hamilton, P. B., Cowx, I. G., Oleksiak, M. F., Griffiths, A. M., Grahn, M., Stevens, J. R. & Tyler, C. R. 2016 Population-level consequences for wild fish exposed to sublethal concentrations of chemicals—a critical review. *Fish and Fisheries* **17** (3), 545–566. <https://doi.org/10.1111/faf.12125>.
- Indian Institute of Technology Roorkee 2018 *Morphological Study of Ganga River Using Remote Sensing Techniques*, Morphology Directorate Central Water Commission. (accessed 20 October 2022).
- Ivorra, L., Cardoso, P. G., Chan, S. K., Cruzeiro, C. & Tagulao, K. A. 2021 Can mangroves work as an effective phytoremediation tool for pesticide contamination? An interlinked analysis between surface water, sediments and biota. *Journal of Cleaner Production* **295**, 126334. <https://doi.org/10.1016/j.jclepro.2021.126334>.
- Jablonkai, I. 2011 *Molecular mechanism of action of herbicides*. In: Hasaneen, M. N. (ed.). *Herbicides - Mechanisms and Mode of Action*. InTechOpen.
- Jain, K., Sreenivas, V., Velpandian, T., Kapil, U. & Garg, P. K. 2013 Risk factors for gallbladder cancer: a case-control study. *International Journal of Cancer* **132** (7), 1660–1666. <https://doi.org/10.1002/ijc.27777>.
- Jayaraj, R., Megha, P. & Sreedev, P. 2016 Organochlorine pesticides, their toxic effects on living organisms and their fate in the environment. *Interdisciplinary Toxicology* **9** (3–4), 90–100. <https://doi.org/10.1515/intox-2016-0012>.
- Jeevanantham, S., Saravanan, A., Hemavathy, R. V., Kumar, P. S., Yaashikaa, P. R. & Yuvaraj, D. 2019 Removal of toxic pollutants from water environment by phytoremediation: a survey on application and future prospects. *Environmental Technology & Innovation* **13**, 264–276. <https://doi.org/10.1016/j.eti.2018.12.007>.
- Jia, M., Liu, M., Wang, Z., Mao, D., Ren, C. & Cui, H. 2016 Evaluating the effectiveness of conservation on mangroves: A remote sensing-based comparison for two adjacent protected areas in Shenzhen and Hong Kong, China. *Remote Sensing* **8** (8), 627. <https://doi.org/10.3390/rs8080627>.
- Júnior, O. G., Santos, M. G. B., Nossol, A. B., Starling, M. C. V. & Trovó, A. G. 2021 Decontamination and toxicity removal of an industrial effluent containing pesticides via multistage treatment: coagulation-flocculation-settling and photo-Fenton process. *Process Safety and Environmental Protection* **147**, 674–683. <https://doi.org/10.1016/j.psep.2020.12.021>.
- Kumari, A., Sinha, R. K. & Gopal, K. 2001a Organochlorine contamination in the fish of the River Ganges, India. *Aquatic Ecosystem Health & Management* **4** (4), 505–510.
- Kumari, A., Sinha, R. K. & Krishna, G. 2001b Concentration of organochlorine pesticide residues in Ganga water in Bihar, India. *Environment and Ecology* **19** (2), 351–356. ISSN 0970-0420.
- Lies, M. & Ohe, P. C. V. D. 2005 Analyzing effects of pesticides on invertebrate communities in streams. *Environmental Toxicology and Chemistry: An International Journal* **24** (4), 954–965. <https://doi.org/10.1897/03-652.1>.
- Mahajan, M., Gupta, P. K., Singh, A., Vaish, B., Singh, P., Kothari, R. & Singh, R. P. 2021 A comprehensive study on aquatic chemistry, health risk and remediation techniques of cadmium in groundwater. *Science of The Total Environment*, 151784. <https://doi.org/10.1016/j.scitotenv.2021.151784>.
- Mahmood, I., Imadi, S. R., Shazadi, K., Gul, A. & Hakeem, K. R. 2016 Effects of pesticides on environment. In: Hakeem, K. R., Akhtar, M. S. & Abdullah, S. N. A. (eds). *Plant, Soil and Microbes*. Springer, Cham, pp. 253–269.

