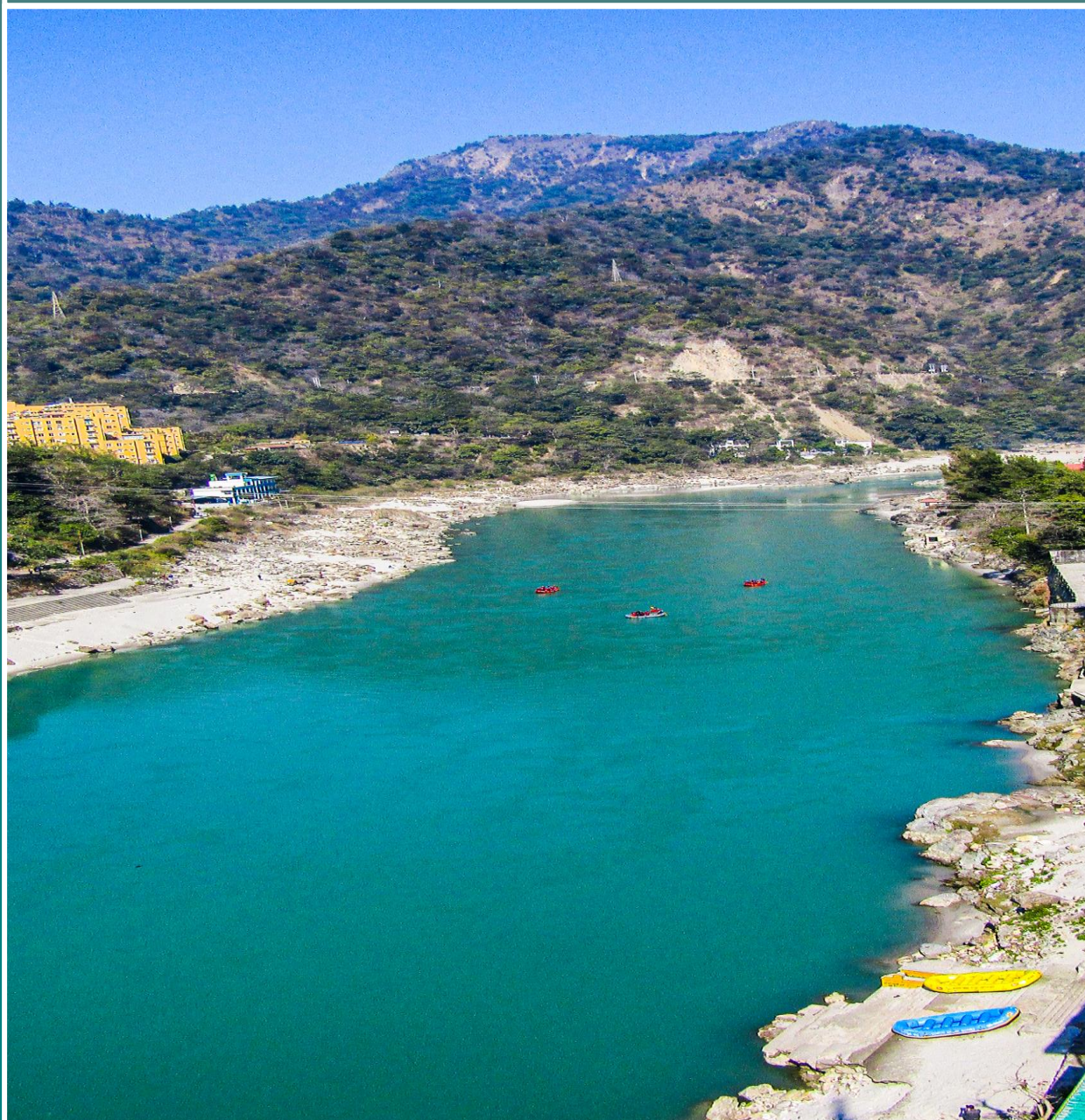


PHASE I REPORT

ECOTOXICOLOGY COMPONENT

POLLUTION ASSESSMENT AND POTENTIAL ECOLOGICAL RISK



भारतीय वन्यजीव संस्थान
Wildlife Institute of India



**BIODIVERSITY CONSERVATION
AND GANGA REJUVENATION
PHASE-I**

**ECOTOXICOLOGY
COMPONENT**



भारतीय वन्यजीव संस्थान
Wildlife Institute of India



PREFACE

Chemical Pollution is identified as one of the major contributors towards the decline in water quality and biodiversity fitness of freshwater ecosystem. More than 80% of river pollution arises from land-based sources and reaches rivers through surface run-offs, direct discharges and atmospheric deposition.

The Ganga River is one of India's largest rivers, covering 26% of India's geographical area and supports 43% of its population. Rapid urbanization, huge agricultural and industrial settlements, along with reduced environmental flow are major drivers for the deterioration of water and sediment quality of Ganga River. The risks posed by continuous inflow of various contaminants from diverse point and non-point sources severely jeopardized the survival and fitness of the freshwater biodiversity.

Since the riverine ecosystem is a complex entity made up of various matrices and influenced by numerous factors such as tributaries and the catchment, it is critical to thoroughly investigate the comprehensive contamination status and ecological risks of diverse contaminants in various matrices of the Ganga River, in order to develop an adequate restoration plan. The scattered spatial and temporal data on contamination profiles of toxicants in the Ganga is a research barrier that must be overcome for adequate restoration of the river.

To achieve this, comprehensive contamination profiles on occurrence, and spatial distribution, of heavy metals, organochlorine pesticides, and organo-phosphorous pesticides in surface water, surface sediments and various fish species of Ganga River were developed. The study quantifies the ecological impact or ecological risks of these contaminants to aquatic biodiversity and discusses the potential sources of contamination. The findings are intended to provide a basis in designing effective monitoring strategies and formulating appropriate mitigation efforts directed towards sustaining the healthy ecological diversity of Ganga River.



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EXECUTIVE SUMMARY

Travelling through diverse geo-climatic zones, the river Ganga accumulates chemicals of natural and anthropogenic origins. The fluvial processes of microbial degeneration, dilution, sequestration and sedimentation provide a limited amount of self-rejuvenating capacity. Due to burgeoning multiple resource use, land use change and discharges from various point and non-point sources along its route, the carrying capacity of the Ganga is often exceeded by the organic and persistent pollutants (pesticides and heavy metals) load.

The organochlorines pesticides (OCPs) such as DDT, HCH, Aldrin and organophosphorus pesticides (OPPs) such as Methyl parathion, Chlorpyrifos constitute 40% and 30% of total insecticides that are used in agricultural sectors, annually. The pesticides and heavy metals from agricultural and industrial origin contaminate the river water through surface runoffs and effluent discharge. These chemicals are highly toxic even at low concentration, persistent in environment, accumulate in animal tissue, and can affect physiology, hormonal balance, breeding of aquatic wildlife and cause health hazard to humans. Bioaccumulation of pesticides and heavy metals in fishes and Gangetic dolphin in the Ganga River has been reported earlier. The slow, steady and long-term exposure and bioaccumulation of these contaminants could bring about gradual and striking changes, such as decline in biodiversity, over an extended period of time. Therefore, it is imperative to assess the concentration, distribution and bioaccumulation path of these toxic compounds to identify eco-toxicological risk zones and potential human health hazard. The data from this study can be used to identify eco-toxicological risk zones and potential human health hazards along the route of the Ganga. The objectives of the study are:

1. To quantify the current status and spatial-temporal distribution pattern of the select contaminants (pesticides, heavy metals, polychlorinated biphenyls and microplastics).
2. To evaluate the potential eco-toxicological risks posed by each target contaminants towards aquatic organisms in Ganga River.

On the basis of geology, hydrology, land use, wastewater discharge, demography and pesticide use the Ganga River was demarcated into five zones as follows.

1. Upper Zone (UZ): Uttarakhand
2. Upper Middle Zone 1 (UMZ1): Bijnor to Yamuna confluence at Prayagraj, Uttar Pradesh
3. Upper Middle Zone 2 (UMZ2): Downstream Yamuna confluence to Balia, Uttar Pradesh
4. Lower Middle Zone (LMZ): Bihar and Jharkhand
5. Lower Zone (LZ): West Bengal

Representative sampling sites were selected on the basis of presence/absence of agricultural and industrial belts, wastewater discharge points, and the existing monitoring stations prescribed by the Central Pollution Control Board (CPCB), India. Samples were collected during Post-Monsoon (October to November 2017) and Post-Winter (April to May 2018) periods. The sampling sites were selected on the basis of secondary information on high historic usage, high toxicity, detection frequency, and CPCB directive. In total 150 water, 150 sediment, and 160 fish samples were collected in each season. The samples were tested to quantify i) pesticides ii) heavy metals, in both the biotic and abiotic matrices and iii) Polychlorinated biphenyls and iv) microplastics in sediment (abiotic) matrix.

