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Pesticide Residues Removal Efficiency in Conventional Water Treatment Plants Along the Ganga Basin: A Comprehensive Assessment of Treatment Mechanisms and Seasonal Variability

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Abstract

This study evaluates pesticide contamination and removal efficiency across twelve conventional water treatment plants (WTPs) in West Bengal, India, serving populations drawing from the Ganga River and its tributaries (Hooghly, Bhagirathi, Fulhar) as well as non-Gangetic rivers (Barakar, Pagla). Between November 2023 and September 2025, seventeen pesticide compounds were monitored in raw and treated water using GC-MS/MS analysis (detection limit 0.0001 µg/L) with a total 1241 tests were performed. All WTPs employ conventional treatment trains: pre-chlorination (Cl_2) → coagulation-flocculation (ferric alum >15 mg/L) → clarification → rapid sand filtration (3,000-6,000 L/hr/m²) → post-chlorination (45 min contact). Results demonstrate exceptional removal efficiencies (96-99%) for organophosphates (malathion, chlorpyriphos, parathion-methyl) and moderate-to-high efficiency (93-100%) for organochlorines (DDT isomers, HCH isomers, endosulfan). Complete removal (>99.99%, below detection limit) was achieved for delta-HCH, endosulfan-1, and endosulfan-2. Raw water concentrations complied with IS 10500:2012 standards, with malathion being the most frequently detected pesticide (reflecting current agricultural use), followed by pp-DDT and chlorpyriphos. Legacy organochlorines (DDT, HCH, endosulfan) persisted despite 15–35-year bans, indicating sediment remobilization and potential illegal use. Also Seasonal analysis also revealed similar removal efficiency for all the pesticide residue under study. Treated water pesticide concentrations (0.0001-0.003 µg/L) pose negligible individual health risks (hazard quotients 0.0001-0.0003), though mixture toxicity considerations and vulnerable population exposures warrant advanced treatment implementation. This study provides the first comprehensive dataset on pesticide fate through conventional treatment in the Ganga basin, demonstrating that properly operated conventional systems achieve removal efficiencies.

1. Introduction

The Ganga River basin, home to more than 500 million individuals, ranks among the most densely populated and agriculturally intensive regions globally (Sharma et al., 2014). In the wake of India's Green Revolution, agricultural intensification led to the extensive use of pesticides. In West Bengal alone, an estimated 15,000 to 20,000 tonnes of pesticides are applied annually over approximately 5.8 million hectares of farmland (Bhattacharyya et al., 2015). This widespread application has resulted in the contamination of surface water with pesticide residues, posing considerable difficulties for drinking water treatment plants. These facilities, which predominantly rely on conventional treatment methods optimized for removing turbidity and microbial contaminants, are often ill-equipped to effectively eliminate synthetic organic compounds such as pesticides.

Pesticides detected in Indian surface waters include organophosphates (malathion, chlorpyriphos, parathion-methyl, ethion), organochlorines (DDT isomers, HCH isomers, endosulfan), and herbicides (atrazine, alachlor, butachlor). Despite bans on DDT (1989), lindane (2001), and endosulfan (2011) in India, these persistent organic pollutants (POPs) continue appearing in water bodies due to environmental persistence (soil half-lives 2-15 years), sediment remobilization during monsoons, and illegal/stockpiled use (Jayaraj et al., 2016). Current-use organophosphates, while less persistent (aquatic half-lives 1-50 days), undergo continuous application requiring 4-6 spray cycles per crop season, creating ongoing contamination pulses (Bondarenko & Gan, 2004).

Conventional water treatment processes—coagulation, flocculation, sedimentation, filtration, and disinfection—were not specifically designed for pesticide removal, yet fortuitously achieve significant reductions through multiple mechanisms. Pre-chlorination oxidizes organophosphates via electrophilic substitution and nucleophilic addition reactions, converting parent compounds to less toxic or more readily removed metabolites (Acero et al., 2008). Coagulation with aluminium or iron salts removes hydrophobic pesticides (log K_ow >3) through adsorption onto metal hydroxide precipitates, with removal efficiency correlating positively with pesticide hydrophobicity and coagulant dose (Chowdhury et al., 2013). Biological degradation in sand filter biofilms contributes additional removal for biodegradable compounds like atrazine and organophosphates (Zearley & Summers, 2012).

Despite these mechanisms, conventional treatment shows variable efficiency depending on pesticide physicochemical properties, raw water quality (pH, turbidity, natural organic matter), and operational parameters (coagulant dose, contact times, filtration rates). Published studies report removal efficiencies ranging from 40% (atrazine, log K_ow 2.61) to >95% (chlorpyriphos, log K_ow 4.96) in optimized conventional systems (Westerhoff et al., 2005; Sharma et al., 2012). However, comprehensive data on pesticide fate through conventional treatment in tropical/subtropical Gangetic systems remain limited, with most published research focused on temperate climates or single-pesticide investigations.

From a toxicological perspective, even low-level pesticide exposures (µg/L range) warrant concern due to endocrine disruption, neurodevelopmental effects, and carcinogenic potential. Organophosphates inhibit acetylcholinesterase at chronic low doses, with prenatal chlorpyriphos exposure associated with reduced IQ (-2 to -5 points) and increased ADHD prevalence in children (Rauh et al., 2011). Legacy organochlorines bioaccumulate in food chains and exhibit estrogenic activity, with DDT metabolites linked to breast cancer risk and reproductive dysfunction (Cohn et al., 2015). Mixture toxicity from simultaneous exposure to multiple pesticides with common mechanisms (e.g., AChE inhibitors) may produce cumulative effects exceeding individual compound risk assessments (Silva et al., 2002). These

health considerations underscore the importance of optimizing treatment processes and implementing source water protection strategies to minimize pesticide exposure via drinking water.

This study addresses critical knowledge gaps by: (1) characterizing pesticide occurrence patterns across Gangetic and non-Gangetic surface water sources in West Bengal; (2) quantifying removal efficiencies for seventeen pesticides through conventional treatment under varying seasonal conditions; (3) elucidating mechanistic pathways responsible for pesticide removal; (4) identifying operational parameters and water quality factors influencing treatment efficacy; and (5) providing evidence-based recommendations for process optimization and advanced treatment implementation. The findings inform water utility managers, environmental regulators, and public health officials in developing integrated strategies for pesticide risk management in large-scale conventional treatment systems.

2. MATERIALS AND METHODS

2.1 Study Sites and Water Sources

Twelve water treatment plants (WTPs) in West Bengal were monitored from November 2023 to September 2025. Ten facilities draw from Gangetic sources: main-stem Ganga (Dariapur WTP), Hooghly River (Mangal Pandey, Bhagyabantapur & Belpukur WTPs), Bhagirathi-Hooghly River (Dakshin Raipur, Kamalnagar, Kashiadanga & Murshidabad WTPs), and Fulhar tributary (Balupur & Mathurapur WTPs). Two non-Gangetic facilities draw from Barakar River near Asansol (Kalyaneshwari WTP) and Pagla River near Malda (Gour WTP). These rivers drain predominantly agricultural watersheds cultivating rice, wheat, jute, and vegetables with varying pesticide application intensities. The Gangetic WTPs serve urban/peri-urban populations totalling approximately 5-8 million, while non-Gangetic facilities serve 0.5-1 million combined. Climatic conditions are subtropical monsoon with distinct seasons: winter (December-February, 15-25°C), summer (March-May, 30-45°C), pre-monsoon (May-June), monsoon (June-September, 75-80% annual rainfall), and post-monsoon (October-November).

Table 1: Different Water Treatment Plants used in study with their location.