- Mansouriieh, N. & Khosravi, M. 2015 Optimization of profenofos organophosphorus pesticide degradation by zero-valent bimetallic nanoparticles using response surface methodology. *Arabian Journal of Chemistry* **12** (8), 2524–2532. <https://doi.org/10.1016/j.arabjc.2015.04.009>.
- Marques, J. M. G. & Silva, M. V. D. 2021 Estimation of chronic dietary intake of pesticide residues. *Revista de Saúde Pública* **55**.
- Mishaqa, E. S. I. 2017 Biosorption potential of the microchlorophyte *Chlorella vulgaris* for some pesticides. *Journal of Fertilizers & Pesticides*. <https://doi.org/10.4172/2471-2728.1000177>.
- Mitra, A., Chowdhury, R. & Banerjee, K. 2012 Concentrations of some heavy metals in commercially important finfish and shellfish of the River Ganga. *Environmental Monitoring and Assessment* **184** (4), 2219–2230. <https://doi.org/10.1007/s10661-011-2111-x>.
- Mojiri, A., Zhou, J. L., Robinson, B., Ohashi, A., Ozaki, N., Kandaichi, T., Farraji, H. & Vakili, M. 2020 Pesticides in aquatic environments and their removal by adsorption methods. *Chemosphere* **253**, 126646. <https://doi.org/10.1016/j.chemosphere.2020.126646>.
- Murdiyarsa, D., Purbopuspito, J., Kauffman, J. B., Warren, M. W., Sasmito, S. D., Donato, D. C., Solichin, M., Krisnawati, H., Taberima, S. & Kurnianto, S. 2015 The potential of Indonesian mangrove forests for global climate change mitigation. *Nature Climate Change* **5** (12), 1089–1092. <https://doi.org/10.1038/nclimate2734>.
- N'diaye, A. D., Boudokhane, C., Elkory, M. B., Kankou, M. & Dhaouadi, H. 2018 Methyl parathion pesticide removal from aqueous solution using Senegal River *Typha australis*. *Water Supply* **18** (5), 1545–1553. <https://doi.org/10.2166/ws.2017.220>.
- Netto, M. S., Georgin, J., Franco, D. S., Mallmann, E. S., Foletto, E. L., Godinho, M., Pinto, D. & Dotto, G. L. 2021 Effective adsorptive removal of atrazine herbicide in river waters by a novel hydrochar derived from *Prunus pinosada* bark. *Environmental Science and Pollution Research*, 1–14. <https://doi.org/10.1007/s11356-021-15366-4>.
- Nie, J., Sun, Y., Zhou, Y., Kumar, M., Usman, M., Li, J., Shao, J., Wang, L. & Tsang, D. C. 2020 Bioremediation of water containing pesticides by microalgae: mechanisms, methods, and prospects for future research. *Science of The Total Environment* **707**, 136080. <https://doi.org/10.1016/j.scitotenv.2019.136080>.
- Ntzani, E. E., Ntritsos, G. C. M., Evangelou, E. & Tzoulaki, I. 2013 Literature review on epidemiological studies linking exposure to pesticides and health effects. *EFSA Supporting Publications* **10** (10), 497E. <https://doi.org/10.2903/sp.efsa.2013.EN-497>.
- Ogbeide, O., Tongo, I. & Ezemonye, L. 2015 Risk assessment of agricultural pesticides in water, sediment, and fish from Owan River, Edo State, Nigeria. *Environmental Monitoring and Assessment* **187** (10), 1–16. <https://doi.org/10.1007/s10661-015-4840-8>.
- Palma, P., Köck-Schulmeyer, M., Alvarenga, P., Ledo, L., Barbosa, I. R., De Alda, M. L. & Barceló, D. 2014 Risk assessment of pesticides detected in surface water of the Alqueva reservoir (Guadiana basin, southern of Portugal). *Science of the Total Environment* **488**, 208–219. <https://doi.org/10.1016/j.scitotenv.2014.04.088>.
- Pretty, J. 2008 Agricultural sustainability: concepts, principles and evidence. *Philosophical Transactions of the Royal Society B: Biological Sciences* **363** (1491), 447–465. <https://doi.org/10.1098/rstb.2007.2163>.
- Rani, L., Thapa, K., Kanojia, N., Sharma, N., Singh, S., Grewal, A. S., Srivastav, A. L. & Kaushal, J. 2021 An extensive review on the consequences of chemical pesticides on human health and environment. *Journal of Cleaner Production* **283**, 124657. <https://doi.org/10.1016/j.jclepro.2020.124657>.
