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A holistic review on trend, occurrence, factors affecting pesticide concentration, and ecological risk assessment

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Abstract Demographic outbursts and increased food demands invoke excessive use of pesticides in the agricultural field for increasing productivity which leads to the relentless decline of riverine health and its tributaries. These tributaries are connected to a plethora of point and non-point sources that transport pollutants including pesticides into the Ganga river's mainstream. Simultaneous climate change and lack of rainfall significantly increase pesticide concentration in the soil and water matrix of the river basin. This paper is intended to review the paradigm shift of pesticide pollution in the last few decades in the river Ganga and its tributaries. Along with this, a comprehensive review suggests the ecological risk assessment method which facilitates policy development, sustainable riverine ecosystem management, and decision-making. Before 2011, the total mixture of Hexachlorocyclohexane was found at 0.004–0.026 ng/mL in Hooghly, but now, the concentration has increased up to 0.465–4.132 ng/mL. Aftermath of critical review, we observed maximum residual commodities and pesticide contamination reported in Uttar Pradesh > West Bengal > Bihar > Uttara Khand possibly because of agricultural load, increasing settlement, and incompetency of sewage treatment plant in the reclamation of pesticide contamination.

Keywords Pesticide · Pollution · Climate change · Risk assessment · Decadal variation

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Introduction

The Ganga River basin (GRB) is among the largest riverine ecosystems in the world. The Ganga mainstream stretch is 2525 km long and begins at Gaumukh (30° 36′ N, 79° 04′ E) at the Gangotri Glacier's snout (CPCB, 2013). At the Gangotri glacier in the higher Himalayan region, at the elevation of 3800 m above mean sea level, initially, the Ganga is called as Bhagirathi (Paul, 2017). When the Bhagirathi meets the Alaknanda River and gets united, it is known as the Ganga River (Singh, 2010). Draining from the Himalayas, the river enters the Ganga Plain at Haridwar in Uttarakhand (UK) and then flows toward Uttar Pradesh (UP), Bihar (BR), and West Bengal (Fig. 1). Finally, after covering 2510 km in the stretch between Gangotri and West Bengal (WB), the river joins the Brahmaputra River and flows into the Bay of Bengal (Malik et al., 2021). There are several tributaries and distributaries that congregate in the mainstream of the Ganga draining from different states, for example, Yamuna, Rind, Ramganga, Kosi, Ghaghara, Gomati, Gandak, and Hooghly (CWC, 2014).

Tributaries of Ganga contribute 60% of the total water of the river (Paul, 2017). Ghaghara accounts for 20% and 16% of water fed by the Yamuna in the mainstream of Ganga (Agarwal, 1994). Ganga's tributaries and distributaries play a crucial role in the transportation of pollutants such as pesticide in the mainstream; this leads to change in physicochemical properties of water and sediments of the river and its associated waterbodies (Ahammad et al., 2014). Industrial wastewater is another factor affecting the water quality of the river Ganga, contributing 20% of the total volume of wastewater pouring into the river (NMCG, 2022). Approximately 12,000 million liter per day (MLD) of sewage is generated from the Ganga River basin. Of this, only 1/3rd amount is treated, and the rest is directly discharged into the river without treatment (NMCG, 2022).

Indo-Gangetic Plain (IGP) is a very productive and fertile land in India, and thus it witnesses the enormous use of pesticides. Excessive and limitless use of pesticides in agricultural production leads to environmental pollution, ultimately ending up in the Ganges through interrupted runoff or via tributaries (Mutiyar & Mittal, 2013; Yadav et al., 2015; Central

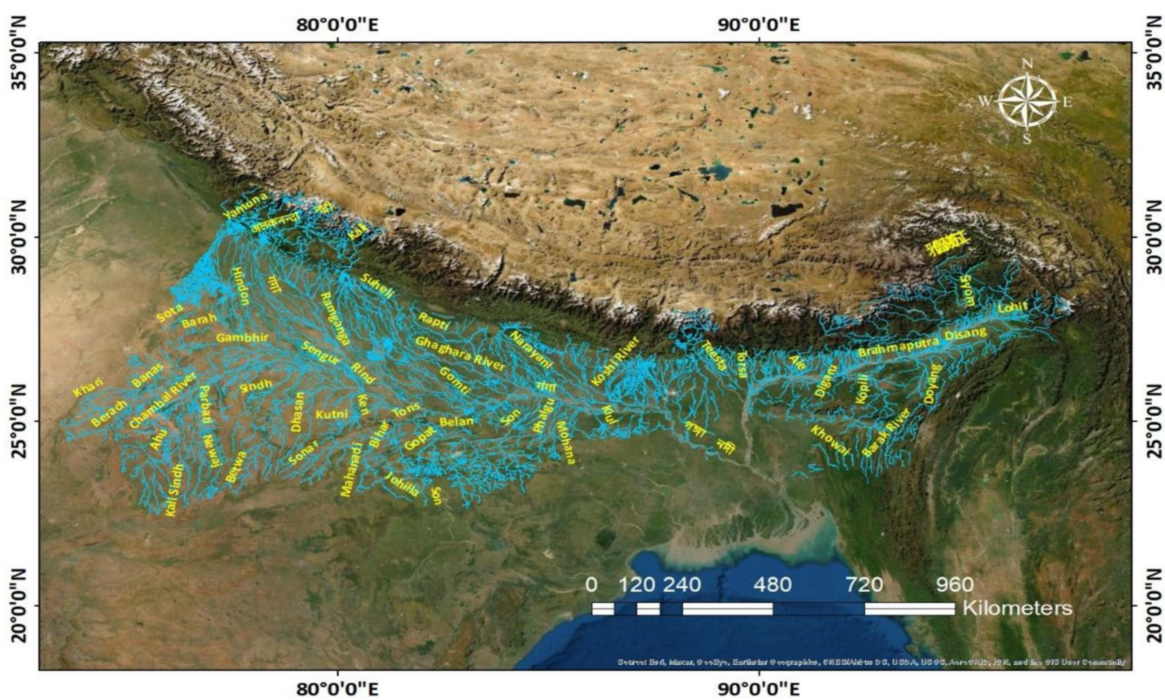

Fig. 1 Stretch of Ganga River basin from Gangotri to the Bay of Bengal

Pollution Control Board, 2016a, b). According to the report of Jayaraj et al. (2016), only 0.3% of applied pesticides reach the target pest, while the rest (99.7%) has wasted and polluted the environment. Most pesticides are lipophilic, so they bioaccumulate and biomagnify at higher trophic levels (Ivorraet al., 2021). Some pesticides are persistent and have a long half-life, along with the potency of long-range transport, even after many years of application.