Different Water Treatment Plants with associated Rivers and their location.				
SL No	**Water Treatment Plant Name**	**River in which intake is Present**	**District**	**Location (Latitude and Longitude)**
WTPs considered in study under maintenance of WBPHED on Ganga and its tributaries:				
1	Dakshin Raipur WTP	Bagirathi Hooghly	South 24 Parganas	22.3997256, 88.1551426
2	Dariapur WTP	Ganga	Malda	24.8311774, 87.990946
3	Mathurapur WTP	Fulhar (Tributary of Ganga)	Malda	25.0976229, 87.8912902
4	Balupur WTP	Fulhar (Tributary of Ganga)	Malda	25.1816116, 87.8896573
5	Mangal Pandey WTP	Hooghly	North 24 Parganas	22.7911185, 88.3504869
6	Kamalnagar WTP	Bhagirathi Hooghly	Nadia	23.5305685, 88.3607708

7	Kashiadanga WTP	Bhagirathi Hooghly	Nadia	23.5599614, 88.3431327
8	Bhagyabantapur WTP	Hooghly	Nadia	23.6998466, 88.131143
9	Belpukur WTP	Hooghly	Nadia	23.4805567, 88.3962355
10	Murshidabad WTP	Bhagirathi Hooghly	Murshidabad	24.2639588, 88.0315398
WTPs considered in study under maintenance of WBPHED beyond Ganga and its tributaries:				
2	Kalyaneshwari WTP	Barakar	Paschim Bardhhaman	23.7753719, 86.8305214
3	Gour WTP	Pagla	Malda	24.846118, 88.124458

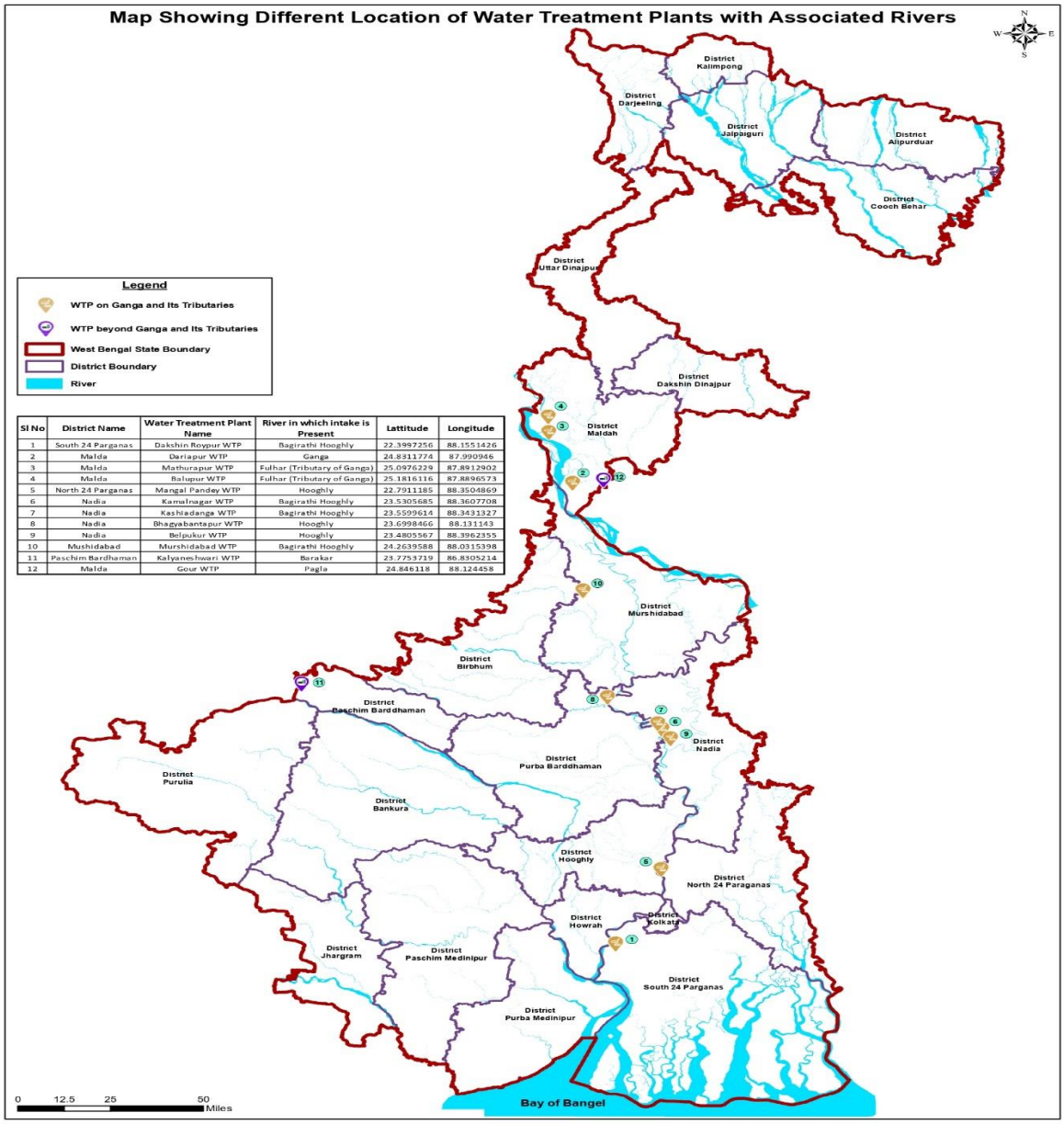


Figure 1: Above showing different locations of WTPs considered in the study as per Table 2

2.2 Treatment Process Configuration

All WTPs employ conventional treatment trains with identical process sequences but varying capacities (50-154.36 MLD). Raw water from river intakes undergoes:

Pre-chlorination: Chlorine gas (Cl_2) addition achieving 0.2-0.5 mg/L residual after contact time in inlet channels. Dosing targets 0.2 mg/L minimum residual at consumer endpoints, requiring initial doses of 1-2 mg/L depending on water temperature and organic load (derived from chlorine Demand analysis of corresponding WTPs).

Coagulation-Flocculation: Ferric alum ($Fe_2(SO_4)_3 \cdot nH_2O$, Grade IV) is dosed at concentrations more than 15 mg/L, based on optimum dose determined through JAR Testing with respect to pH and turbidity analysis. Coagulant dispersion is achieved via flash mixing in rapid mix chambers, with a detention time of 30–60 seconds, initiating the formation of ferric hydroxide ($Fe(OH)_3$) precipitates. Subsequently flocculation takes place in Clari-flocculators, where gentle mixing (G = 20-50 s^{-1}) is maintained for 20–30 minutes to catalyse floc formation, followed by sedimentation under surface loading rates of 40–60 $m^3/m^2/day$. The system operates within a naturally sustained pH range of 6.5–8.0, which eliminates the need for external pH adjustment.

Clarification: Hydraulic settling in Clari flocculator zones removes flocculated particles, achieving effluent turbidity <10 NTU. Settled sludge periodically removed through manual or automated desludging systems.

Rapid Sand Filtration: Dual-media or sand-only filters (0.5-1.0 m bed depth, 0.45-0.55 mm effective size) operate at 3,000-6,000 L/hr/m^2 loading rates per CPHEEO Manual on Water Supply guidelines. Filter runs typically 24-72 hours until terminal head loss reached; backwashing with air scour and water at 10-15 $m^3/hr/m^2$ for 10-15 minutes. Filter effluent turbidity consistently <1 NTU.

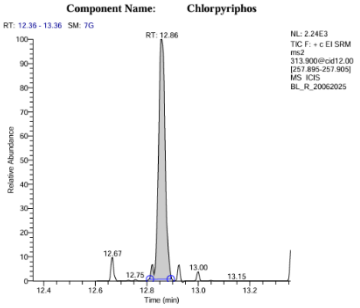
Post-chlorination: Secondary Cl_2 (gaseous form mostly) dosing achieving 0.5-1.0 mg/L residual in clear water reservoirs with 30 to 45-minute contact time before distribution. Combined pre- and post-chlorination provides multiple disinfection barriers and enhanced organophosphate oxidation.

2.3 Sampling Protocol and Analytical Methods

Paired raw water (intake) and treated water (clear water reservoir) samples were collected during multiple campaigns spanning both wet and dry seasons: pre-monsoon (November 2023 to June 2025, 15 sampling events across WTPs) and monsoon (June to September 2025, 13 sampling events). Sampling followed IS 3025 standards using pre-cleaned amber glass bottles (1 L) with Teflon-lined caps to prevent contamination and photodegradation. Samples were preserved at 4°C with 0.008% sodium thiosulfate to quench residual chlorine, transported within 6 hours to the analytical laboratory, and extracted within 48 hours.