- Rath, B. 2012 Microalgal bioremediation: current practices and perspectives. *Journal of Biochemical Technology* **3** (3), 299–304. ISSN: 0974-2328.
- Rawtani, D., Khatri, N., Tyagi, S. & Pandey, G. 2018 Nanotechnology-based recent approaches for sensing and remediation of pesticides. *Journal of Environmental Management* **206**, 749–762. <https://doi.org/10.1016/j.jenvman.2017.11.037>.
- Riaz, G., Tabinda, A. B., Iqbal, S., Yasar, A., Abbas, M., Khan, A. M., Mahfooz, Y. & Baqar, M. 2017 Phytoremediation of organochlorine and pyrethroid pesticides by aquatic macrophytes and algae in freshwater systems. *International Journal of Phytoremediation* **19** (10), 894–898. <https://doi.org/10.1080/15226514.2017.1303808>.
- Richards, L. A., Fox, B. G., Bowes, M. J., Khamis, K., Kumar, A., Kumari, R., Kumar, S., Hazra, M., Howard, B., Thorn, R. M. S., Read, D. S., Nel, H. A., Schneidewind, U., Armstrong, L. K., Nicholls, D. J. E., Magnone, D., Ghosh, A., Chakravorty, B., Joshi, H., Dutta, T. K. & Polya, D. A. 2022 A systematic approach to understand hydrogeochemical dynamics in large river systems: development and application to the river Ganges (Ganga) in India. *Water Research* **211**, 118054. <https://doi.org/10.1016/j.watres.2022.118054>.
- Saad, M., Shams, D., Khan, W., Ijaz, A., Qasim, M., Hafeez, A. & Ahmed, A. N. 2017 Occurrence of selected pesticides and pcps in surface water receiving untreated discharge in Pakistan. *Journal of Environmental and Analytical Toxicology* **7** (500). DOI: 10.4172/2161-0525.1000500.
- Saaristo, M., Brodin, T., Balshine, S., Bertram, M. G., Brooks, B. W., Ehlman, S. M. & Arnold, K. E. 2018 Direct and indirect effects of chemical contaminants on the behaviour, ecology and evolution of wildlife. *Proceedings of the Royal Society B* **285** (1885), 20181297. <https://doi.org/10.1098/rspb.2018.1297>.
- Saini, A., Jainth, S., Saini, R., Gupta, A., Grover, R. & Gupta, M. 2015 Ganga deterioration and conservation of its sanctity. *International Journal of Recent Scientific Research* **6**, 3786–3787.
- Salman, J. M. & Abid, F. M. 2013 Preparation of mesoporous activated carbon from palm-date pits: optimization study on removal of bentazon, carbofuran, and 2, 4-D using response surface methodology. *Water Science and Technology* **68** (7), 1503–1511. <https://doi.org/10.2166/wst.2013.370>.
- Samanta, S. 2013 Metal and pesticide pollution scenario in Ganga river system. *Aquatic Ecosystem Health & Management* **16** (4), 454–464. <https://doi.org/10.1080/14634988.2013.858587>.



- San Román, I., Alonso, M. L., Bartolomé, L., Galdames, A., Goiti, E., Ocejó, M. & Vilas, J. L. 2013 Relevance study of bare and coated zero valent iron nanoparticles for lindane degradation from its by-product monitorization. *Chemosphere* **93** (7), 1324–1332. <https://doi.org/10.1016/j.chemosphere.2013.07.050>.
- Sarkar, U. K., Dubey, V. K., Singh, A. K., Gupta, B. K., Pandey, A., Sani, R. K. & Lakra, W. S. 2012 The recent occurrence of exotic freshwater fishes in the tributaries of river Ganga basin: abundance, distribution, risk, and conservation issues. *The Environmentalist* **32** (4), 476–484. <https://doi.org/10.1007/s10669-012-9412-7>.
- Sarker, S., Akbor, M. A., Nahar, A., Hasan, M., Islam, A. R. M. T. & Siddique, M. A. B. 2021 Level of pesticides contamination in the major river systems: a review on south Asian countries perspective. *Heliyon* **7** (6), e07270. <https://doi.org/10.1016/j.heliyon.2021.e07270>.