Primarily agrochemicals are used for pest abolishment; approximately 90% of chemicals are released into the environment as remanent without degradation (Shah & Parveen, 2022). Among the group of persistent pesticides, organochlorine pesticides have become a serious concern worldwide owing to their persistent nature, toxicity, long-range spread, and their bio-accumulative nature (Briz et al., 2011; Gao et al., 2013). Due to bioaccumulation in the body, OCPs are carcinogenic for human health (Ennour-Idrissi et al., 2019; Louis, 2019), teratogenic (Kalra et al., 2016; Kim et al., 2017; Ramakrishnan & Jayaraman, 2019), endocrine disruptors (Dwivedi et al., 2018; Frye et al., 2012), neurotoxic (Heusinkveld & Westerink, 2012; Yadav et al., 2015), and genotoxic (Ennaceur et al., 2008). Pesticides not only exert an effect on human health but induce toxicity, directly and indirectly, in fish as well (Ali et al., 2018).

The effects of pesticide contamination on fish behavior, endocrine disruption, genotoxicity, hematological changes, enzyme alteration, and biochemical modifications are well documented by many researchers (Ullah & Zorriehzahra, 2015). As per the report of the National Cancer Registry program, the significant number of cancer patients has amplified around the Ganga basin (Jain et al., 2013; Saini et al., 2015). A total of 1291 carcinoma gall bladder cases were reported in the hospital-based cancer registry (HBCR) in the year 2014–2016. A total of 16% of gall bladder carcinoma cases have been reported in Patna followed by Vaishali (5.8%), Sitamarhi (5%), Madhubani (4.7%), Gaya (4%), and Samastipur (4%) (Madhawi et al., 2018). Kumar et al. (2022) have taken 2000 cancer patients' blood samples at Mahavir Cancer Sansthan and Research Centre, Patna, Bihar, and prepared the geospatial map of the Ganga basin. Kumar et al. (2022) study strongly correlate the relation of toxic elements with the increasing cancer cases incidence in the Gangetic basin. Similar results were previously reported by Madhawi et al. (2018) that the gall bladder cancer has increased in the Indo-Gangetic basin especially in Bihar.

The Stockholm Convention on POPs (Persistent Organic Pollutants) was an international environmental treaty that was signed in 2001 and became effective in 2004, which enlists POPs such as pesticides (Olisah et al., 2022). India has banned the export, manufacturing, use, and import of all 12 initial POPs listed in the convention, except for Di chloro-diphenyl-trichloroethane (DDT) (Sharma et al., 2014). Furthermore, 16 new POPs were added, among which pesticides were in the major group. Several steps have been taken by the government to exterminate the problem of pollution from the sacred river Ganga, such as Ganga action plan-I, Ganga action plan-II, and Namami Gange Mission. Government of India have banned many insecticides and pesticide such as Acephate, Atrazine, Butachlor, Captan, Carbofuran etc. to reduce the ill impacts of pesticide on environment (The Gazette of India, 2020).

The Union Government launched the "Namami Gange Programme," which is an integrated conservation mission in June 2014 to accomplish the twin objectives of (i) reduction of pollution as conservation and (ii) rejuvenation of the National River Ganga (Fig. 1). However, after launching numerous synergistic schemes, this review is an attempt to a comprehensive study on decadal change before and after 2011 of pesticide contamination in the river Ganga along with its major tributaries and distributaries in water, sediment quality, and on aquatic biota (NMCG, 2022). A comparison of pesticide contamination levels in Ganga and other important rivers around the globe has also been done.

The review raises the problem of pesticide pollution in the river Ganga and its tributaries. Water pollution is a barrier to attaining sustainable development targets by 2030. The review is an attempt to fill the research gap in the field among numerous studies on Ganga. Aftermath of critical review analysis in the last decades, very meager studies emphasize the trends of pesticide pollution in the mainstream of Ganga and its significant tributaries and ecological risk assessment. It affirms the critical need to engage society and collectively adopt proper strategies for sustainable management. The conservation of river water quality is intrinsically associated with aquatic and riparian ecosystems. It motivates the hydrobiologist, hydrogeologist, and sustainable development manager to fill the gap.

Source of pesticide contaminations

Point sources

Municipal/sewage discharge

There were several efforts made by the government to get rid of contamination in the river Ganga. In this queue of promising efforts, one was registered as a society under Society Registration Act 1860 in 2011, i.e., NMCG. This society has been formed with two major objectives: (1) effective pollution abatement and rejuvenation of the river Ganga and (2) to protect water quality and promote long-term development in the river basin. To fulfill the vision of NMCG, the government has established numerous sewage treatment plants (STP), the maximum number of 34 STPs in WB, 8 in UP, 5 in BR, and 4 in UK. In class I cities, out of 2601.3 MLD, less than 50% (approx. 1192 MLD) were treated, and in-class II towns out of 122 MLD, only 13% (approx. 16.4 MLD) were treated (CPCB, 2013) (Fig. 2). Around 43.78 crore people reside near the GRB (CPCB, 2013). Four immensely populated states UK, UP, Bihar (BR), and WB, and two metro cities are situated near the vicinity of the Ganga basin.

IGP has the most fertile soils, and its region is fully embraced with agriculture and flourishing civilization. The characteristics of the IGP make this region one of the ideal places for residents as well as the establishment of industries. Ganga River Basin Planning Assessment Report (2018) stated total demography of the Ganga basin is estimated to elevate by 45% from 485 million in 2011 to 706 million projected in 2040. The rural population is likely to be enhanced by 35%, from 341 to 463 million, while the urban population is projected to increase by 68% from 144 to 243 million (Ganga River Basin Planning Assessment Report, 2018). A total of 72,741 MT of pesticide usage has been reported in Ganga basin between 2012 and 2017 which is 27% of the total consumption of the nation (Shah and Parveen, 2022). According to Ghosh et al. (2009), approximately 9000 MT of pesticides were used per year in the agricultural sector. The assemblage of pesticide consumption pattern has been reported as 80% insecticide + 15% herbicide + 2% fungicide in 2014 (Shah & Parveen, 2022). So, its consequences will likely be severe, like a discharge of non-treated wastewater from urban centers.