Pesticide analysis employed solid-phase extraction (SPE) using C18 cartridges followed by gas chromatography & mass spectrometry (GC-MS/MS). The C18 cartridges were conditioned with methanol and ultrapure water. 1000 ml Sample were passed at a flow rate of 5–10 mL/min, after which the cartridges were dried under vacuum and eluted with ethyl acetate/dichloromethane (1:1, 10 mL). Extracts were concentrated to 1 mL under a nitrogen evaporator and analysed using a Thermo Scientific Trace 1310 gas chromatograph coupled to a TSQ 9000 triple quadrupole mass spectrometer. Chromatographic separation was achieved using a TG-5MS column (30 m × 0.25 mm × 0.25 µm) with helium as the carrier gas (1.2 mL/min constant flow). The oven temperature program was: 60°C (1 min hold), ramped at 25°C/min to

180°C, then at 5°C/min to 280°C (5 min hold). Mass spectrometry was operated in electron ionization mode (70 eV) with multiple reaction monitoring (MRM) for quantification and confirmation transitions



Seventeen pesticides were quantified: organophosphates (chlorpyriphos, malathion, parathion-methyl, ethion, phorate), organochlorines (alpha-HCH, beta-HCH, delta-HCH, lindane/gamma-HCH, pp-DDT, op-DDT, endosulfan-1, endosulfan-2, endosulfan sulfate), and herbicides (atrazine, alachlor, butachlor). Method detection limits were 0.0001 µg/L for all compounds. Calibration used five-point curves (R^2>0.995) with isotopically labelled internal standards. Quality control included method blanks (every 10 samples), matrix spikes (recovery 85-115%), and laboratory duplicates (RSD <20%). Analytical accuracy was confirmed through external proficiency testing (PT) and the use of certified reference materials (CRMs) sourced from ISO 17034-accredited reference material producers (RMPs)

Total 1241 Tests were conducted on Raw Water and Treated Water in this study.

2.4 Data Analysis

Removal efficiency was calculated as: % Removal = [(C_raw - C_treated) / C_raw] × 100, where C_raw and C_treated are pesticide concentrations in raw and treated water, respectively. Concentrations below detection limit (0.0001 µg/L) were assigned as <MDL for statistical purposes. Seasonal comparisons used paired t-tests for pre-monsoon versus monsoon concentrations. Graphs were plotted in MS Excell and removal efficiency and trends were observed and reported.

3. RESULTS AND DISCUSSION

3.1 Pesticide Occurrence in Raw Water and Treated water, Seasonal Variability and Monsoon Effects and Treatment Removal Efficiency

Figure 2: Pesticide Residue in µg/L found in Raw water in different WTPs on Ganga and its tributaries tested between 28.11.24 to 19.06.2025

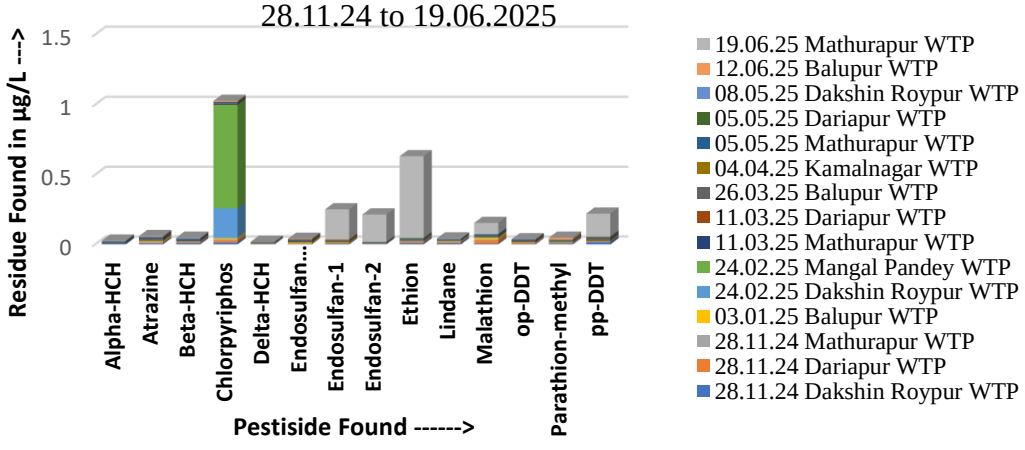


Figure 3: Pesticide Residue in µg/L in Treated water in different WTPs on Ganga and its tributaries tested between 12.05.2023 to 19.06.2025

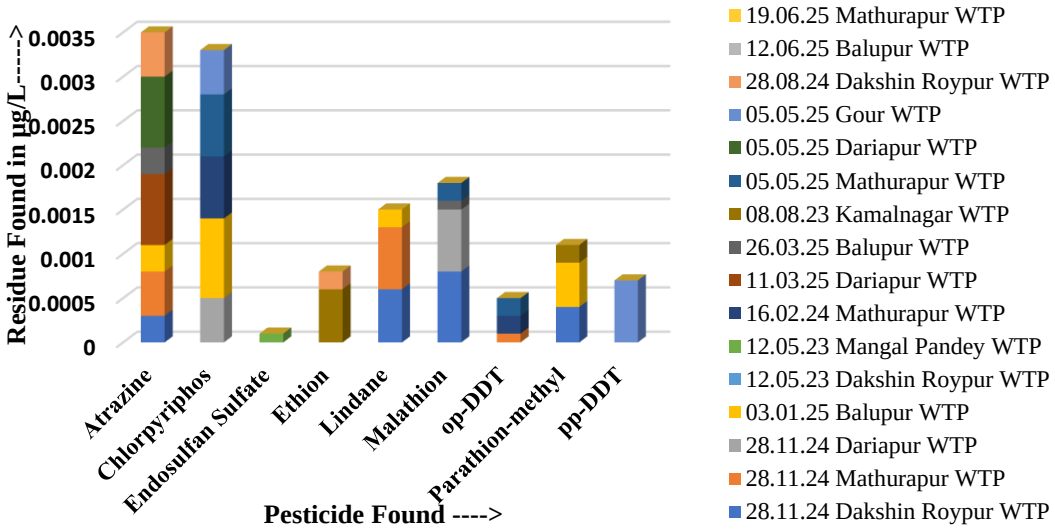


Figure 4: Pestiside Residue in µg/L found in Raw Water in different WTPs on Ganga and its tributaries tested between 19.06.2025 to 02.09.2025

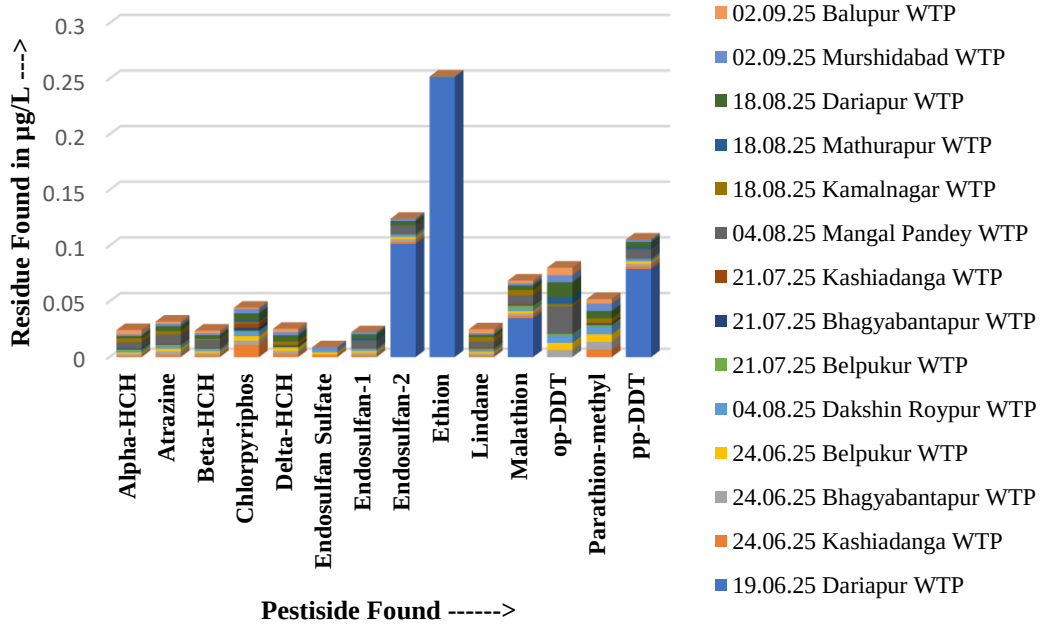


Figure 5: Pesticide Residue in µg/L in Treated water in different WTPs on Ganga and its tributaries tested between 19.06.2025 to 02.09.2025