- Sathiakumar, N., MacLennan, P. A., Mandel, J. & Delzell, E. 2011 A review of epidemiologic studies of triazine herbicides and cancer. *Critical Reviews in Toxicology* **41** (sup1), 1–34. <https://doi.org/10.3109/10408444.2011.554793>.
- Senthilkumar, S., Krishna, S. K., Kalaamani, P., Subburamaan, C. V. & Ganapathi, S. N. 2010 Adsorption of organophosphorous pesticide from aqueous solution using “waste” jute fiber carbon. *Modern Applied Science* **4**, 68–83.
- Shalaby, S. E., El-Saadany, S. S., Abo-Eyta, A. M., Abdel-Satar, A. M., Al-Afify, A. D. G. & Abd El-Gleel, W. M. M. 2018 Levels of pesticide residues in water, sediment, and fish samples collected from Nile river in Cairo, Egypt. *Environmental Forensics* **19** (4), 228–238. <https://doi.org/10.1080/15275922.2018.1519735>.
- Shamsollahi, Z. & Partovinia, A. 2019 Recent advances on pollutants removal by rice husk as a bio-based adsorbent: a critical review. *Journal of Environmental Management* **246**, 314–323. <https://doi.org/10.1016/j.jenvman.2019.05.145>.
- Sharma, A. K., Tiwari, R. K. & Gaur, M. S. 2016 Nanophotocatalytic UV degradation system for organophosphorus pesticides in water samples and analysis by Kubista model. *Arabian Journal of Chemistry* **9**, S1755–S1764. <https://doi.org/10.1016/j.arabjc.2012.04.044>.
- Shen, W., Mu, Y., Wang, B., Ai, Z. & Zhang, L. 2017 Enhanced aerobic degradation of 4-chlorophenol with iron-nickel nanoparticles. *Applied Surface Science* **393**, 316–324. <https://doi.org/10.1016/j.apsusc.2016.10.020>.
- Singh, P. B., Singh, V. & Nayak, P. K. 2008 Pesticide residues and reproductive dysfunction in different vertebrates from north India. *Food and Chemical Toxicology* **46** (7), 2533–2539. <https://doi.org/10.1016/j.fct.2008.04.009>.
- Sudhakar, U. B. 2014 Effect of pollutants on the fishes of Ganga and Sai River of Raebareilly District in Uttar Pradesh in India. *Research Journal of Animal, Veterinary and Fishery Sciences* **11**, 1–6.
- Thapa, S., Lv, M. & Xu, H. 2017 Acetylcholinesterase: a primary target for drugs and insecticides. *Mini Reviews in Medicinal Chemistry* **17** (17), 1665–1676. <https://doi.org/10.2174/1389557517666170120153930>.
- Thrall, P. H., Oakshott, J. G., Fitt, G., Southerton, S., Burdon, J. J., Sheppard, A., Russell, R. J., Zalucki, M., Heino, M. & Ford Denison, R. 2011 Evolution in agriculture: the application of evolutionary approaches to the management of biotic interactions in agro-ecosystems. *Evolutionary Applications* **4** (2), 200–215. <https://doi.org/10.1111/j.1752-4571.2010.00179.x>.
- Torrens, F. & Castellano, G. 2014 Molecular classification of pesticides including persistent organic pollutants, phenylurea and sulphonylurea herbicides. *Molecules* **19** (6), 7388–7414. <https://doi.org/10.3390/molecules19067388>.
- Tsimbiri, P. F., Moturi, W. N., Sawe, J., Henley, P. & Bend, J. R. 2015 Health impact of pesticides on residents and horticultural workers in the Lake Naivasha Region, Kenya. *Occupational Diseases and Environmental Medicine* **3** (02), 24. doi:10.4236/odem.2015.32004.
- USEPA 1991 Risk assessment guidance for superfund. In: Vol. I. Human Health Evaluation Manual (Part B, Development of Risk-Based Preliminary Remediation Goals), Office of Emergency and Remedial Response U.S. Environmental Protection Agency Washington, DC 20460 EP A/5401R-92/003. (accessed 15 June 2021).
- USEPA 1992 National Study of Chemical Residues in Fish. Vol. I. United States Environmental Protection Agency, Office of Science and Technology Standards and Applied Science Division U.S. Environmental Protection Agency Washington, DC 20460 (EPA 823-R-92-008a).
- USEPA 2017 USEPA Regional Screening Level (RSL) Summary Table. June 2017. Available from: <https://semspub.epa.gov/work/03/2245073.pdf>. (accessed 11 June 2021).