Untreated sewage constitutes an abundance of organic (viz., macronutrients), including pesticides (Singh et al., 2018; Vega et al., 1998). Numerous studies of the CPCB (Central Pollution Control Board, India) reported more than 144 drains and 767 grossly polluting industrial wastewater entering the entire stretch of Ganga (PIB, GOI, Ministry of Water Resources). Recent trends of sewage generation and treatment at five major states of Ganga pathway (Wastewater Management for Efficacious Use of Water Resources, 2022) are shown in Fig. 3.

Industrial sources

Previous studies on river Ganga indicate the occurrence of hexachlorocyclohexane (HCH), di-chloro diphenyl trichloroethane (DDT), endosulfan, and metabolites of these compounds in the river water (Mutiyar et al., 2011; Samanta, 2013; Chakraborty et al., 2016). Sankaramakrishnan et al. (2005) have analyzed the Ganga water quality from Kanpur (upstream of Bithoor) to the intensely contaminated Jajmau region. This study confirmed the occurrence of hexachlorocyclohexane (α-HCH) and malathion at a concentration of 0.190 μg/L ± 0.020and 2.618 μg/L ± 0.050, respectively. In Bithoor, γ-HCH 0.260 μg/L was reported downstream of Kanpur Gangabharaj and Dieldrin (1.671 μg/L ± 0.036) was reported in the Chakeri area (Sankararamakrishnan et al., 2005). Another study of) detected DDT with a maximum concentration of 0.58 μg/L downstream of Allahabad. Besides this, in BR, untreated or partially treated wastewater from industries or agriculture is discharged directly. It will gradually deteriorate the Ganga's water quality in BR (CPCB, 2009) (Tables 1 and 2).

There were 59 priority drains releasing tonnes of reclaimed/non-reclaimed municipal/industrial wastewater (highest organic load: 190.41 tonnes/day) into the river Ganga (Sah et al., 2020). Some studies have been performed in the deltaic region of river Ganga, WB, and their conclusion has been laid on the same front about pesticide contamination (Agarwal et al., 2015; Chakraborty et al., 2016) (Tables 1 and 2). In the study, the concentration of OCPs has investigated in river Ganga, Kolkata, WB (Naresh et al., 2009). The study was based on a seasonal investigation of OCP residues in various sources, such as tanks, lakes, and rivers. Lindane (0.01–0.43 μg

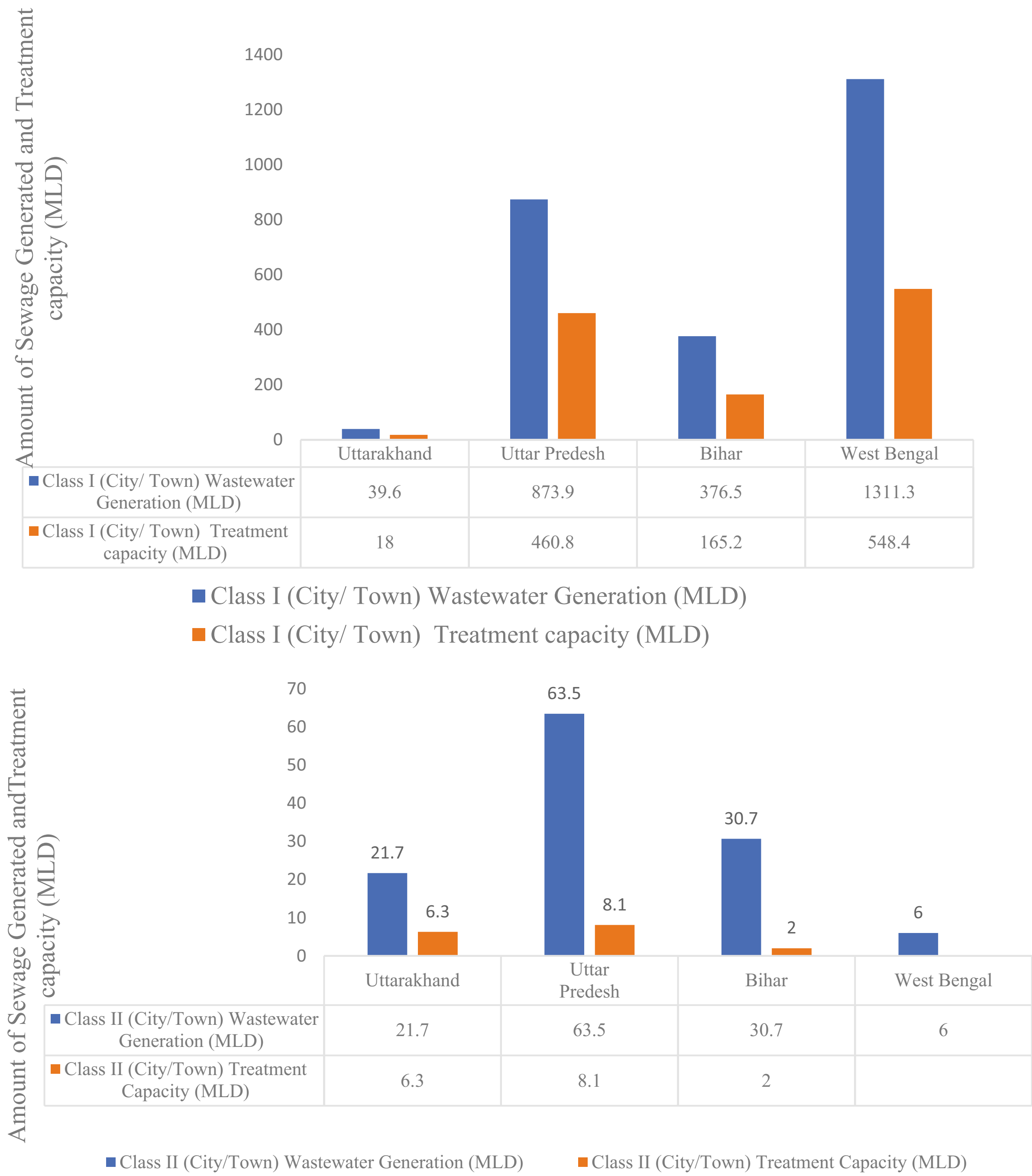

Fig. 2 The graph is showing the gap of wastewater generated and treated (MLD) in class I and class II cities/towns (CPCB, 2013)

L^{-1}) was the pesticide most often reported across all sources, followed by DDT (0.01–1.4 μg L^{-1}). Aldrin and dieldrin concentrations were found to be extremely high (0.9 μg L^{-1}) in the river Hooghly between Barrackpur and Sheoraphuli, approximately 20 km north of Kolkata. Lindane was identified in surface water in the Greater Kolkata, Baksara, and Andul (Naresh et al., 2009).