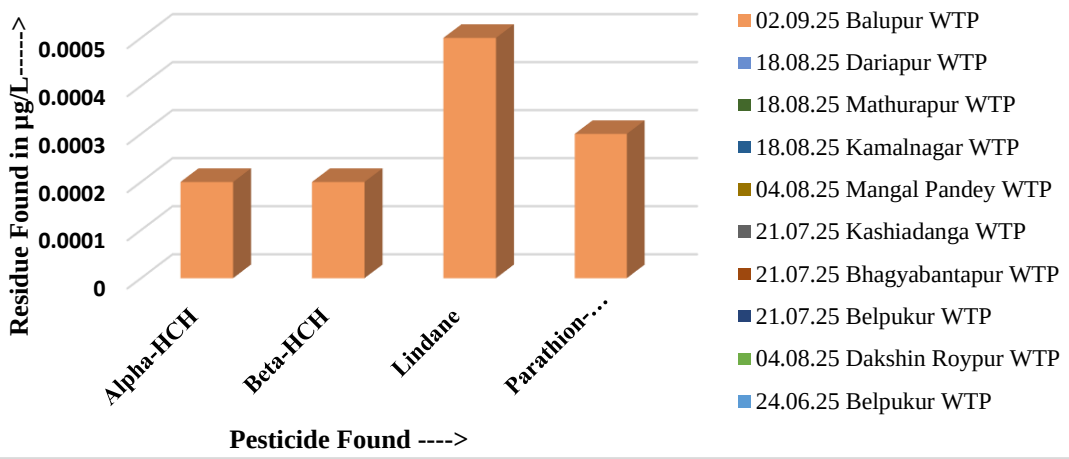


Figure 5.1: **Average % Removal of Pesticide Residue in different WTPs on Ganga and its tributaries tested between 12.05.2023 to 19.06.2025**

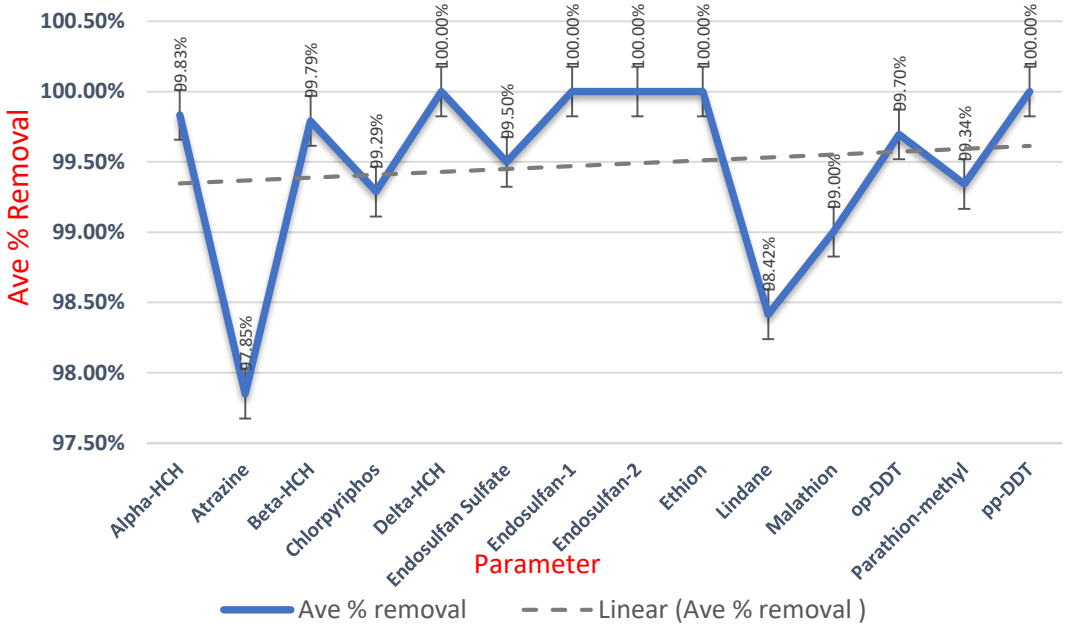
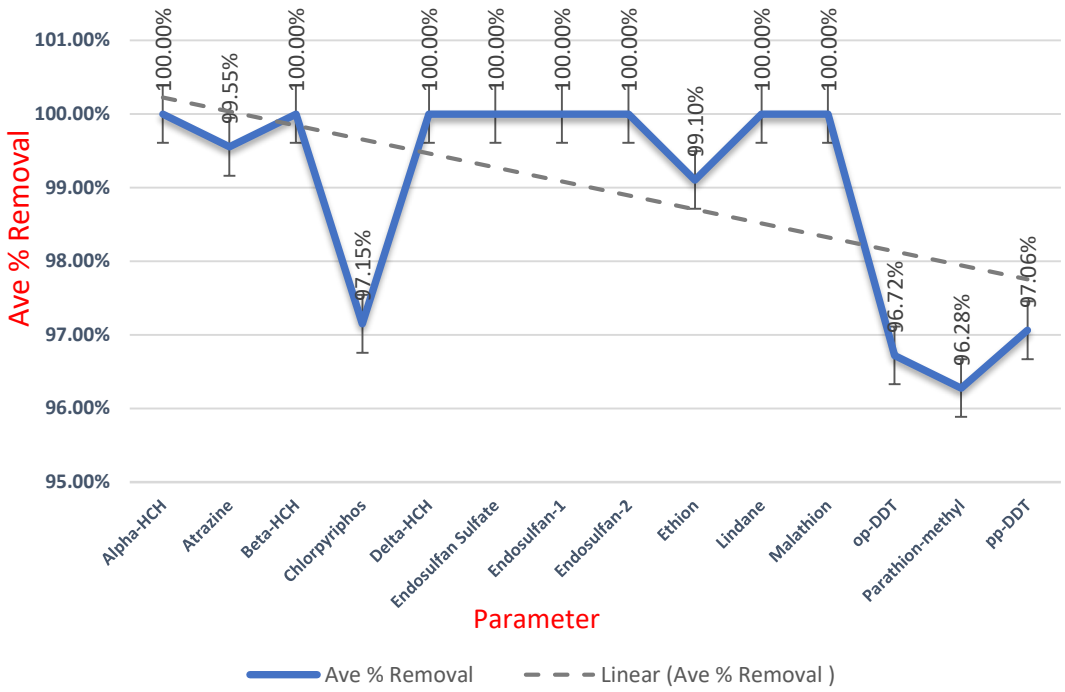
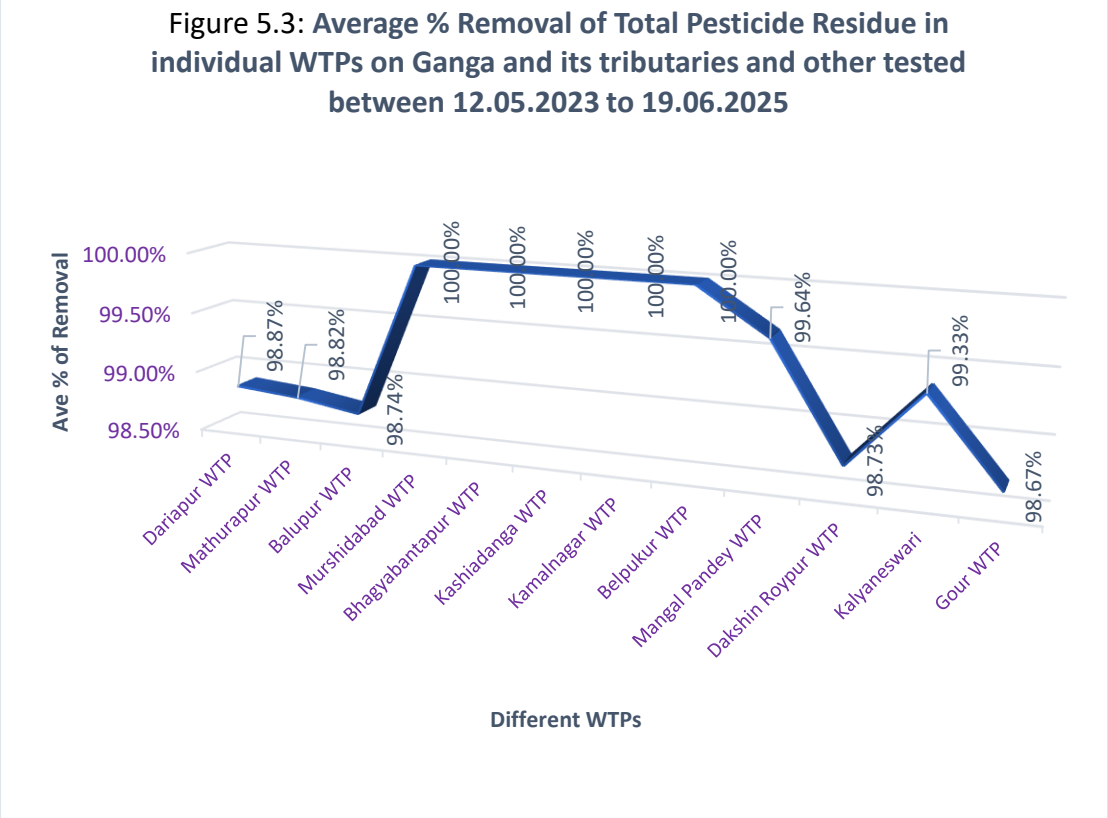