- Varol, M. & Sünbül, M. R. 2017 Organochlorine pesticide, antibiotic and heavy metal residues in mussel, crayfish and fish species from a reservoir on the Euphrates River, Turkey. *Environmental Pollution* **230**, 311–319. <https://doi.org/10.1016/j.envpol.2017.06.066>.
- Varshney, S., Hayat, S., Alyemeni, M. N. & Ahmad, A. 2012 Effects of herbicide applications in wheat fields: is phytohormones application a remedy? *Plant Signaling & Behavior* **7** (5), 570–575. <https://doi.org/10.4161/psb.19689>.
- Vaseem, H. & Banerjee, T. K. 2013 Contamination of the River Ganga and its toxic implication in the blood parameters of the major carp Labeorohita (Ham). *Environmental Science and Pollution Research* **20** (8), 5673–5681. <https://doi.org/10.1007/s11356-013-1570-8>.
- WHO 1997 *Guidelines for Predicting Dietary Intake of Pesticide Residue*. Programme of Food Safety and Food Aid World Health Organization. Available from: [www.who.int](http://www.who.int) (accessed 26 November 2021).
- WHO/FAO 2016 *Manual on Development and use of FAO and WHO Specifications for Pesticides*, 1st edn. 3<sup>rd</sup> revision. ISSN 0259-2517. Available from: [www.fao.org/3/i57/13e/i15713e.pdf](http://www.fao.org/3/i57/13e/i15713e.pdf). (accessed 14 October 2022).
- Wildlife Institute of India 2018 *Assessment of the Wildlife Values of the Ganga River from Bijnor to Ballia Including Turtle Wildlife Sanctuary, Uttar Pradesh*. Available from: [www.forestsclearance.nic.in](http://www.forestsclearance.nic.in). (accessed 26 November 2022).
- Yadav, I. C., Devi, N. L., Syed, J. H., Cheng, Z., Li, J., Zhang, G. & Jones, K. C. 2015 Current status of persistent organic pesticides residues in air, water, and soil, and their possible effect on neighboring countries: a comprehensive review of India. *Science of the Total Environment* **511**, 123–137. <https://doi.org/10.1016/j.scitotenv.2014.12.041>.

- Yahia, D. & Elsharkawy, E. E. 2014 Multi pesticide and PCB residues in Nile tilapia and catfish in Assiut city, Egypt. *Science of the Total Environment* **466–467**, 306–314. <https://doi.org/10.1016/j.scitotenv.2013.07.002>.
- Yamashita, N., Urushigawa, Y., Masunaga, S., Walsh, M. I. & Miyazaki, A. 2000 Organochlorine pesticides in water, sediment and fish from the Nile River and Manzala Lake in Egypt. *International Journal of Environmental Analytical Chemistry* **77** (4), 289–303. <https://doi.org/10.1080/03067310008032698>.
- Yilmaz, B., Terekeci, H., Sandal, S. & Kelestimur, F. 2020 Endocrine disrupting chemicals: exposure, effects on human health, mechanism of action, models for testing and strategies for prevention. *Reviews in Endocrine and Metabolic Disorders* **21** (1), 127–147. <https://doi.org/10.1007/s11154-019-09521-z>.
- Zhang, L. & Fang, M. 2010 Nanomaterials in pollution trace detection and environmental improvement. *Nano Today* **5** (2), 128–142. <https://doi.org/10.1016/j.nantod.2010.03.002>.
- Zhang, H., Lu, X., Zhang, Y., Ma, X., Wang, S., Ni, Y. & Chen, J. 2016 Bioaccumulation of organochlorine pesticides and polychlorinated biphenyls by loaches living in rice paddy fields of Northeast China. *Environmental Pollution* **216**, 893–901. <https://doi.org/10.1016/j.envpol.2016.06.064>.
- Zhou, Y., Xia, X., Yu, G., Wang, J., Wu, J., Wang, M., Yang, Y., Shi, K., Yu, Y., Chen, Z. & Yu, J. 2015 Brassinosteroids play a critical role in the regulation of pesticide metabolism in crop plants. *Scientific Reports* **5** (1), 1–7. <https://doi.org/10.1038/srep09018>.

First received 30 December 2022; accepted in revised form 22 February 2023. Available online 7 March 2023