The concentration of pesticides also varies with the variation of seasons. Concentrations have been

Fig. 3 State-wise sewage generation and treatment capacity (in MLD) planned/proposed

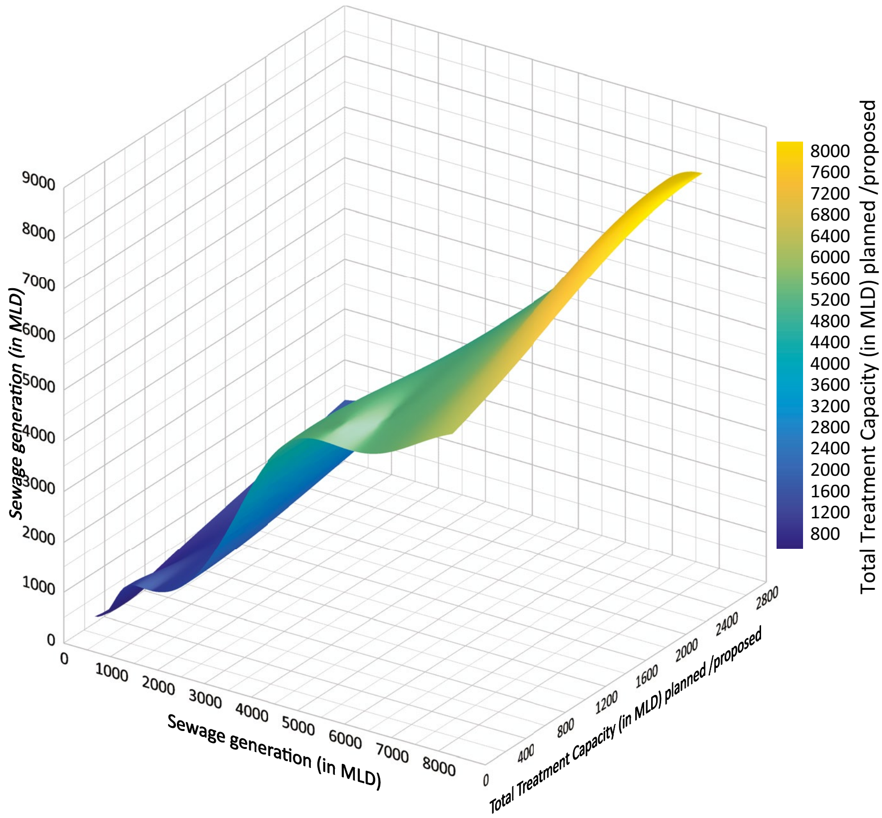

Chart 1. State wise sewage generation and treatment capacity (in MLD) planned/proposed

(Wastewater Management for Efficacious Use of Water Resources (2022))

	Sewage generation (in MLD)	Total Treatment Capacity (in MLD) planned /proposed
Uttarakhand	627	515
Uttar Pradesh	8263	3374
Bihar	2276	631
Jharkhand	1510	639
West Bengal	5457	337

reported to be significantly higher in winter due to its more significant pesticide application and minimum in monsoon (rainy season), possibly due to dilution. Again, pesticide concentration was marginally higher in summer compared to monsoon season (Naresh et al., 2009; Chakraborty et al., 2016) (Tables 1 and 2).

Nonpoint source

Contamination from agricultural uses

Among the total agricultural production of the nation, nearly half is produced from the Gangetic basin to fulfill the needs of 40% of the population (Schneider & Asch, 2020). The Ganga River basin congregated 9000 tonnes of pesticides from agriculture and public health runoff (Naresh et al., 2009; Samanta, 2013).

Among the insecticides, the use of organochlorines was 16%, organophosphates were 50%, synthetic pyrethroids 19%, carbamates 4%, bioinsecticides 1%, and others were about 10% (Karunya & Saranraj, 2014) (Fig. 4). Agricultural use of pesticides could easily find its mode of transmission reaching into the river via runoff streams and tributaries (Syafrudin et al., 2021). Leena et al. (2012) collected samples from different sites in Bhagalpur, BR, and found OCPs

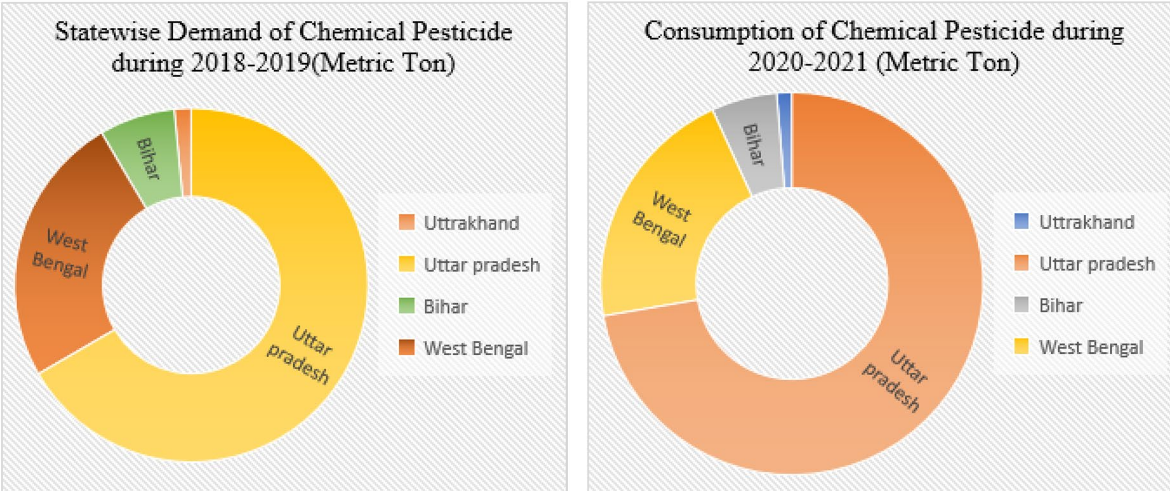

Fig. 4 State-wise demand and consumption of chemical pesticide during 2018–2019 and 2020–2021 (Directorate of Plant Protection, Quarantine and Storage, GOI)

and organophosphate at different sites. The presence of lindane, methyl parathion, isomers of endosulfan (108.02–739 ng L^{-1}), and isomers of DDT (78.22–489.0 ng L^{-1}) was identified in different sites and seasons. It could be because of agricultural runoff or surface runoff contributing to a heavy load of pesticide pollution in water. DDT concentration has been reported to be significantly high because of a slow degradation rate, i.e., 75–100% in 4–30 years (Leena et al., 2012) (Fig. 4).