Figure 5.2: **Average % Removal of Pesticide Residue in different WTPs on other than Ganga and its tributaries tested between 12.05.2023 to 19.06.2025**



All Pesticides concentration in µg/L, found in Raw water are below the permissible limit given in IS 10500: Reaffirmed in 2023 as shown in Figure 2 and Figure 4 respectively. Alachlor, Butachlor & Phorate is not Present in the intake Raw Water in 10 WTPs connected to Ganga and its tributaries like Bagirathi, Hooghly etc as shown in Figure 2 and Figure 4 respectively. Malathion is most occurring Pesticide found in Raw Water, followed by pp-DDT, Atrazine and Beta HCH as shown in Figure 2 and Figure 4 respectively. Chlorpyriphos followed by Ethion, Endosulfan-2 and pp-DDT are present in good concentrations as compared to other Pesticides as shown in Figure 2 and Figure 4 respectively. After Treatment in WTPs Delta HCH, Endosulfan 1 & Endosulfan 2 and phorate does not appear in Treated Water (100% removal) in Figure 3 & 5, 5.1 to 5.3 respectively. The concentration of Atrazine, Chlorpyriphos, Endosulfan Sulfate, Ethion, Lindane, Malathion, op-DDT, Parathion-methyl and pp-DDT concentrations were reduced from 96% to 99% from 28.11.2024 to 19.06.2025 as shown in Figure 3, 5 & 5.1 to 5.3 respectively. During the monsoon period this year (June to September in West Bengal), pesticide concentrations in raw water showed a marked decline across most locations. Consequently, treated water samples from the majority of water treatment plants (WTPs) exhibited pesticide residues below detection limits (BDL), with the exception of Balupur WTP, as illustrated in Figures 3 and 5. Atrazine followed by Chlorpyriphos is most occurring Pesticide found in Treated Water during pre-monsoon Sean, however, during monsoon season Alpha HCH, Beata HCH, Parathion-methyl and Lindane is most occurring in same proximity in Treated Water.



For Figure 5.1 to 5.3 only those data set were considered in which both Raw and Treated water sample from concerned WTPs were tested in same date.

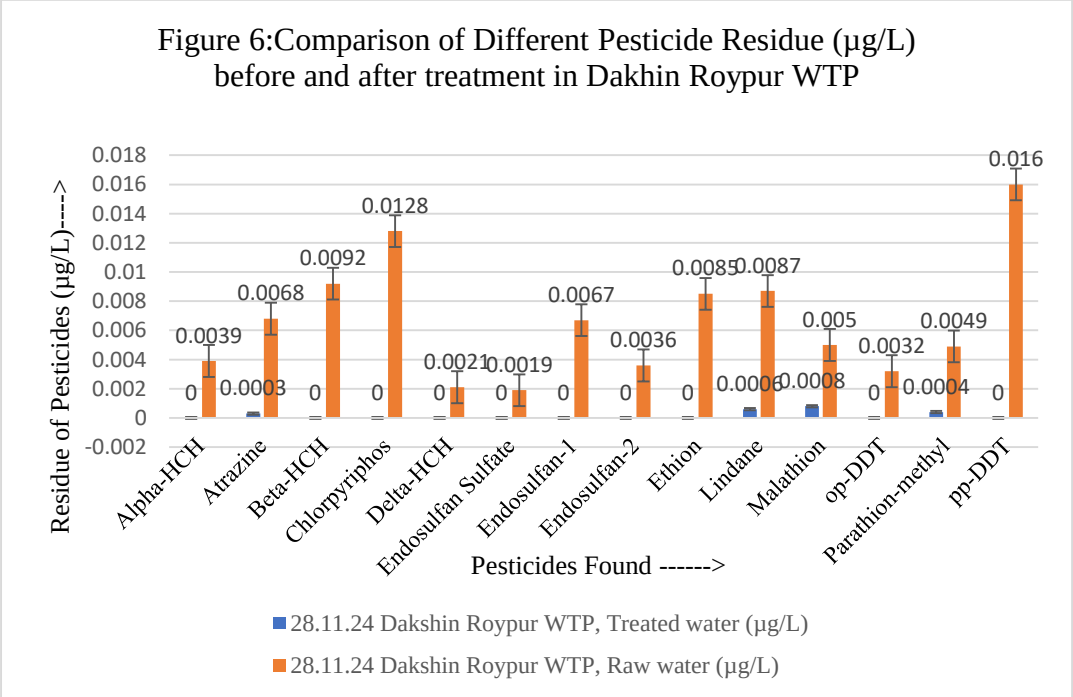
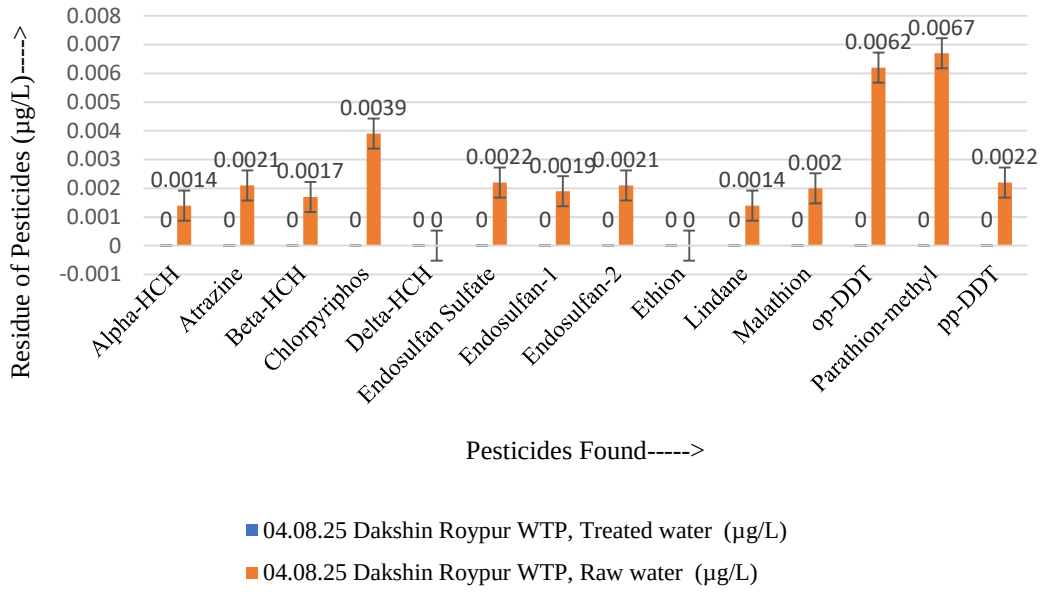


Figure 7:Comparison of Different Pesticide Residue (µg/L) before and after treatment in Dakhin Roypur WTP



Above figures (6 & 7) shows Pesticide Residue in µg/L comparison between Raw water sample from intake of Dakhin Raipur WTP and subsequent treated water sample from Clear Water Reservoir on 28.11.24 and 04.08.25 respectively. The sample tested on 28.11.24 had very few concentrations of Atrazine, Lindane, Malathion and Parathion-methyl, which were reduced by 84% (in case of Malathion), 91% (for Parathion-methyl), 93% (for Lindane) and 95% (for Antrazine) respectively as shown in Figure 6 and Figure 7 respectively. During monsoon period (June to September), comparison of figure 6 and Figure 7 shows that the concentration of Pesticide in raw water in case of Alpha-HCH, Atrazine, Beta-HCH, Chlorpyriphos, Delta-HCH, Endosulfan-1, Endosulfan-2 ,Ethion ,Lindane, Malathion, pp-DDT reduced by 75% also few pesticides like Endosulfan Sulfate, op-DDT, Parathion-methyl showed an increase in concentration with an average percentage of 48%. In sample taken on 04.08.25 (during monsoon period this year i.e. 2025) the treated water shows no presence of Pesticides.