The selected parameters were analysed in laboratory using standard protocols. The toxicological risk to aquatic species due to pesticides and heavy metals was assessed based on Risk Quotient approach and the pollutants and river stretches were categorised as high, medium, low, and negligible ecological risk.

Key Outcomes

1. Spatial-temporal assessment highlights that the Ganga River is subjected to high contamination by pesticides (banned and restricted), heavy metals, PCBs, and microplastics.
2. 23 pesticides investigated in this study mostly belonged to banned and restricted category in India. High concentration of these pesticides in all components of the Ganga, viz water, sediment and fishes point towards serious gap in understanding the toxic effects of these pesticides at the local level and follow up of ban at regional and national level.
3. Lower zone i.e. the sampling stretch in the West Bengal emerged as the most contaminated zone with pesticides and heavy metals, which was manifested in this zone being the high ecological risk. PCBs posed considerable ecological risk in UMZ2.
4. Fresh inputs of HCH in all the zones and continued use of DDT and HCH in upper pristine region of Uttarakhand is a matter of concern.
5. High levels of Chromium in UMZ bioaccumulation of Mercury in fish from Uttar Pradesh and high ecological risk due to Cadmium in UZ, UMZ and LMZ may lead to biomagnification along the food chain and potential health risk to humans..
6. Accumulation of pesticides and heavy metals in fishes from all the zones was an indicator of extensive and continuous use of banned toxic pesticides and

discharge of untreated industrial waste. These pollutants can pose health hazards to humans.

7. High quantities of microplastics in the UMZ, need attention before it start leaching in other zones and affect the aquatic wildlife.
8. Accumulation of toxic compounds in commercially exploited fish species such as snow trout, seenghala, hilsa, bata, rita and mottled eel is potential health hazard for humans.
9. Ecological Risk map supports that pesticides such as Drins, Heptachlors, p, p' DDT, p, p' DDE, Methyl Parathion, Malathion, Chlorpyrifos, and heavy metals such as Cadmium, Arsenic, Copper, Lead, Chromium and Mercury should be prioritized for risk management.

Recommendations

1. Given the findings from this study, it is recommended that authorities should take zonewise action and prioritize the regions for implementing the improvement measures. Highest efforts are required in the LZ (West Bengal).
2. National Implementation Plan (NIP) on pesticides should be strictly implemented by each zone and continuous monitoring must be carried out to evaluate the success of the implementation
3. We suggest that awareness campaigns and training programs for farmers must be taken up on a priority basis in all the zones to eliminate the use of banned pesticides and adopt integrated pest management, mixed intercropping systems, and organic agroforestry systems.
4. Contaminants such as *Drins, Heptachlors, p, p' DDT, p, p' DDE, Methyl Parathion, Malathion, and Chlorpyrifos, Copper, Iron, Chromium, and Lead*)

should be prioritized for risk management, particularly because Ganga River is home to endangered species and high risks and continuous exposure of these contaminants can compromise the normal function of key physiological processes, which can ultimately affect the fitness and biodiversity of its aquatic ecosystem.

5. This is the first systematic and comprehensive study on the quantification and potential ecological risk of conventional and emerging contaminants along the entire Ganga River. The results from this study can be used as baseline for future monitoring and research studies on pollution and pollutant risk management.
6. This study clearly highlights the contaminants, zones and sites which need to be focused for making strategies on cleaning the Ganga
7. Findings from this study will be helpful for the policymakers in identifying the status and ecological risks of pesticide, heavy metal, PCB and microplastics at the state/zone level. This in turn will help in designing effective monitoring strategies and formulating appropriate mitigation efforts that would be directed toward sustaining the healthy ecological diversity of the Ganga.
8. The Ecological risk assessment conducted in this study will act as decision support for prioritizing risk zones and site-specific action plans for management of the environmental toxicants.
9. The risk map will also aid in focussed enforcement of the National Implementation Plan of the Stockholm Convention on Persistent Organic Pollutants (POPs) in high ecological risk zones such as LZ.
10. It is recommended that long term monitoring of the sites along Ganga is essential for the contaminants taken up in the study. Other emerging

contaminants, pharmaceutical and personal care products, by products and monomer residues etc. must be taken up for future studies to gain holistic understanding of synergistic as well as antagonistic effects of the chemicals and impact on the biodiversity of the Ganga.

Chapter 1

Project Background and Objectives

The Ganga River is one of the largest rivers in India with huge cultural, socio-economic, and environmental significance. Besides aquatic flora and fauna, the river has also been the lifeline for millions of people through the centuries. However, the biodiversity of Ganga River is declining fast due to various factors such as water pollution, habitat destruction, overexploitation, land use change etc. Water pollution has been identified as one of the major contributor towards the decline in water quality and biodiversity fitness of Ganga ecosystem.

The project "Biodiversity Conservation and Ganga Rejuvenation", funded by National Mission for Clean Ganga, Ministry of Jal Shakti, Department of Water Resources, River Development and Ganga Rejuvenation, Government of India, at Wildlife Institute of India is aimed at developing comprehensive measures to conserve and safeguard the aquatic biodiversity of the Ganga River. The project has six main components (Figure 1.1), with objectives covering all the important domains mandatory for a successful river restoration effort. The second component i.e. "Planning Aquatic Restoration for Ganga River" has eight sub-components namely: Invertebrates, fish, Birds and mammals, herpetology, toxicology, genetics, IT & GIS, and Flora. This is a detailed report dealing with Ecotoxicology sub-component.

The Ecotoxicology Component

The water of the Ganga is subjected to several anthropogenic stressors (organic and inorganic) contributing significantly towards decline in its water quality. With incessant flow of contaminants from point and non-point sources, the survival and biodiversity

fitness of freshwater ecosystem of Ganga River is severely jeopardized. Aquatic species are particularly at higher risk because exposure to these contaminants can be life-long and through multiple routes, thus bioaccumulation is frequent. This continuous exposure can compromise the normal function of key physiological processes, which can ultimately affect the survival of its aquatic species. Considering, that the entire stretch of Ganga is also home to rich and diverse fauna and several endangered species like otters, crocodiles, turtles, fishes and the iconic Gangetic dolphin, the threat to biodiversity and ecological risks posed by the contaminants needs special attention.

Therefore, the objectives of this component are:

1. To systematically inspect the current contamination status and characterize the spatio-temporal distribution pattern of the target contaminants
2. To evaluate the potential eco-toxicological risks posed by each target contaminant towards aquatic organisms in Ganga River

The contamination profiles and ecotoxicological studies are intended to provide a basis to regulatory authorities in designing effective monitoring strategies and formulating appropriate contamination mitigation efforts that would be directed towards sustaining the healthy ecological diversity of Ganga River