A study performed on river Ganga by Sah et al. (2020) reported the mean concentrations of $\sum$ OCPs (0.126–10.402 μg L^{-1}) were higher (~2 to 5 times) in the post-monsoon season in comparison to post-winter values ranging from 0.053–3.010 μg L^{-1}. The study witnessed the dominance of lindane (γ-HCH) in all the states UK, UP, BR, and WB. Lindane detection indicated probably frequent application in the paddy field (Sah et al., 2020). The spatial dispersal of OCPs exposed the maximum concentrations in agriculture-intensive areas and estuarine lower zone (WB) (Sah et al., 2020). The high cropping intensities in this region and the decrease in river flow because of the redirection of river water to Bangladesh and the absorption of water for irrigation at the Farakka Barrage may be the conceivable explanation for the maximum concentration seen in WB (Sah et al., 2020). The state consumes 0.679 kg/ha of pesticides. The usage is higher than that of its neighboring state, UP, which is nearly 2.7 times bigger area than WB (Devi et al., 2017). Compared to previous studies on the Ganga concentration of pesticides, DDT and endosulfan reported a 50% decrease, and HCH reported a 60% decline (Sah et al., 2020).

Role of tributaries of river Ganga in pesticide pollution

Major tributaries that contribute water to the Ganga River in India are Kali, Yamuna, Ghaghara, Ramganga, Gandak, Damodar, Gomti, Kosi, Tamsa, Mahananda, Son, and Punpun (Trivedi, 2010). Tributaries supply 60% of the Ganga's total water volume. The tributaries of Ganga transport a substantial amount of pesticides. The Yamuna River has carried a fair amount of pesticide (Parween et al., 2021), it passes through a few major cities including Delhi, Mathura, Vrindavan, and Agra and joins at Allahabad with the Ganga.

A researcher (Pandey et al., 2011) has conducted an experiment and collected six sediment samples from Ramghat, Najafgarh Upstream, Najafgarh downstream, ITO, Okhla, and Kalindi Kunj along the river Yamuna at Delhi. Pandey et al. (2011) reported the composition of HCHs (alpha, beta, gamma), Endrin aldehyde, Heptachlor, Aldrin, Endosulfan, DDD, and DDT at all the sampling sites (Ramghat, Najafgarh upstream, Najafgarh downstream, ITO, Okhla, Kalindi Kunj) in every season:

Table 1 A comparative table of pesticide concentration in water and sediment of Ganga and its major tributaries or distributaries (before and after year 2011)

Pesticide	Hooghly water ng/mL[a]	Hooghly sediment ng/g[b]	Hooghly water ng/mL[c]	Hooghly sediment ng/g[c]	Ganga water ng/mL[d]	Ganga sediment ng/g[d]	Ganga water ng/mL[e]	Ganga sediment ng/g[e]
	Before 2011		After 2011		Before 2011		After 2011	
α- HCH	-	0.05–0.26	0–0.836	0–0.616	BDL to 1.02	BDL to 0.74	BDL to 3.4	BDL to 1.6
β-HCH	-	BDL to 0.06	0.06–2.01	0–0.856	BDL to 1.32	BDL to 4.51	BDL to 19.7	BDL to 8.4
γ-HCH	-	0.06–0.15	0–0.115	0–0.287	BDL to 0.71	BDL to 1.80	BDL to 24.5	BDL to 19.8
δ-HCH	-	BDL	0.206–2.940	0–0.987	BDL to 0.30	BDL to 2.71	BDL	BDL
T-HCH	0.004–0.026	0.11–0.40	0.465–4.132	0–2.216	BDL to 0.30	-	-	-
2,4′-DDE	-	BDL to 0.03	0–0.926	0–0.186	BDL to 0.13	-	-	-
4,4′-DDE	-	BDL to 0.04	0–0.180	0–0.732	BDL to 0.04	BDL to 5.10	BDL to 9.7	BDL to 2.6
2,4′-DDD	-	BDL to 0.07	0–0.160	ND	-	-	-	-
4,4′-DDD	-	BDL to 0.34	0–0.659	0–0.592	BDL to 0.03	BDL to 9.12	BDL to 6.6	BDL to 1.2
2,4′-DDT	-	0.04–0.14	0–0.746	0–0.258	BDL to 0.14	BDL to 42.39	BDL to 17.3	BDL to 4.3
4,4′-DDT	-	0.12–1.2	0–1.311	0–0.826	BDL to 0.03	BDL to 19.73	BDL to 20.6	BDL to 2.4
T-DDT	0.009–0.072	0.18–1.93	0–2.214	0–1.400	BDL to 0.23	BDL to 4.06	-	
α-Endosulfan	-	-	0–0.614	0–0.270	BDL to 0.13	BDL to 1.78	BDL	BDL
β-Endosulfan	-	-	0–0.717	0–0.056	BDL to 0.07	BDL to 11.30	BDL	BDL
T-Endosulfan	BDL to 0.002	-	0–1.331	0–0.027	-	-	-	-
Aldrin	-	-	-	-	BDL to 1.88	BDL to 1.57	BDL to 13.4	BDL

Source: [a]Sarkar et al. (2008)

[b]Guzzella et al. (2005)

[c]Mondal et al. (2018)

[d]Singh et al. (2007)

[e]Raghubansi et al. (2014)

pre-monsoon, monsoon, post-monsoon. The ΣOCPs level varied from about 157.7 to 307.6 ng g^{-1} in pre-monsoon to 195.8 to 577.7 ng g^{-1} in monsoon and 306.9–844.4 ng g^{-1} in the post-monsoon season. Extensive agriculture in Haryana, industrial effluent, sewage discharge can induce ample pesticides cocktail in the Yamuna River (Pandey et al., 2011) (Tables 1 and 2).