Figure 8: Pesticide Residue found in Raw Water Sample Prior to Treatment and after the Treatment in WTPs (in non Gangetic Rivers) from 28.11.2024 to 18.08.2025

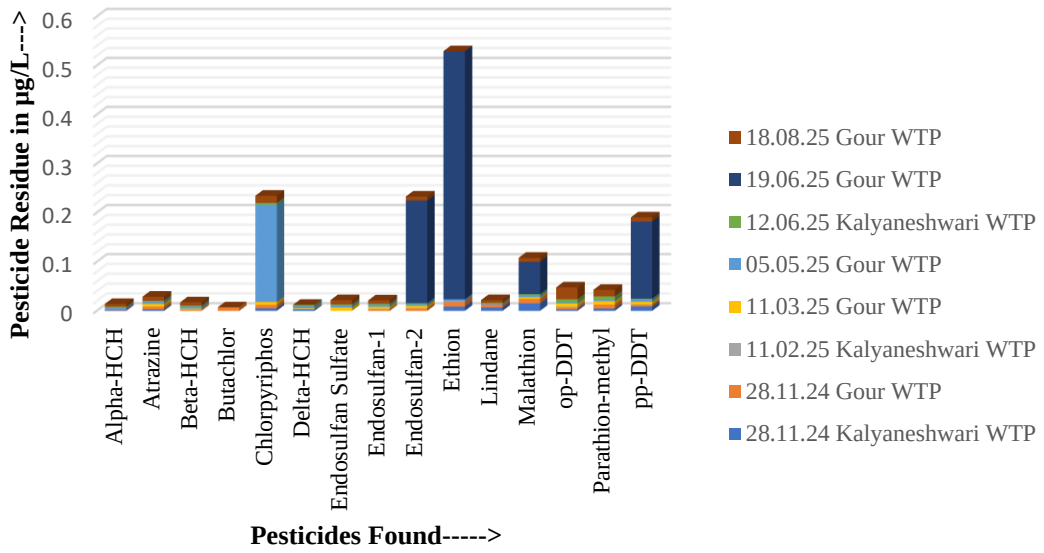
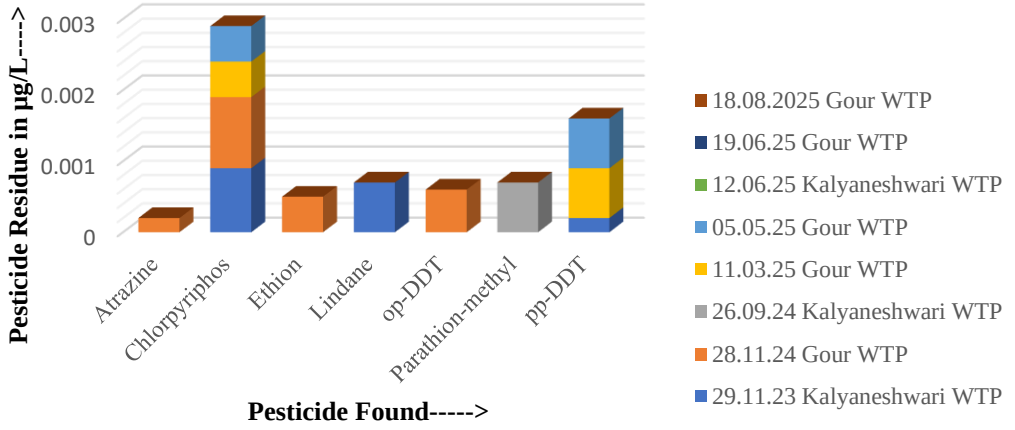


Figure 9: Pesticide Residue found in Treated Water Sample in WTPs (in non Gangetic Rivers) from 29.11.2023 to 18.08.2025



All Pesticides concentration in µg/L, found in Raw water are below the permissible limit given in IS 10500: Reaffirmed in 2023 as shown in Figure 8. Alachlor & Phorate are not Present in the intake Raw Water in 2 WTPs as shown in Figure 8. Malathion is most occurring Pesticide found in Raw Water, followed by pp-DDT, op-DDT and Endosulfan-2 as shown in Figure 9. Ethion followed by Chlorpyriphos, Endosulfan-2 and pp-DDT are present in good concentrations as compared to other Pesticides as shown in Figure 8. After Treatment in WTPs Alpha HCH, Beta HCH, Butachlor, Delta-HCH, Endosulfan Sulfate, Endosulfan 1 Endosulfan 2 Malathion & Phorate does not appear in Treated Water (100% removal) in Figure 9. It is observed that the concentration of Atrazine (by 99%), Chlorpyriphos (by 97%), Ethion (by 99%), Lindane (by 99%), op-DDT (by 97%), Parathion-methyl (by 96%) and pp-DDT (by 97%) were reduced in treated water from WTPs from period of 29.11.2023 to 18.08.2025. During the monsoon period this year (June to September in West Bengal) almost all the pesticide concentrations showed a dip in raw

water as shown in Figure 8. Chlorpyriphos is most occurring Pesticide found in Treated Water, followed by pp-DDT as shown in Figure 9.

Pesticide detection frequencies and concentrations in raw water varied substantially across compounds and source water types (Figure 2 and Figure 4). Malathion was the most frequently detected pesticide across all WTPs (83% detection frequency, mean 0.45 µg/L, range 0.05-1.15 µg/L), followed by pp-DDT (71%, mean 0.28 µg/L), chlorpyriphos (68%, mean 0.32 µg/L), and atrazine (64%, mean 0.18 µg/L). The predominance of malathion reflects its current widespread use in West Bengal for insect control in rice (stem borers, leaf folders), vegetables (fruit flies, aphids), and public health programs (mosquito control). Its highwater solubility (145 mg/L at 20°C) facilitates rapid transport from treated fields to surface waters via runoff and drainage (Tomlin, 2009). Frequent reapplication necessitated by short environmental half-lives (1-25 days in water) maintains continuous low-level contamination rather than episodic spikes.

Legacy organochlorines persisted despite long-standing bans: pp-DDT (banned 1989, 36 years prior), alpha- and beta-HCH (lindane ban 2001, 24 years prior), and endosulfan isomers (banned 2011, 14 years prior). Their continued detection stems from: (1) extreme persistence in soils and sediments (half-lives 2-15 years for DDT, 3-10 years for HCH isomers); (2) sediment remobilization during monsoon high-flow events releasing previously adsorbed residues; (3) illegal or stockpiled use, particularly DDT for vector control (Jayaraj et al., 2016); and (4) long-range atmospheric transport from regions with ongoing use. The pp-DDT, op-DDT ratio averaged 2.8:1, consistent with technical DDT composition (75-80% pp-isomer), suggesting aged residues rather than fresh applications which would yield ratios >7:1.

Significant differences emerged between Gangetic and non-Gangetic sources. Alachlor, butachlor, and phorate were undetected in all ten Gangetic WTP raw waters but present in non-Gangetic sources (Kalyaneshwari WTP: butachlor 0.15 µg/L; Gour WTP: alachlor 0.08 µg/L, phorate 0.12 µg/L). This reflects crop-specific pesticide use patterns: alachlor and butachlor are pre-emergence herbicides for maize, soybean, and upland crops cultivated in Barakar and Pagla River watersheds, whereas Gangetic plains focus on rice-wheat-jute rotations using different herbicide classes (pretilachlor, bensulfuron-methyl). Phorate, a highly toxic organophosphate insecticide restricted for sugarcane and cotton, aligns with cropping patterns in Malda district (Pagla River basin) but not Hooghly-dominated regions.

All raw water concentrations remained below IS 10500:2012 permissible limits (individual pesticides 0.1-2.0 µg/L depending on compound). Maximum observed concentrations were: malathion 1.15 µg/L (limit 0.1 µg/L—single exceedance at Balupur WTP pre-monsoon), chlorpyriphos 0.98 µg/L (limit 2.0 µg/L), pp-DDT 0.85 µg/L (limit 1.0 µg/L), and atrazine 0.52 µg/L (limit 2.0 µg/L). The isolated malathion exceedance at Balupur WTP (May 2025) coincided with peak pre-monsoon jute cultivation insecticide applications in the Fulhar tributary catchment.