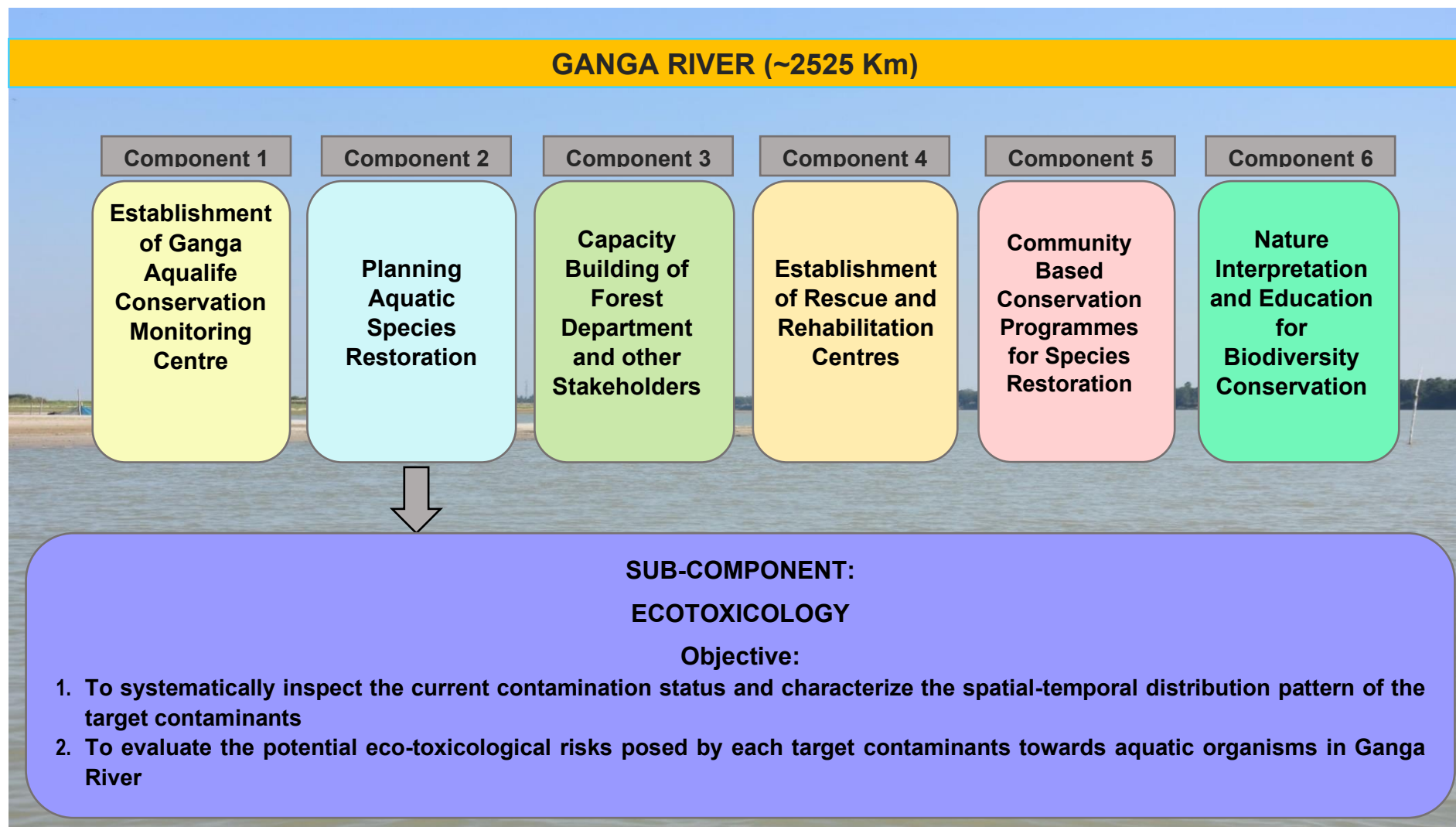


Figure 1.1: The six components of the project “Biodiversity Conservation and Ganga Rejuvenation”

Chapter 2

Introduction

The Ganga: Physical Attributes

Ganga River (the Ganges) is the second-largest river in India, and has exceptional value in the country owing to its religious, economic and ecological significance. It lies between North latitudes of 30°49' 59.99" and 22°1' 43.284" and East longitudes of 79°09'60.00" and 88°12' 37.584. Ganga originates from the Gangotri glacier of the Himalayas, flows for 2525 km, and outfall into the Bay of Bengal. The Ganga river basin has a total catchment area of 861452 km² which accounts for 26% of India's land area and its average annual discharge is 12400 m³/s. During its course, from origin to outfall, the river flows through five states, henceforth referred to as Ganga states in this report, namely Uttarakhand, Uttar Pradesh, Bihar, Jharkhand and West-Bengal, from North to East. (Table 1.1).

Table 1.1: Physical attributes of Ganga River in five Ganga States

States	River length (Km)	Geographical Area (Sq Km)
Uttarakhand	450	53483
Uttar Pradesh	1000	240928
Bihar	400	94163
Jharkhand	45	79716
West Bengal	540	88752

The drainage in Ganga is a combination of precipitation, contribution of tributaries, and snowmelt water from the Himalayas. The seasonal variation of flow of the river is presented in Table 1.2. The river is joined by major tributaries, Yamuna, Ramganga, Ghaghra, Gandak, Burhi Gandak, Kosi, Mahananda and Sone and their annual drainage contribution to Ganga River is presented in Table 1.3. The river together with its tributaries forms the vast and highly fertile Indo-Gangetic plain in the northern and

eastern parts of India supporting intensive agriculture practices along the middle and lower stretches of Ganga. The net irrigated and sown areas of the Ganga basin account to about ~30% and 21% respectively, of the total cultivated area in India (2013-2014) whereas the remaining non-arable land is extensively utilized for urban expansion and industrial establishments

Table 1.2: Seasonal variation of flow in Ganga River

Months	Season	Mean Seasonal Flow (Range in Million cubic metres)
July to September	Monsoon	12,817-2,35,357
October to November	Post-Monsoon	947-54,494
December to February	Winter	167-18055
March to June	Post-Winter/Summer	281-12,474

Central Water Commission (CWC), MoEF

Table 1.3: Annual drainage contribution of major tributaries in Ganga River

Major Tributaries	Annual Drainage (%) into Ganga River	Rate of Flow (Cumecs/s)
Ramganga	3.3	484
Yamuna	16.2	2,410
Ghaghara	20.1	2,993
Kosi	13.1	1,952
Gandak	11.1	1,655
Son	4.8	711
Burhi Gandak	1.5	225
Punpun	0.8	114

Land and Resource Use

Agriculture

The Ganga basin is one of the most widely and heavily irrigated agricultural lands in the world (Karnick, 2011). The highly fertile land of the Ganga states has net irrigated to sown ratio of 62.6% as compared to 44% in the entire country. The farmers of this region practice multiple cropping; hence, the fields are irrigated more than once a year and a variety of seasonal crops including cereals, pulses, paddy, vegetables, fruits, and flowers are grown along the river belt (ESMF, 2011). Terrace farming, and fruit

orchards (apples, plums, peaches, walnut etc.) dominate in the high altitude (Uttarakhand) Himalayan region. The major crops cultivated in the middle and lower Ganga states (Uttar Pradesh, Bihar, Jharkhand, and west Bengal) are Rabi and Kharif. The Kharif crops like rice, maize, and sugarcane are sown in June and July and are harvested in autumn months (September and October), whereas the Rabi crops like wheat, pulses, and peas are sown in the period between October and December and harvested in April and May. Besides, during dry seasons (January to May), riverbed cultivation for seasonal vegetables is a common practice in dry riverbeds of Ganga River (Uttar Pradesh Biodiversity Board, 2013, Kumari et al., 2018).

Further, to maximize the availability of water for irrigation, and to support agricultural yield, substantial amounts of water from the river is abstracted and diverted through barrages and canal systems. There are three main barrages in the main stem Ganga utilizing water for irrigation and the average quantity of water abstracted for irrigation from these barrages are presented in Table 1.4.

Table 1.4: Diversion of Ganga water for irrigation use

Name of Barrages	Associated Canals	Water Discharge through Canals for irrigation (m ³ /s)	Annual irrigation (million Ha)
Bheem Gaura Barrage, Haridwar	East Ganga Canal	237	0.233
	Upper Ganga Canal	297	0.924
Ch. Charan Singh Barrage, Bijnor	Madhya Ganga Canal (First Phase)	234	0.306
Ch. Charan Singh Ganga Barrage, Narora Bulandsharhar	Lower Ganga Canal Parallel Lower Ganga Canal	157	0.5

* Status Paper on River Ganga

Industrial Settlements

The arable land (net irrigated and sown area) along the Ganga states is largely used for agricultural activities whereas the remaining non-arable land is extensively utilized for urban expansion and industrial establishments. There is a cascade of small,

medium and large-scale industries located across Ganga River. The major industrial units located along the Gangetic Plain are tannery, sugar, pulp and paper, chemicals (mainly include pesticides, pharmaceuticals, fertilizer, food & beverage and petro-chemical), distillery, textile, bleaching & dyeing, dairy, and other (paint, cement, electronics & electrical house, ordinance, packaging & printing, thermal, electroplating, metallurgical, automobile etc.) (CPCB, 2013). The sector-wise distribution of industrial units along the Ganga is given in Figure 1.2. Tannery industries (58%, majority located in Uttar Pradesh) dominate among the sector-wise distribution of industrial units in Ganga states followed by the pulp and paper industries (9%, majority located in Uttarakhand), and sugar mills (9%, most of which is located in Uttarakhand & Uttar Pradesh).