Likewise, the Gomti river is also surrounded by pesticide contamination via the settlement of major cities like Lucknow and Jaunpur. A total of 150 MLD mixed wastewater of domestic, industrial, and agricultural input was received by Gomti between Gaughat and mid-Lucknow (Malik et al., 2007). Malik et al. (2007) found aldrin, HCH isomers, HCB, endrin, endosulfan isomers (α and β), DDT isomers/metabolites, dieldrin, endosulfan sulfate, heptachlor, and its metabolites, methoxychlor, α-chlordane, and γ-chlordane at eight different sampling sites in Gomti. ΣOCPs residues ranged between 2.16 and 567.49 ng L^{-1} in river water and 0.92–813.59 ng g^{-1} in the sediment of river Gomti. The maximum detection frequency of α and δ HCH pesticide has been found near the area of mid-Lucknow in river water and sediments. The maximum level of β-HCH (24.21 ± 53.96 ng L^{-1}) was reported in the water sample of Gomti. DDT pollution was found to originate in river catchments from weathered agricultural soils that showed the mark of freshly sprayed DDT (Malik et al., 2007).

The levels of organochlorine pesticides varied from ND (non-detectable) to 38.80 ng L^{-1} for aldrin in Son River, an important tributary of the river Ganga in BR (Mutiyar & Mittal, 2013). In WB near Murshidabad, Ganga splits into two major tributaries:

the Hooghly and the Padma. An experiment has been done by Mondal et al. (2018) to introspect the health of rivers due to pesticide contamination. ∑ DDT (0.838 ± 0.671 ng mL^{-1}) and isomers of DDT 4,4’ -DDT (0.526 ± 0.477 ng mL^{-1}) concentration were reported to be maximum in Hooghly. DDT concentration was found high probably because of old sources and new applications in agriculture as well as vector control for public health (Mondal et al., 2018).

Effect of global climate change on pesticide pollution in a river basin

The global climate is expected to warm in the future, increasing the frequency and intensity of extreme weather (Climate Change, 2013). Climate change can have a direct impact on pesticide contamination of aquatic ecosystems, such as the impacts of warming on pesticide residue decomposition (Kookana et al., 2010) and pesticide transport via changing precipitation patterns (Steffens et al., 2014). Furthermore, higher temperatures are expected to contribute to greater pesticide applications (Delcour et al., 2015) as a result of the increasing demand to control an increased number of pests as a result of climate change (Delcour et al., 2015). However, only a few quantitative estimates have been produced about how pesticide discharge may change in lotic ecosystems as a result of future climate change and how this will affect macroinvertebrate biodiversity and community structure. Freshwater communities in Europe are expected to see a significant rise in pesticide application and the danger of insecticide exposure as a result of future climate change (Kattwinkel et al., 2011).

The Ganga–Brahmaputra Basin was the subject of a pattern analysis by Parajuli et al. (2021), which examined precipitation trends between 1983 and 2020. The study’s findings revealed a 5.8 mm/year decrease in precipitation rates. Declining trends could jeopardize the river ecosystem through a high concentration of pesticide intermix from source discharge in river sediment. It could not be able to dilute the contamination.

Decadal status of persistent organic pesticide level in river Ganga

The aquatic environment is vulnerable to pesticide intrusion through various routes and sources. There are a few major routes of pesticides that are common for water contamination: (i) air–water exchange processes (Guzzella et al., 2011), (ii) malarial combat purposes (Ahad et al., 2010; Tariq et al., 2004), (iii) ponding irrigation, (iv) underground leaching (Flury et al., 1994), (v) unconscious disposal of pesticide containers, (vi) agricultural runoff, and (vii) washing of equipment (Ahad et al., 2010; Tariq et al., 2004).

According to Khuman and Chakraborty (2019), the air and water can exchange persistent pesticide pollutants in the lower stretch to transboundary Ganga. The samples have been collected from four districts, two urban such as North 24 Parganas and Kolkata and two suburban Howrah and Hooghly. Among all these districts average concentration of ∑DDT ranged from 0.88 to 192 ng L^{-1} with a mean concentration of 10 ng L^{-1} and ∑HCHs in Hooghly River varied between 0.5 and 1157 ng L^{-1} with a mean of 41 ng L^{-1}. According to their study, β-hexa chloro hexane and γ-hexa chloro hexane were the most dominant isomers in the Hooghly River. Isomers of DDT like p,p’ DDT and p,p’ DDE and HCH were found dominant in urban sites might be because of prominent use in the last 5 years or maybe some localized point source in Hooghly river (Kumar et al., 2012). The result concluded with the presence of total endosulfan concentration varied between 18 and 106 ng L^{-1} and contributed to nearly half of the entire OCs (organochlorine) concentration in the urban and suburban areas. In this study, α-endo has contributed more than half (55%) of the ∑ENDOs concentration followed by β-endosulfan (37%) and endosulfan sulfate (9%). The supremacy of α-endo in surface water is in line with other studies in Indian rivers such as the Bhagalpur region of river Ganga (Leena et al., 2012).

Middle stretch of Ganga such as Kanpur, Allahabad, and Varanasi region are agglomerate with an abundant population, industrial effluent, and regressing agriculture activities. The Allahabad belt is predominated by an agricultural occupation that promotes the application of pesticide and herbicide in bulk amounts, and further, it reaches in the aquatic system. In a study performed by Raghubansi et al. (2014), pesticide residues of o′p′-DDT, p′p-′DDT, p′p′-DDE, aldrin, α-HCH, β-HCH, and γ-HCH were found in almost every sample of Rasoolabad ghat, Sangam, and Chatnaag Ghat water at a significant level. Investigated result revealed that the residues of concentration of lindane (BDL (below detection limit) to 24.5 ng mL^{-1}) > pp′-DDT (BDL to

20.6 ng mL^{-1}) > o′p′-DDT (BDL to 17.3 ng mL^{-1}) respectively.

Mutiyar and Mittal (2013) reported the detection of pesticides in different states: UK, UP, BR. Results indicated the occurrence of sixteen major OCPs in three states encroaching up to 72% stretch of Ganga. The total pesticide residue level was spotted underneath the safe limit (1 μg L^{-1}) BIS (Bureau of Indian Standard). This is probably the bottled drinking water quality limit and 0.5 μg L^{-1} EU (European Union) standard. In UK stretch, OCPs were perceived, and HCHs were detected in all the samples, but both DDT and heptachlor were not detected in any samples of UK. The concentration of pesticide detection increased significantly in the stretch of UP where endosulfan was perceived in about (75%) > aldrin (11%) > DDT (9%) > HCH (5%) group. The β-endosulfan is the pivotal pesticide, which was found to occur frequently in many of the samples at UP, in relatively higher concentrations (up to 133.11 ng L^{-1}) (Mutiyar & Mittal, 2013).