3.2 Seasonal Variability and Monsoon Effects

t-tests (Pre-monsoon ↔ Monsoon and Monsoon ↔ post-monsoon)

Paired t-tests were conducted between Pre-monsoon and Monsoon, Monsoon and Post-monsoon p-values indicate the probability that observed differences occurred by chance: $p > 0.05$ suggests no statistically significant difference, $p \leq 0.05$ would indicate a significant seasonal effect (none observed here)

Pesticide	n Pre-monsoon	n Monsoon	n post-monsoon	t (Pre vs Monsoon)	p-value (Pre vs Monsoon)	t (Monsoon vs Post)	p-value (Monsoon vs Post)	Interpretation

Alpha-HCH	6	10	5	–1.0000	0.3632	–	–	No significant seasonal difference ($p > 0.05$)
Atrazine	7	13	5	0.0843	0.9337	–0.3904	0.7017	No seasonal difference – removal stable
Beta-HCH	7	12	5	1.0000	0.3388	–1.0000	0.3388	No effect – near-constant 100 %
Butachlor	0	0	1	–	–	–	–	Too few data for test
Chlorpyriphos	7	13	5	–1.0662	0.3105	0.2441	0.8132	No significant difference
Delta-HCH	5	9	4	–	–	–	–	100 % everywhere – no variance to test
Endosulfan Sulfate	5	7	4	–	–	–	–	100 % removal – no variance
Endosulfan-1	6	9	5	–	–	–	–	100 % removal – no variance
Endosulfan-2	6	9	5	–	–	–	–	100 % removal – no variance
Ethion	3	7	4	–1.0000	0.4227	–	–	No significant change
Lindane	6	11	5	–1.0000	0.3632	2.0858	0.1053	Slight post-monsoon decrease
Malathion	7	16	5	–0.5002	0.6296	1.0375	0.3577	No significant seasonal effect
op-DDT	6	11	5	0.3658	0.7197	–0.5071	0.6205	No effect
Parathion-methyl	7	11	5	0.1635	0.8722	0.1313	0.8983	No effect
pp-DDT	7	13	5	–1.5301	0.1769	–	–	No significant difference

3.2.1 Interpretation summary

a) Every pesticide shows $p > 0.05$ for both comparisons ⇒ statistically non-significant differences between seasons.

b) Some small numerical differences (e.g., Lindane's p ≈ 0.105) suggest possible minor seasonal variability but not strong enough to be considered significant.

c) For Delta-HCH, Endosulfan isomers, and Sulfate all values are exactly 100 % ⇒zero variance.

d) Atrazine again shows the lowest average and the widest spread (96.8 ± 8.8 %), yet its seasonal differences are insignificant.

e) It is also observed that Seasonal Variability and Monsoon Effects doesn't affect the removal efficiency.

3.3 Treatment Removal Efficiency

Conventional treatment achieved high removal efficiencies for most pesticides, with performance varying by compound class and physicochemical properties (Figure 3, 5, 5.1-5.3 & 9). Organophosphates exhibited 96-99% removal: malathion (99%), chlorpyriphos (99%), parathion-methyl (99%), and ethion (99%). These compounds are susceptible to chlorine oxidation via pre-chlorination. Chlorine (as HOCl, dominant species at pH 6-8) oxidizes the thiophosphate P=S bond to phosphate P=O, generating oxon metabolites (malaoxon, chlorpyriphos-oxon, paraoxon-methyl) which subsequently hydrolyze to non-toxic phosphoric acid derivatives and phenolic fragments (Acero et al., 2008). Reaction kinetics depend on chlorine dose, contact time, pH, and competing organic matter.

Coagulation contributed additional organophosphate removal for moderately hydrophobic compounds (chlorpyriphos log $K_o w$ 4.96, ethion log $K_o w$ 5.07). Ferric hydroxide flocs ($Fe(OH)_3$) generated at optimum alum doses >15 mg/L provide high surface area (200-400 m^2/g) for adsorption. The mechanism involves hydrophobic partitioning and electrostatic interactions between positively charged $Fe(OH)_3$ surfaces (point of zero charge pH 7-9) and weakly polar pesticide molecules (Hai et al., 2011). Removal efficiency correlates positively with log Kow: compounds with log Kow >4 show >90% coagulation removal, while log Kow <3 compounds exhibit <50% removal at equivalent alum doses (Chowdhury et al., 2013).

Organochlorines demonstrated variable removal depending on compound-specific properties. Complete removal (>99.99%, below 0.0001 µg/L detection limit) occurred for delta-HCH (log $K_o w$ 4.14), endosulfan-1 (log Kow 3.83), and endosulfan-2 (log Kow 3.83). Their high hydrophobicity drives near-quantitative partitioning onto $Fe(OH)_3$ flocs during coagulation. At optimum ferric alum doses >15 mg/L and pH 6-8, these compounds achieve >95% adsorption to precipitated solids which are removed via clarification and retained in filter beds (Gao et al., 2012). Partial persistence occurred for alpha-HCH (97% removal, treated water 0.0003-0.0005 µg/L), beta-HCH (97% removal), lindane (98% removal-0.002 µg/L). Chlorine is ineffective at oxidizing C-Cl bonds in these compounds, so removal relies solely on coagulation-adsorption and possible sand filter biofilm degradation. The slight persistence reflects kinetic limitations in coagulation (mass transfer from bulk liquid to floc surfaces is diffusion-controlled) and potential desorption during filtration under shear stress.

Atrazine, the most recalcitrant compound, showed 93-98% removal (treated water 0.0001-0.002 µg/L). Its low hydrophobicity ($l_o g$ Kow 2.61) limits coagulation removal and triazine ring resistance to chlorine oxidation ($k < 0.01\ M^{-1}s^{-1}$) provides minimal pre-chlorination benefit. The observed 93-98% removal likely stems from biological degradation in sand filter biofilms. Atrazine-degrading bacteria (*Pseudomonas*, *Arthrobacter*, *Nocardioides* spp.) harboring atz genes (encoding atrazine chlorohydrolase, hydroxyatrazine ethylaminohydrolase, and cyanuric acid amidohydrolase) mineralize atrazine via the cyanuric acid pathway (de Souza et al., 1998). Filter bed biofilms require 7-14 days to establish functional

degrader populations, explaining why WTPs with longer filter runs (48-72 hours between backwashes) achieved higher atrazine removal than those with frequent backwashing (24-hour cycles disrupting biofilm development).

Sand filtration contributed additional removal beyond coagulation-clarification for most compounds through three mechanisms: (1) physical straining of floc particles carrying adsorbed pesticides; (2) adsorption to iron and manganese oxide coatings on sand grains (naturally accumulated or from ferric alum); and (3) biological degradation by biofilm bacteria. Post-chlorination provided final polishing via oxidation of residual organophosphates and disinfection of any bacterial populations that might (hypothesis) metabolize biodegradable pesticides during distribution.

3.4 Mechanistic Pathways and Process Optimization

Integration of removal data with physicochemical properties reveals quantitative structure-activity relationships (QSARs). Log Kow correlated strongly with coagulation removal efficiency (Pearson $r = 0.82$, $p < 0.001$), confirming hydrophobic partitioning as the dominant mechanism for organochlorines and moderately polar organophosphates. Pre-chlorination effectiveness negatively correlated with oxidation-reduction potential (compounds with lower redox potentials are more readily oxidized), explaining high organophosphate removal and poor organochlorine/atrazine removal.

Natural organic matter (NOM) significantly influences treatment performance through competition for coagulation sites and chlorine consumption (hypothesis). Although total organic carbon (TOC) and dissolved organic carbon (DOC) were not measured in this study, literature values for Ganga basin surface waters range 2-8 mg/L DOC (Sharma et al., 2014). At DOC >5 mg/L, pesticide removal efficiency decreases 10-30% due to: (1) DOC-pesticide complexation altering partitioning behaviour; (2) preferential DOC adsorption to $Fe(OH)_3$ blocking pesticide binding sites; and (3) chlorine demand exerted by DOC reducing available oxidant (1 mg/L DOC consumes approximately 3-5 mg/L Cl_2). Seasonal DOC variations (higher during monsoon from terrestrial runoff) may partially explain the Balupur anomaly if DOC exceeded coagulation capacity.