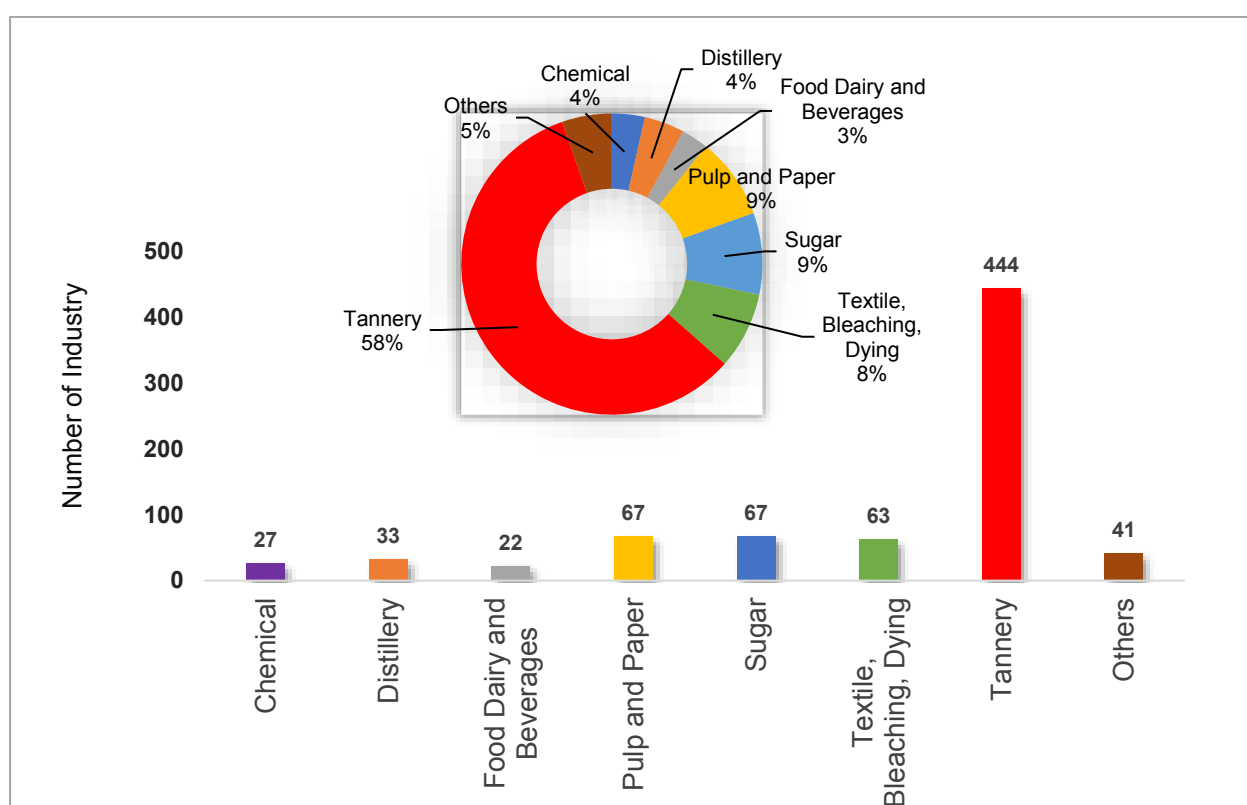


Figure 1.2: Sector-wise distribution of industrial units in five Ganga States

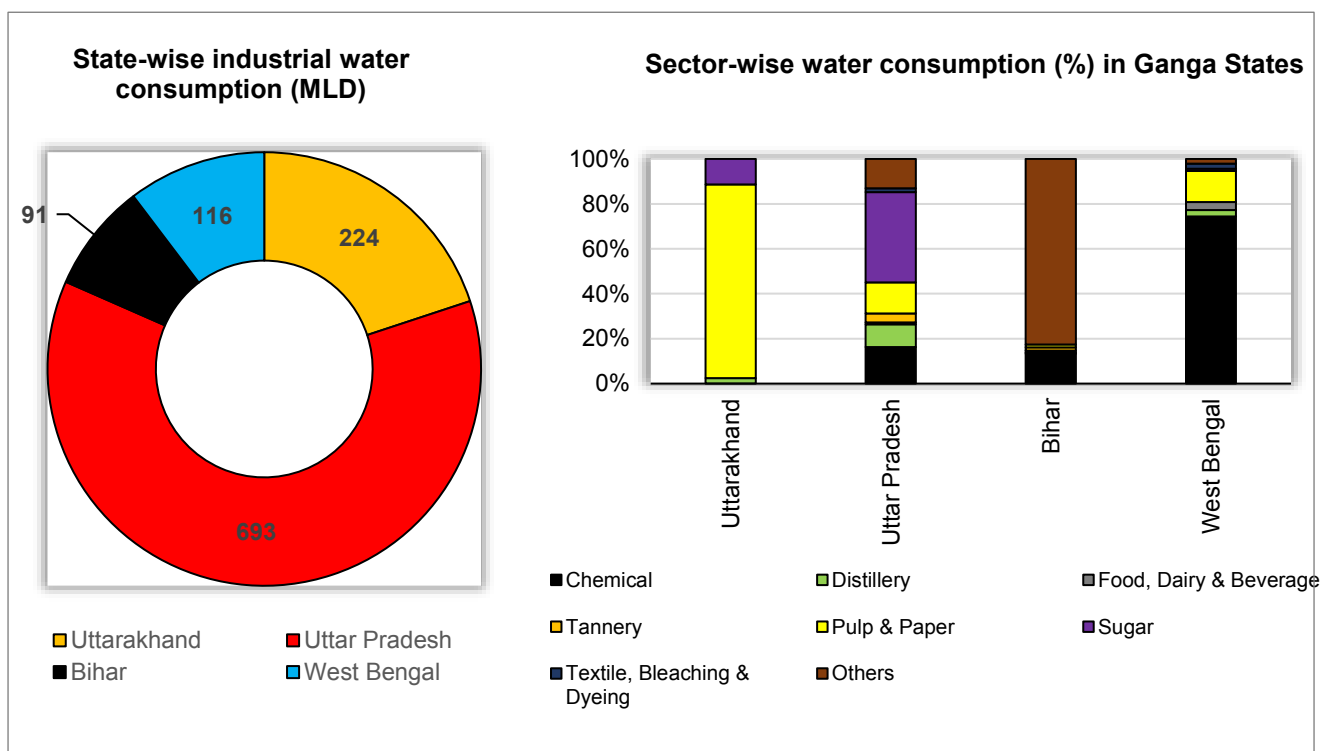
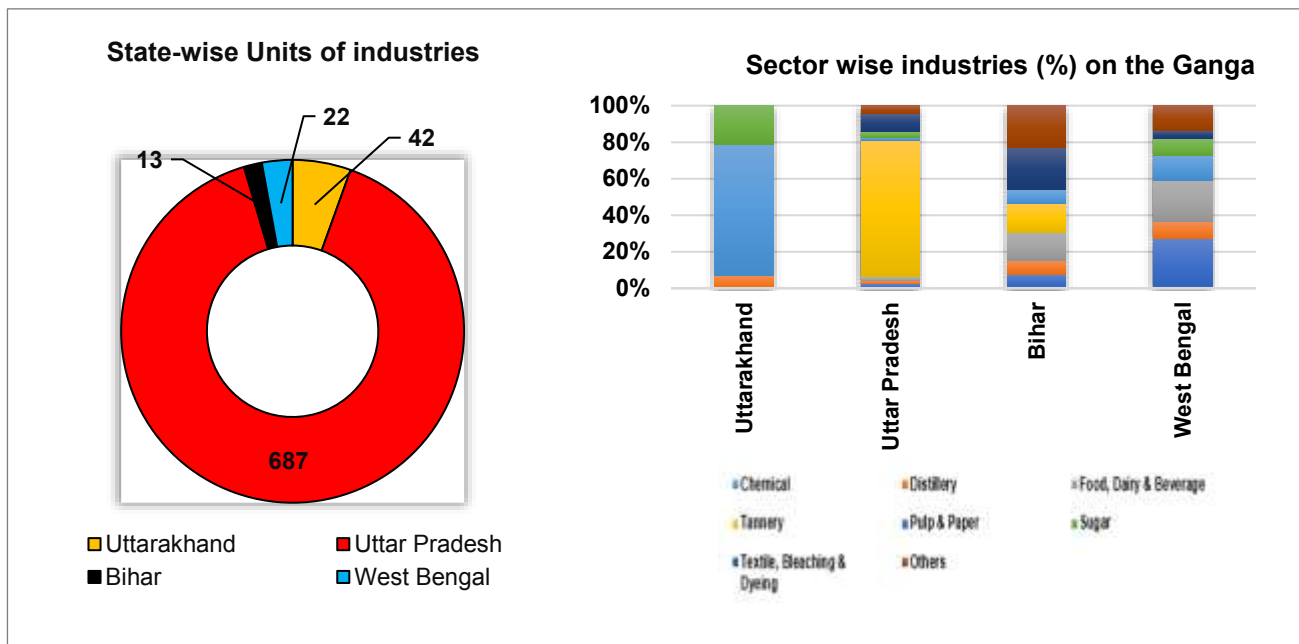