The concentration of pesticide found in BR was relatively antagonistic to UP. Maximum frequency present was for the aldrin group (34%) > HCHs (21%) > endosulfan (20%) > heptachlor group (13%) > DDT group (12%). Thus, the study concluded with the supremacy of pesticides was different in different states such as HCHs in UK, endosulfan in UP, and aldrin (aldrin and dieldrin) in BR (Mutiyar & Mittal, 2013). Endosulfan (783 ng L^{-1}) use was majorly present in BR (Bhagalpur) followed by DDT group (489 ng L^{-1}) and HCH (74.04 ng L^{-1}) among the tested pesticides (Mutiyar & Mittal, 2013). Some studies have happened in WB stretch; Chakraborty et al. (2014) found many OCPs and their isomers at the mouth of Ganga distributaries near the tip of Bay of Bengal BDL to 114 ng L^{-1} in the order of maximum concentration Heptachlor > HCH > DDT > dieldrin > aldrin > endosulfan. Aforesaid studies reveal the supremacy of different pesticides in different states (Tables 1 and 2).

Global trend of pesticidal contamination in river

Along with India, the pollution of pesticides touches numerous important rivers around the globe. In a study done by Navarro et al. (2010) on Ebro River basin pesticide contamination, a study has done between 2004 and 2006 in an industrial-influenced area, where the concentration of organophosphorus, acetanilids, tributyl phosphate, octyl phenol, and nonylphenol were found between 0.005 and 2.575 μg/L. Ccanccapa et al. (2016) analyzed 50 pesticides in the Ebro River basin, Spain in water, sediment, and biota. Results illustrated the pathetic condition of the river; Imazalil and Diuron were found to be at levels of 409.73 ng/L and 150 ng/L, respectively; and a significant amount of chlorpyrifos, diazinon, and carbendazim was also frequently detected. A similar situation was observed in Owan River, Edo state, Nigeria, where a high concentration of bezenehexachloride was reported in river water (Ogbeide et al., 2015, Richards et al., 2022). The concentration of α-BHC, β-BHC, γ- BHC varied from ND-0.43 μg/L. According to the above-mentioned studies, global river water recites similar pesticide contamination like Ganga (Tables 1 and 2).

Ecological risk assessment

Ecological risk assessment, a key procedure analyzing the potential detrimental environmental impact of the resistant pesticide inflicting harmful effects on non-target organism, is receiving more and more attention. Ecological risks of pollutants to ecosystems are commonly analyzed using different methodologies (Mansano et al., 2016; Thomaidi et al., 2017; Qian et al., 2017) to provide a more thorough and trustworthy forecast of risks and uncertainties. The calculation of risk quotients is based upon ecological impacts data, pesticide use statistics, fate and transport data, and estimates of exposure to the pesticide (USEPA, 2017).

The conventional risk assessment methodologies concentrate on the projections of risk of a specific type of chemical. Such analysis may depreciate the risk of an environment that frequently confronts to chemical mixture rather than a single component (Cao et al., 2021; Wang et al., 2022). In mixture risk assessment, a chemical with beneath (NOEC) no observed effect concentration can generate a synergistic effect. Therefore, ecological risk assessments (ERA) of simultaneously exposed contaminates based on the mixture risk models (MRM) can provide accurate estimates of numerous chemical pollutants (Zheng et al., 2016). The significant MRM is a two-tiered structure. In the two tires, it primarily improves the use of (1) available exposure data and (2) single chemical toxicity data, and lastly, it conveys an estimate of the risk quotient by adding up the measured environmental

Table 2 A comparative table of pesticide concentration in water and sediment of Ganga and its major tributaries or distributaries

Pesticide	Yamuna water ng/ml[a]L	Yamuna sediment ng/g[b]	Yamuna water ng/ml[c]	Yamuna sediment ng/g[d]	Gomti water ng/ml[e]	Gomti sediment ng/g[a]	Gomti water ng/ml[b]	Gomti sediment ng/g
	Before 2011		After 2011		Before 2011		After 2011	
α- HCH	BDL to 0.166	0.24–25.49	BDL to 0.067	135–248	BDL to 0.0445	BDL to 32.06	BDL	-
β-HCH	0.012–0.242	0.37–27.85	BDL to 0.165	37–48	BDL to 0.301	BDL to 14.88	BDL	-
γ-HCH	BDL to 0.207	0.31–30.27	BDL to 0.220	73–81	BDL to 0.063	BDL to 30.39	BDL	-
δ-HCH	BDL to 0.058	0.11–20.99	-	12–35	BDL to 0.098	BDL to 81.23	BDL	-
T-HCH	0.012–0.593	-	BDL to 0.285	-	-	-	-	-
2,4′-DDE	BDL to 0.006	-	-	-	-	-	-	-
4,4′-DDE	0.0228–0.402	-	BDL to 0.146	-	BDL to 0.010	BDL to 14.03	BDL to 129	-
2,4′-DDD	BDL to 0.17	-	-	-	-	-	-	-
4,4′-DDD	BDL to 0.057	-	BDL to 0.070	-	BDL to 0.015	BDL to 95.73	BDL	-
2,4′-DDT	BDL to 0.02	-	-	-	BDL to 0.068	BDL to 345.66	BDL	-
4,4′-DDT	0.025–0.470	-	BDL to 0.23	-	BDL to 0.013	BDL to 206.12	BDL	-
T-DDT	0.066–0.722	-	BDL to 0.354	-	-	-	-	-
α-Endosulfan	-	-	-	-	BDL to 0.087	BDL to 1.00	BDL to 127	-
β-Endosulfan	-	-	-	-	BDL to 0.005	BDL	BDL	-
T-Endosulfan	-	-	-	-	-	-	-	-
Aldrin	-	-	-	-	BDL to 0.077	BDL to 10.89	BDL to 24	-

Source: [a]Kaushik et al. (2008)
[b]Pandey et al. (2011)
[c]Kumar et al. (2012)
[d]Verghese (2015)
[e]Malik et al. (2009)
[f]Trivedi et al. (2016)

concentrations to the predicted no-effect concentration ratios ($RQ_{MEC/PNEC}$) or toxic units (RQ_{STU}) (Table 3).

Risk assessment of pesticide

The ecological risk assessment of pesticide is estimated by RQ (risk quotient) (Palma et al., 2014).

$$RQ = \frac{MEC}{PNEC}$$

MEC is the maximum and mean detected concentration of pesticides.

PNEC symbolizes the concentration of pesticides predicted to have no effect.