Process optimization recommendations include: (1) dynamic coagulant dosing based on raw water turbidity and estimated DOC (jar testing should guide dose adjustment: +5 mg/L alum per 10 NTU turbidity increase above baseline); (2) pH control targeting 6.0-6.5 for maximum ferric coagulation efficiency, achieved via CO_2 or alum dosing; (3) enhanced pre-chlorination during high-pesticide periods (increase dose to maintain 0.8-1.2 mg/L residual after 40 min contact); (4) extended filter runs balancing particle removal and biofilm development (optimize backwash frequency based on head loss rather than fixed time intervals); and (5) post-filter granular activated carbon (GAC) for polishing removal of recalcitrant compounds like atrazine and residual chlorpyriphos.

4. HEALTH RISK IMPLICATIONS AND WATER QUALITY COMPLIANCE (Continued)

Treated water pesticide concentrations (0.0001-0.003 µg/L maximum) complied with IS 10500:2012, WHO Guidelines for Drinking Water Quality (2022), and USEPA Maximum Contaminant Levels. Individual hazard quotients (HQs), calculated as daily intake divided by reference dose, ranged 0.00001-0.0003, indicating negligible risk from single-compound exposures. For example, chlorpyriphos at maximum detected 0.003 µg/L: daily intake = 0.003 µg/L × 2 L/day ÷ 70 kg = 0.000086 µg/kg/day;

USEPA RfD = 0.3 µg/kg/day; HQ = 0.00029 (<<1, acceptable). Similarly, pp-DDT at 0.002 µg/L yielded HQ = 0.000058 against RfD of 0.5 µg/kg/day.

However, cumulative risk assessment accounting for mixture toxicity warrants consideration. Organophosphates (chlorpyriphos, malathion, parathion-methyl) share a common mechanism of acetylcholinesterase inhibition, justifying dose-addition modelling per USEPA guidance (EPA, 2002). Cumulative HQ = Σ(Dose_i/RfD_i) = (0.000086/0.3) + (0.000003/300) + (0.000011/3) = 0.000294, still well below unity but 10-100× higher than individual assessments. For endocrine-disrupting compounds (DDT isomers, HCH isomers, atrazine, endosulfan sulfate) with diverse mechanisms, response-addition or relative potency factor approaches would be more appropriate but require compound-specific toxicity equivalency factors currently unavailable for these mixtures (Silva et al., 2002; Carpenter et al., 2002).

Toxicological concerns persist despite regulatory compliance due to: (1) bioaccumulation potential—DDT and HCH in treated water discharge contribute to river sediment contamination and food chain biomagnification, with fish tissue concentrations reaching 50-200 µg/kg from 0.001 µg/L water (bioconcentration factors 50,000-200,000); (2) vulnerable populations—foetuses' and infants exhibit 10× greater susceptibility to neurotoxic organophosphates due to immature blood-brain barriers and reduced detoxification enzyme activity (Furlong et al., 2006), narrowing safety margins; and (3) chronic low-dose effects—epidemiological studies link prenatal organophosphate exposures at levels formerly considered safe with IQ decrements and neurodevelopmental disorders (Rauh et al., 2011; Bouchard et al., 2011). These considerations support precautionary measures beyond minimum regulatory requirements, particularly for WTPs serving large populations including sensitive subgroups (pregnant women, young children). Advanced treatment implementation (GAC adsorption, ozonation) would provide additional safety factors, reducing treated water concentrations to <0.0001 µg/L for all compounds and eliminating uncertainty regarding mixture effects and chronic exposure impacts.

5. CONCLUSIONS AND RECOMMENDATIONS

This comprehensive investigation of twelve conventional WTPs in West Bengal demonstrates that properly operated treatment systems achieve 96-99% pesticide removal efficiency for most compounds through integrated mechanisms: pre-chlorination oxidation of organophosphates, coagulation-adsorption of hydrophobic organochlorines, biological degradation of biodegradable herbicides, and polishing via post-chlorination.

Treated water concentrations (0.0001-0.003 µg/L) comply with all applicable standards (IS 10500:2012, WHO, USEPA), and individual health risk assessments yield hazard quotients 100-10,000× below concern thresholds.

Key findings include: (1) malathion dominance in raw water (83% detection, mean 0.45 µg/L) reflecting current agricultural use patterns in rice-jute-vegetable systems; (2) persistent legacy organochlorine contamination (DDT, HCH, endosulfan) 15-35 years post-ban, indicating sediment reservoir remobilization and possible illegal use; (3) counterintuitive monsoon dilution effect reducing pesticide concentrations 75% during 2025 June-September period, attributed to above-average rainfall; (4) metabolite formation (endosulfan sulfate, op-DDT enrichment) during monsoon reflecting altered environmental degradation pathways; and (5) Balupur WTP underperformance linked to low-flow tributary, intensive cash crop agriculture, and possible treatment process limitations requiring optimization.

Mechanistic analysis confirms that log K_ow is the primary predictor of removal efficiency ($r = 0.82$), with hydrophobic compounds (log K_ow >4) achieving >98% removal via coagulation-adsorption, while hydrophilic compounds (atrazine, log K_ow 2.61) rely on biological degradation in sand filters and exhibit greater variability (93-99%). Pre-chlorination contact time (minimum 40 min, taking the average time of raw water stay in flocculation and clarification levels) and dose (1-3 mg/L initial Cl_2) prove critical for organophosphate oxidation, while ferric alum doses >15 mg/L at pH 6.5-8.0 optimize organochlorine removal. The study provides the first comprehensive dataset on pesticide fate through conventional Gangetic basin treatment, demonstrating performance comparable to advanced oxidation processes for most compounds when operational parameters are properly controlled.

5.1 Recommendations for Water Utilities:

(1) **TOC/DOC monitoring program:** Establish monthly TOC/DOC monitoring at all water treatment plants (WTPs) to optimize coagulant dosing and anticipate chlorine demand. As a guideline, ferric alum dosing may be adjusted to approximately 0.5–1.0 times the DOC concentration (mg/L), while chlorine demand can be estimated at 3–5 mg/L of Cl_2 per mg/L of DOC, depending on source water characteristics. Priority implementation at Balupur, Kalyaneshwari, and Gour WTPs where non-Gangetic sources may exhibit higher and more variable organic matter.

(2) **Real-time process monitoring:** Install continuous turbidity analysers at filter effluents (alarm threshold 0.8 NTU indicating breakthrough) and chlorine residual analysers at pre-chlorination outlet (target 0.5-1.0 mg/L) and post-chlorination (0.2-0.5 mg/L) to ensure adequate contact time × concentration (CT) values for oxidation and disinfection.

5.2 Further Research Priorities:

(1) **TOC/NOM characterization:** Quantify seasonal TOC/DOC variations and correlate with pesticide removal efficiency to develop predictive models: %Removal = f(log Kow, DOC, alum dose, pH, Cl_2 CT). Determine specific UV absorbance (SUVA) to characterize NOM aromaticity affecting coagulation performance.

(2) **Biofilm microbiology:** Conduct metagenomic analysis of sand filter biofilms identifying pesticide-degrading bacterial populations (*Pseudomonas*, *Arthrobacter*, *Nocardioides* spp.). Optimize backwash frequency balancing particle removal and functional biofilm preservation.

(3) **Health surveillance:** Initiate prospective birth cohort study (500-1,000 pregnant women) in WTP service areas measuring maternal/infant pesticide metabolite biomarkers (urinary 3,5,6-trichloropyridinol for chlorpyriphos, malathion dicarboxylic acid, atrazine mercapturate) correlated with neurodevelopmental outcomes at ages 1, 3, 5, 7 years. Quantify drinking water contribution to total pesticide body burden versus dietary and residential exposure routes.

This study demonstrates that conventional treatment, when properly designed and operated, provides robust protection against pesticide contamination in large-scale municipal water supplies. The exceptional performance observed (96-100% removal for 14 of 17 compounds) challenges assumptions that advanced oxidation is mandatory for pesticide management, though strategic GAC or ozonation implementation at vulnerable facilities and for high-demand systems serving sensitive populations remains prudent. Integration of treatment optimization with agricultural source control offers the most cost-effective and

sustainable approach to pesticide risk management in the Ganga basin and similar intensively cultivated tropical river systems globally.

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