Figure 1.3: State-wise and sector-wise (a) industries (b) industrial water consumption

The state-wise count of industrial units, water consumption for industrial purpose, and sector wise consumption is given in Figure 1.3 whereas the state wise and sector wise

wastewater generation from industries in the Ganga states is shown in Fig 1.4. A recent report from CPCB (CPCB, 2016) revealed that there are 764 Grossly Polluting Industries (GPI); discharging more than 100KLD waste water and/or hazardous chemicals used by the industry) located on the main stem of the Ganga. In Uttarakhand, there are forty-two GPIs and out of these seven units discharge their effluent in the main stem of Ganga whereas rest discharge in the Ramganga. Among the Ganga states, Uttar Pradesh leads with respect to industrial settlements (90%), water consumption (62%) and waste water generation (54%) followed by Uttarakhand>West Bengal>Bihar. No industries are located on the Jharkhand stretch of the Ganga. Majority of the industries are settled in urban city centres such as Kanpur, Patna, and Kolkata etc.

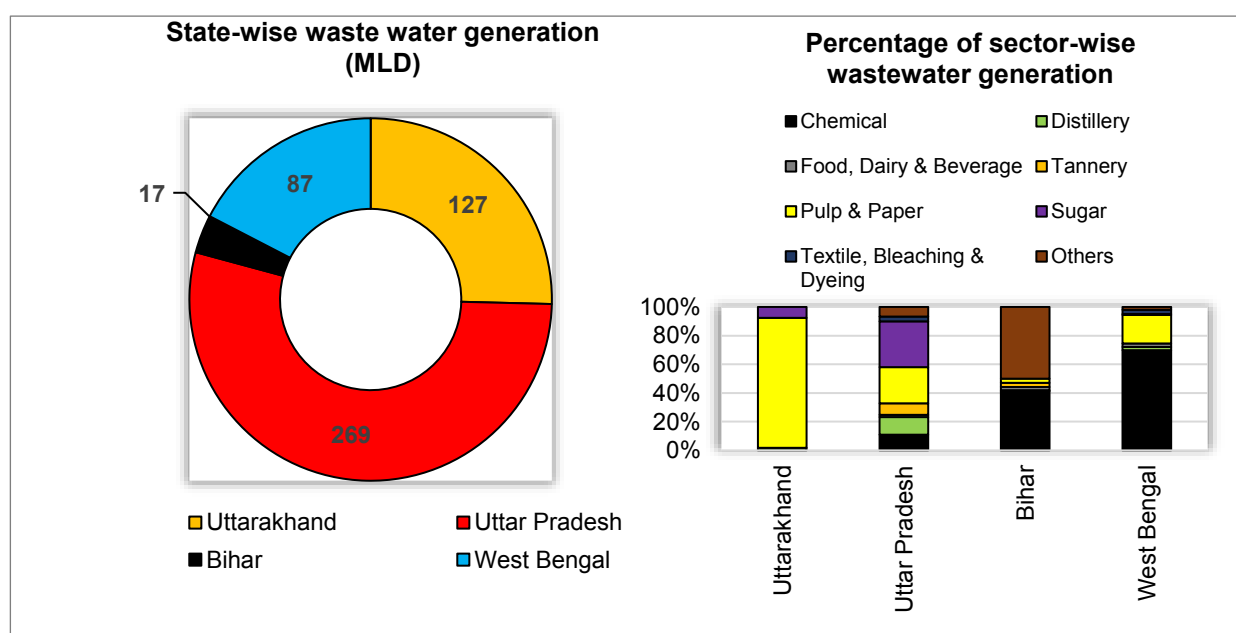


Figure 1.4: State-wise and sector-wise industrial wastewater generation

Amongst the industrial wastewater generation capacity, the Pulp and paper industries (34%) contributes highest (Figure 1.4) followed by chemical industries (31%), and

sugar mills (10%), and these three major industrial sectors together generate ~ 80% of the total waste water effluents.

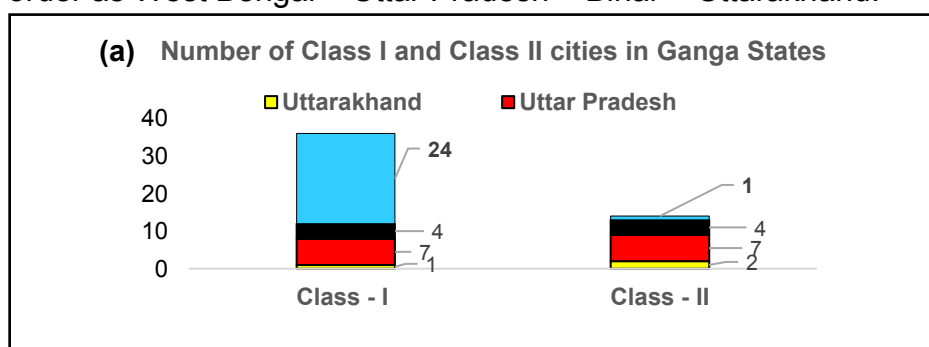
Urban Expansion

The five Ganga states support 36.1% of the country's population (438.2 million), that lives in cities, towns, and villages along the Ganga River including some of the most densely populated areas of India (Table 1.5). Agriculture is the main source of revenue and about 70% population is dependent on agriculture for income.

Table 1.5: Geographic Area and demography of Ganga States

State	Geographical Area (Sq Kms)	Demography (Billions) Census 2011
Uttarakhand	53483	0.01
Uttar Pradesh	240928	0.2
Bihar	94163	0.1
Jharkhand	79716	0.03
West Bengal	88752	0.09

Over the last few decades, these states have witnessed rapid urbanization and many large cities and towns have expanded along the river. There are thirty-six Class I cities (having population over 100,000) and fourteen Class II cities (having population between 50,000 to 100,000) along the main stem of the Ganga River. Out of thirty-six Class I cities, 24 are in West Bengal alone, followed by Uttar Pradesh (7), Bihar (4), and Uttarakhand (1). Among the fourteen Class II cities, seven are in Uttar Pradesh, followed by Bihar (4), Uttarakhand (1), and West Bengal (1), respectively (Figure 1.5 a). The state-wise municipal sewage generation from Class I cities are arranged in descending order as West Bengal > Uttar Pradesh > Bihar > Uttarakhand.