Table 3 Studies of ecological risk assessment in Ganga

S.N	Study area	Ecological risk assessment	References
1	Upper zone (Uttarakhand), upper middle zone (Uttar Pradesh),upper middle zone (Uttar Pradesh), lower middle zone (Bihar), lower zone (west Bengal)	Ecological risk (> 1) at entire studied sites for p, p′ DDE Lower zone found high ecological risk zone	Sah et al. (2020)
2	Hoogly river water	Risk quotient (RQ) (fish) = T-endosulfan (1220) = chronic RQ (fish) = phorate = (0.015) = chronic RQ (fish) = T-HCH (0.686) = acute RQ (fish) = T-endosulfan (0.061) = Acute	Mondal et al. (2018)
3	Middle stretch (Ganga in Uttar Pradesh) (aquatic fishes and invertebrates)	RQ = (> 1)	Shah and Parveen (2021)
4	Varanasi and Prayagraj	RQ = (< 1)	Satyanarayana et al. (2023)

The no-observed-effect concentration (NOEC) of sensitive species is used to figure out the PNEC.

In the risk assessment study, the PNEC values were based on the NOEC values of the pesticide for 3 trophic levels: (1) the primary producer (2) the primary consumer (3) the secondary consumer. According to Palma et al. (2014) and Zheng et al. (2016), the risk ratio results were put into four risk levels:

Negligible risk ($RQ < 0.01$)
Low risk ($0.01–RQ < 0.1$)
Medium risk ($0.1–RQ < 1$)
High risk ($RQ \geq 1$)

The presence of DDT and aldrin at the middle Indo Gangatic plain poses a high risk, i.e., RQs > 1 for both average (RQm using mean MEC) and worst-case scenarios (RQex using maximum MEC) (Shah & Parveen, 2022). Toxicity assessments of exposed pesticide are important for reducing risks, making laws, and policy (Alengebawy et al., 2021). Pesticides have toxicological and eco-physiological effects synergistically and cause concern (Johns et al., 2012). To alleviate the risk factor, monitoring and management of the environment are necessary. Risk assessment and management will positively affect water quality, aquatic life, and the health of the public. Along with environmental quality, risk assessment is important for making standards and guidelines that help people make good decisions in different areas.

Risk characterization

(a) Single pesticide

Risk quotient (RQ) and toxicity-exposure ratio (TER) are common assessment methods for ecological risk evaluation (Bhandari et al., 2021). Calculating TER will establish a relation between toxicity and exposure (Bhandari et al., 2021). The TER for each pesticide was estimated by using the TER for the test organisms ($TER_{species}$) and the following Eq. (1).

$$TER\ species = \frac{NOE\ C\ species}{MSCmaximum\ or\ mean} \quad (1)$$

where NOEC stands for no observed effect concentration, and MSC denotes measured pesticide concentration.

EC (2002) established threshold values of 5 and 10 for chronic and acute soil toxicity, respectively. If the TER exceeded the cut-off values, the pesticide risk was deemed minimal. TER values of ≥ 10 or ≥ 5, which are appropriate acute and chronic exposure at threshold values respectively, and showed a tolerable risk for the organisms (JaabiriKamoun et al., 2018).

(b) Cocktail of pesticide

The concentration addition (CA) approach has been used for calculating the toxicity of pesticide mixtures (Bhandari et al., 2021; Hadrup et al., 2013). Multiple pesticide exposures can lead to concentration addition approach (Hadrup et al., 2013). The RQ_{mix}(RQ mixture) of the cocktail of pesticide was estimated by summing up RQ_i of each pesticide. The total risk assessment of multi-pesticide residue of a site ($\sum RQ_{site}$) was evaluated using concentration addition (CA) based on the mixture risk assessment (Bundschuh et al., 2014). In ecotoxicological analysis, concentration addition is suitable model because its assumption include pesticide in a cocktail (Escher et al., 2020) have the same mode of action which equated in Eq. 2.

$$\sum(RQ_{site})OR\sum(RQ_{mix}) = \sum_{k=1}^{n} RQ_i = \sum_{k=1}^{n}(MSC_i/PNEC_i) \quad (2)$$

where,

MSC_i = measured soil concentration of a pesticide i.

n = number of pesticides.

$PNEC_i$ = predicted no-effect concentration of a pesticide i.

RQ_{site} = risk quotient of a site.

RQ_{mix} = risk quotient of pesticide mixtures.

RQ_i = risk quotient of a pesticide i.

Risk assessment impact crucially on whole water quality and public health concern because it will further help in designing of policy development, guidelines, and standards for living beings. In extended research, this review will fill the gap of policy-making and sustainable goals achievement for "Aviral" and " Nirmal" Ganga.

Future research prospect

In the outcome of an extensive literature review, we have noticed the vital gaps as per our present understanding that opens a wide spectrum of future research:

1. Real-time monitoring of pesticide concentrations in Ganga and its tributaries is necessary specially in Bihar and Jharkhand.
2. Identification of zone of urgent actions.
3. Evaluate the effect of pesticide risk assessment on human health.
4. Estimation of uncertainty as well as variability-related ecological risk assessment.
5. To understand the fate of pesticide load, concerted research is a demand of time. There have been several studies done on hydrology and hydro-geochemistry, but meager research has been done from 2013 to 2022 on the Ganga River basin on pesticide contamination other than organochlorine.
6. There is no study available on riverine agriculture and their biomagnification contamination rate.

Conclusion

The presented review is extensively focused on the decadal trend of pesticide adulteration in Ganga and its tributaries compared with major global rivers. It covers sources of contamination, role of tributaries in the transportation, and contribution of toxicants in the mainstream from agricultural landscapes. The presence of isomers of HCH and DDT has been reported maximum in UP, BR, and WB. Before 2011, the concentration of pesticide was elevated in Ganga water of UP stretch > WB > BR > UK. The risk quotient analysis should be less than 1, but lower stretches of river Ganga were found to be higher ecological risk zone.

Pesticide residues and their rate of persistence in the environment are high, thereby promoting the increased spread in the streams. Climate change, lack of rainfall, and demand for food invoke pesticide use in agriculture. However, there is a dearth of data on the actual figures of pesticides in Ganga water and major tributaries in recent decades in the UK, BR, and WB after 2011. Previous studies were majorly based on pesticide concentration, but this review suggests the different ecological risk assessment methods such as RQ and TER evaluation of single pesticide contamination and concentration addition (CA) approach for cocktail of pesticide. This review is an attempt to present emerging concern after numerous establishments of STPs, policy making, etc. In the future, (1) a detailed risk assessment of the entire stretch of Ganga and (2) impact and bioaccumulation of pesticide in the food chain will be highly appreciated.

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