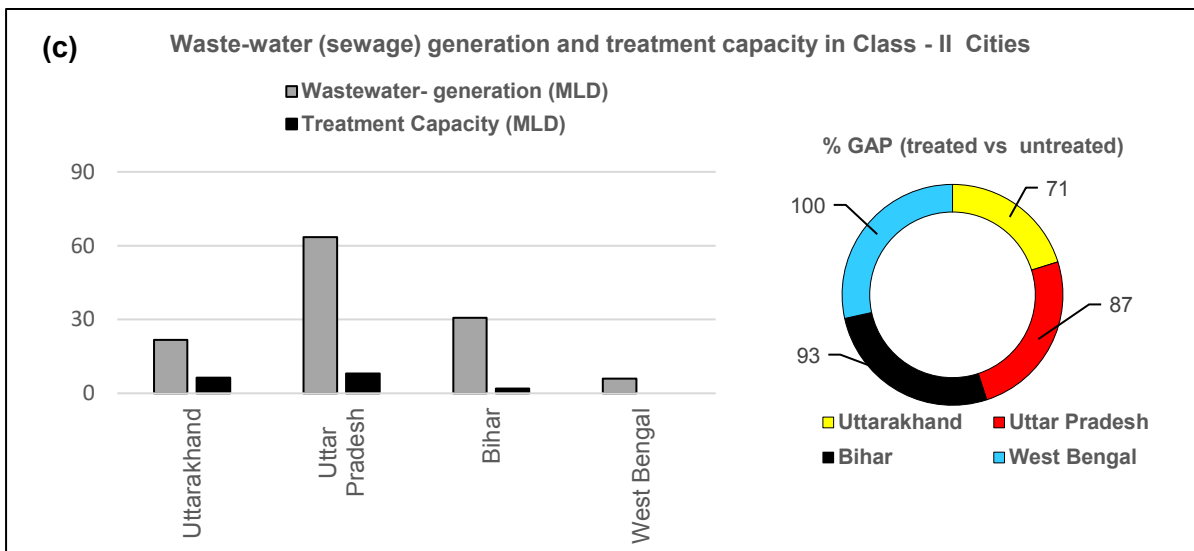
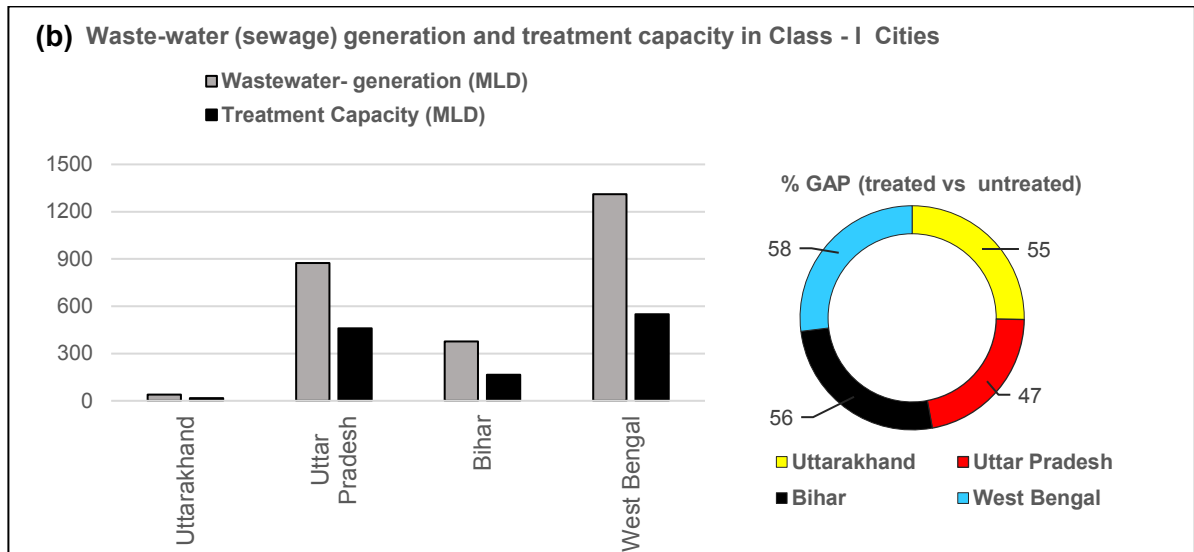


Figure 1.5: (a) Number of Class I and Class II cities in Ganga States (b) & (c) Wastewater (sewage) generation and treatment capacity in Class I Class I and Class II

The main cities that contribute significantly to the municipal sewage input to the Ganga are Kanpur, Allahabad and, Varanasi in Uttar Pradesh, Howrah, and Kolkata in West Bengal and Patna in Bihar. Additionally, the amount of sewage generation is disproportionately more than the sewage treatment capacity in all these states with a percent gap (between treated and untreated municipal sewage wastewater) of 47-58 % in Class I cities and 71-93% in Class II cities, respectively (Figure 1.5 b & c).

Faunal Diversity in Ganga River

The river is of utmost ecological importance and has five protected areas along the river (Figure). The Ganga River is home to rich and diverse fauna including 143 species of freshwater fish, 12 species of freshwater turtles and endangered species like dolphin (*Platanista gangetica gangetica*), otters (*Lutrogale perspicillata*, *Lutra lutra* and *Aonyx cinereus*), Gharial (*Gavialis gangeticus*), crocodiles (*Crocodylus palustris*, *Crocodylus porosus*), turtle (*Batagur kachuga*), and, species of fish like *Tor putitora* and *Tenuulosa ilisha* (WII,2018).

History of contamination and Target Analytes

High population density together with extensive agricultural and industrial activity has resulted in discharge of tons of toxic municipal sewage, agricultural run-off as well as industrial waste into the Ganga River making it seem less “sacred” and more of a “dumping ground” for toxic wastes. The previous studies (Rehana et al., 1995; Nayak et al., 1995; Shankararamakrishnan et al., 2005; Ghose et al., 2009; Singh et al., 2011; Mutiyar et al., 2013; Raghuvanshi et al., 2014; Chakraborty et al., 2016; and Mondal et al. 2018) on the Ganga revealed that the key contributors toward organic and inorganic contamination in the Ganga River are the excessive discharge of pesticides, heavy metals and polychlorinated biphenyls. In addition, microplastics which is another class of contaminants impacting the biodiversity, is found recently in many freshwater and marine ecosystems across the globe.

2.1. Pesticides

Agriculture and its associated sectors are the largest and primary source of livelihoods for 58% of the population in India and play a central role in ensuring steady economic growth and sustainable development of economy. The high proportion of fertile agricultural land (157 million hectares) and diverse agro-climatic conditions are a great

combination for rich agriculture produce that can safeguard the food availability for 1.27 billion Indian population. One of the pivotal contributors towards food security and accelerated agricultural yields is use and application of pesticides to restrict a wide variety of pests that would otherwise adversely affect the quality and quantity of agricultural yield. Consequently, the dependence on pesticides has accrued over the last few decades and agrochemical industry in India has witnessed steep growth. Accordingly, the production of key pesticides (technical grade) during 2010-11 to 2015-16 increased from 133772 M.T (metric tons). to 187524 M.T. Presently, India is the 4th largest global manufacturer and largest exporter of agriculture chemicals with an estimated market size of around \$4.9 billion (Department of Chemicals & Petrochemicals, year). In terms of consumption, pesticides in India are employed mainly in two sectors viz., agriculture and public health programmes. However, the consumption pattern of technical grade chemical pesticides in India showed a decline from 33840 MT in 2010-11 to 24197 MT in 2016-17 (Directorate of Plant Protection, Quarantine & Storage). This steady decline in consumption of pesticides could be attributed to introduction of Integrated Pest Management programme and ban on low cost, and broad spectrum but toxic key pesticides like Lindane (γ -HCH), endosulfan, DDT etc. Amongst the agriculture-dominated stretches of Ganga River, substantial amounts of pesticides are used annually to increase agricultural productivity and yield (Figure 1.6). An analysis of state-wise annual consumption pattern (2015-2016) of pesticides among five Ganga states revealed that Uttar Pradesh is the highest pesticide consuming state followed by West-Bengal > Bihar > Jharkhand > Uttarakhand. Although, over the decades, this continual and reckless use of pesticides has accelerated the agricultural yield and socio-economic growth of the country, it is

often accompanied by steady deterioration of environmental health and change in the ecosystem.

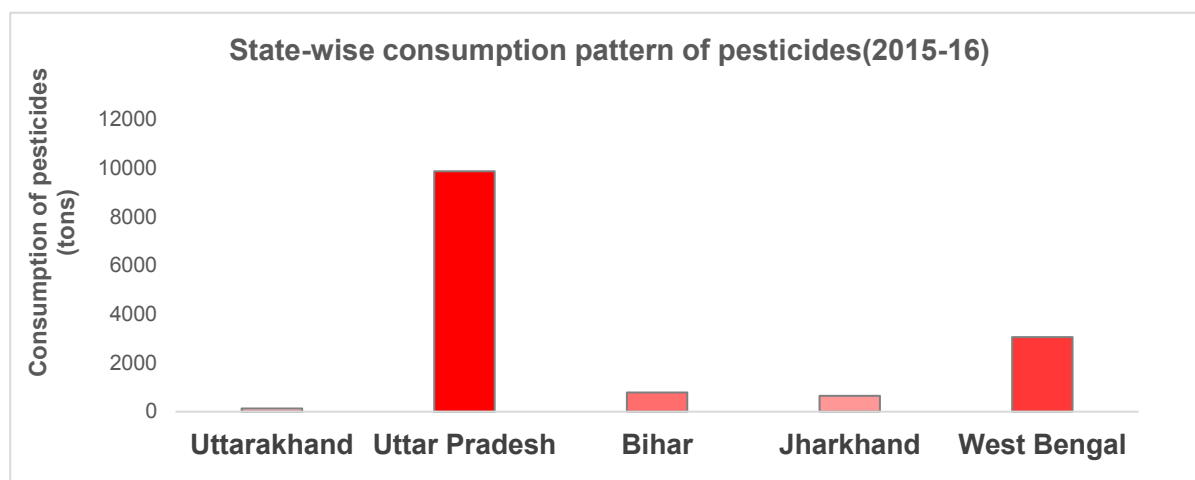


Figure 1.6: State-wise consumption pattern of pesticides (2015-16) in five Ganga states

Globally, the accumulation of these pesticides in the ecosystem and environment is considered as one of the biggest problems linked with agriculture (FAO, 2011). This is because bulk (99.7%) of the pesticide drifts into the ecosystem and environment during application and only a fraction (0.3%) of it reaches the target organisms (Deknock et al., 2019, Pimentel, 1995). Once these pesticides are introduced to the environment they frequently enter and contaminate the nearby waterbodies through agricultural surface runoff, leaching, drainage, atmospheric precipitation, soil percolation, erosion or volatilization (Gavrilescu, 2005; Holvoet et al., 2007; Larson et al., 1995; Schlmz, 2001, Miyamoto et al., 2008). The active ingredients of the pesticide thus drifting away affects the non-target organisms, natural ecosystem and the services it provides (Miyamoto et al., 2008; Carriquiriborde et al., 2014). Unlike developed nations, where herbicides are predominantly used, in India (Figure 1.7) insecticides tops the position (48%) followed by fungicides (36%), herbicides (14%), and others (2%) (Agarwal et al., 2015; Department of Chemicals & Petrochemicals year; Kumari et al., 2018; Yadav et al., 2015). The reason for the high usage of

insecticides in India could be attributed to their low cost and broad-spectrum insecticidal property against various pests. Among these insecticides, Organochlorines pesticides (OCPs) and Organophosphorous pesticides (OPPs) constitute 40% and 30% of total insecticides consumed annually (Figure).

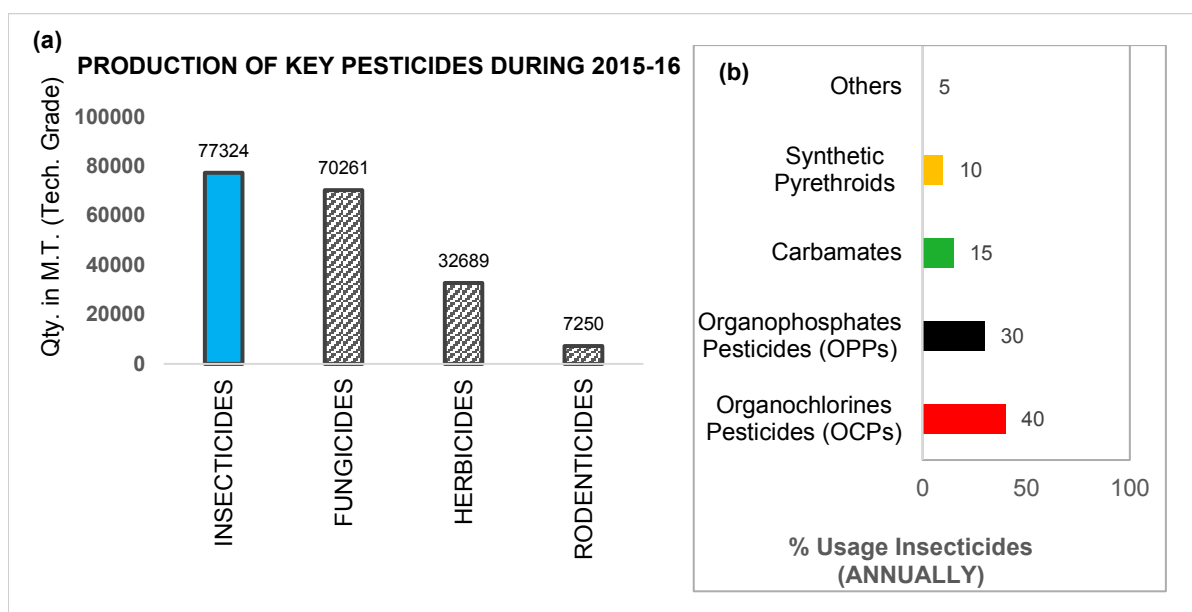


Figure 1.7: (a) Production of key pesticides in India (2015-2016) (b) Percentage Usage of Insecticides in India

Of all the pesticides, the OCPs and OPPs are considered as the pesticide of highest concern due to their persistent, toxic, long-range transmission and bio-accumulative nature (Briz et al., 2011; Contreras López, 2003; Gao et al., 2013; Naqvi and Vaishnavi, 1993; Willet et al., 1998).

2.1.1. Organochlorine Pesticides

Organochlorine pesticides (OCPs) are chemically characterized as lipophilic, semi-volatile and resistant to degradation. The high lipophilicity of OCPs favours their bioaccumulation in tissues of organisms whereas their slow break-down facilitates the biomagnification from lower to higher trophic levels in the food chain. Further, semi-

volatile property of OCPs enable their long-range atmospheric transfer, through air and water, and facilitates their accumulation into the ecosystem far away from the original source of application. Due to their characteristic properties, many of the OCPs like Hexachlorohexane (HCH), chlordane, p,p'-dichlorodiphenyltrichloroethane (p,p'-DDT), endosulfan, aldrin, heptachlor, dieldrin, and, endrin are classified as Persistent Organic Pollutants (POPs) by Stockholm Convention and their production and usage is banned by many nations.

In human beings, possible inter-linkages have been found between OCPs and health whereby studies indicate that OCPs could potentially cause various cancers (Mathur et al., 2002, Rathore et al., 2002; Abdo et al. 2013; Louis, 2019, Ennour-Idrissi et al., 2019), teratogenicity (Kalra et al., 2016; Kim et al., 2017; Ramakrishnan et al., 2019), endocrine disruption (Younglai et al., 2004; Fyre et al., 2011; Fowler et al., 2017), neurotoxicity (Shinomiya and Shinomiya, 2003; Sharma et al., 2010; Song et al., 2012; Heusinkveld and Westerink, 2012) and genotoxicity (Pandey et al., 1990; Ramirez and Cuenca, 2002; Poli et al., 2003; Ennaceur et al., 2008). Similarly, wildlife exposed to OCPs have shown high rates of malformed genitalia (Sonne, 2006), aberrant mating behaviour (Fry, 1995), sterility, cancer, egg-shell thinning, immune system and thyroid dysfunction etc. (Colborn and Smolen, 1996; Briz et al., 2011; Bergmen, 2012; Newton, 2013; WHO 2013; Godfray 2019).

Until the year 2006, when India ratified the Stockholm convention, large amounts of OCPs, banned by other countries, were still manufactured, used, and exported by the country. Post ratification, India banned the manufacturing, import, export, and use of all the 12 Persistent Organic Pollutants (POPs) listed in the convention, except DDT. India is the only major country in the world to still manufacture and use DDT for vector

control and is allowed exemption until 2022. Specific exemption (up to the year 2019) is also allowed for use of DDT as an intermediate in the production of Dicofol. However, the production of DDT has declined in the last decade from 3310 MT in 2008-09 to 1370 MT in 2018-19 (Annual Reports, Dept of Chemicals and Petrochemical, 2011-2019). Among HCHs, only γ -HCH or lindane is banned for production, import, or formulation, since March-2011 and banned for use, since March-2013. However, the country does not have any policy or law for ban or restriction of α -, β and δ -HCHs (PPQS, 2019). A summary of other OCPs listed as POP under Stockholm convention and banned by India is given in **Annexure – I, Table A1**.

Despite the imposed ban, over the last two decades, high levels and distributions of OCPs in freshwaters have frequently been detected across many rivers in India, including the large rivers (**Annexure – I, Table A4**). The potential sources of contamination may include production units, illegal imports as well as stockpiles of obsolete pesticide stocks (UNEP POPs, 2012).

1.1.2. Organophosphorous Pesticides (OPPs)

Organophosphorus pesticides (OPPs), are another group of pesticides that are extensively used in agriculture all over the world. OPPs poison insects and other animals, primarily by inhibiting the acetylcholinesterase enzyme (AChE) at the nerve endings. It is estimated that OPPs are worth nearly 40% of the global market and that they are expected to maintain dominance for some time into the future because they are cheap, readily available and have a wide range of efficacy. They are able to combat a large number of pest species, and have a shorter environmental half-life than their organochlorine predecessors. However, unlike OCPs, they are relatively soluble in water and have significantly higher potential for entering in the aquatic environments through surface runoff, sprays and soil leachate (Tse et al. 2004).

OPPs have been recognized as dangerous for both environment and human health when present above certain critical levels. Literature supports that they can influence body glucose homeostasis through several mechanisms including physiological stress, oxidative stress, inhibition of paraoxonase, nitrosative stress, pancreatitis, inhibition of cholinesterase, stimulation of the adrenal gland, and disturbance in the metabolism of liver tryptophan (Badrane et al. 2014). While high-level exposure to OPPs can lead to death in the short term, many studies have suggested that chronic low-level exposure can also have serious health consequences such as neurological disorders, brain anomalies and compromised cognitive development especially for infants and children (Wang et al. 2009; Ophir et al. 2014; Epstein 2014). As confirmed by numerous studies, the aquatic environment appears to be one of the primary locations for OPPs (Wang et al. 2009; González-Curbelo et al. 2013; Sangchan et al. 2014; Masiá et al. 2014). They represent the group of compounds posing the highest risk to ecosystem and may be a source of contaminants to aquatic biota.

2.2. Heavy Metals

Heavy metals are naturally occurring elements that are found throughout the earth's crust. While, some metals are essential in trace amounts (micronutrients) for normal human and wildlife metabolism (e.g., Cr, Mn, Ni, Cu and Zn), their overexposure may lead to harmful effects. Non-essential heavy metals like arsenic, lead and, cadmium are not required for normal metabolic activity and can have toxic effect on human and wildlife even at trace levels (US EPA, 1999). Most of the heavy metal contamination in the environmental matrices results from anthropogenic activities such as mining and smelting operations, industrial production and use, and domestic and agricultural use of metals and metal-containing compounds. Environmental contamination can also occur through metal corrosion, atmospheric deposition, soil erosion of metal ions and

leaching of heavy metals, sediment re-suspension and metal evaporation from water resources to soil and ground water. Natural phenomena such as weathering and volcanic eruptions have also been reported to significantly contribute to heavy metal pollution.

Due to rapid industrialization and urbanization along the Ganga River, the aquatic ecosystem of the river has increasingly been exposed to heavy metal contaminants. In the aquatic environment, heavy metals are usually distributed as water-soluble species, colloids, suspended and sedimentary forms. However, unlike organic pollutants, natural processes of decomposition do not remove heavy metals. On the contrary, they usually are enriched in sediment by organisms or geochemical processes. In some conditions, more than 99% of heavy metal entering into the river can be stored or fixed in river sediments in various forms. Thus, sediment often acts as both carriers and potential sources for metals in an aquatic environment. However, heavy metals cannot remain inert in sediments forever. With the variation of the physical–chemical characteristics of water conditions, part of these inert metals will re-enter the overlying water and become available to aquatic organisms. Under certain conditions, these metals may accumulate to a concentration level, which may be toxic to flora and fauna of river ecosystem (Jefferies and Freestone, 1984), and also affect other trophic levels including humans via food chain. Some of the heavy metals are highly toxic to aquatic ecosystems because of their environmental persistence, and therefore can be strongly accumulated and biomagnified along water, sediment, and aquatic food chain and could result in sublethal effects or decline in population size of several vulnerable aquatic populations (Megeer et al., 2000; Jones et al., 2001; Almeida et al., 2002; Xu et al., 2004., Xiao R. et al., 2012; Sheykhi V. et al., 29 2013; Kazem et al., 2014).

2.3. Polychlorinated Biphenyls (PCBs)

Polychlorinated biphenyls (PCBs) are used widely as insulating fluids in electrical equipment such as transformers and capacitors, as well as in hydraulic systems, surface coatings, and flame retardants. Their chemical properties, such as non-flammability, chemical and thermal stability, dielectric properties, and miscibility with organic compounds, make them suitable in several industrial applications. PCBs are of anthropogenic origin and do not occur naturally in the environment. They are inert and semi-volatile chlorinated organic compounds synthesized by humans through chlorination of biphenyl molecules. PCBs constitute a class of 209 organic compounds individually called as congeners. Each of the PCB congeners has a high chemical inertness and stability which is why they were found to have a wide range of application. Once released into the environment these chemicals tend to persist and bioaccumulate in the food web and cause toxic effects on humans and the environment.

PCBs are the major group of persistent organic compounds (POPs) included in the Stockholm Convention (UNEP 2008) due to their worldwide spread and global concern as toxic environmental contaminants. These congeners differ in the number and position of the chlorine atoms bound to the biphenyl molecule. Due to this, each congener has different biological activity and toxicity and other physical as well as chemical properties. Though PCBs were banned years ago in most of the western countries due to their highly toxic nature, in India these were banned only in 2016. The Union environment ministry has recently banned the manufacture and import of PCBs and directed complete prohibition on its use in any form by the end of 2025, in a bid to curb pollution. As per estimates, 10,000 tonnes of PCBs have been recorded in India, especially in the power sector. Despite prohibition of their industrial production, they

can still be found in the environment due to their long half-lives and high bioaccumulation potentials. The potential ability of PCBs to move up the food chain is a significant concern and makes it difficult to control in environmental and biological matrix.

Health effects related to PCB exposure include hepatic effects, thyroid, dermal, endocrine effects, developmental & reproductive toxicity, and neurotoxic effects. Many of the effects of PCBs interact with arylhydrocarbon receptor (AhR). PCBs are also known to increase oxidative stress, which may lead to carcinogenesis. PCBs are suspected by some scientists to have contributed to declines in wild fish populations (Rolland et al. 1997; Colborn and Thayer 2000). These chemicals have been associated with alterations in the endocrine function of adult fish (Bortone and Davis 1994; Nimrod and Benson 1996, 1997) and with endocrine-related developmental anomalies in embryos (Walker and Peterson 1991; Walker et al. 1996; Davis 1997).

2.4. Microplastics

Since 1950 the global production of plastic increased from 1.7 MT (million tonnes), to 335 MT in 2016 (Association of Plastics manufacturers, 2018). With increase in population and benefits extended by plastics in day to day life, its production is expected to grow continuously. The major issue does not lie with the use of plastics but its management at the end of life. Data suggests that since 1950 only 9% of the plastic has been adequately recycled (Geyer et al., 2017) and rest continues to end up either in landfill or in open dumps. This mismanaged plastic eventually breaks down in smaller fragments under constant ultraviolet radiations and enter the terrestrial and aquatic ecosystem in various sizes (Lehtiniemi et al., 2018). Such plastic particles which stays in the environment and are of size <5mm are termed a microplastics (hereafter referred to as MPs) and are found distributed horizontally across all aquatic

ecosystems ranging from freshwater to marine (Andrady, 2011; Lambert & Wagner, 2018) and vertically from surface to deep ocean beds (Moore et al., 2001; Woodall et al., 2014). Based on their mode of origin, these MPs can either be called as primary microplastics (originally manufactured in industry as a resin pellet; used as an additive in cosmetics) or secondary microplastics which are formed as a result of breakdown of larger plastic waste items due to heat and mechanical abrasions or from biosolids and effluents from Wastewater Treatment Plants (GESAMP, 2015). Eventually these MPs enter the waterbodies like lakes, rivers and oceans. The fact that MPs are resistant to degradation makes these tiny particles persistent in the environment. As these particles are small in size and often look like prey/food, these are taken up by zooplanktons, bivalves/other macro-sized invertebrates and also fishes (Cole et al., 2013; Gray & Weinstein, 2017; Vendel et al., 2017). Eventually MPs become part of the food chain and start accumulating in the tissues where they have the potential adverse impacts. Laboratory studies have shown the adverse effects of microplastic ingestion like increase in toxicological stress in fin whales (Fossi et al., 2016) and negative effect on algal growth (Sjollema et al., 2015). It is known to cause liver toxicity and inflammation, and cause the accumulation of lipids in the liver of fish (Lu et al., 2016). MPs can also serve as vector for the assimilation of persistent organic pollutants (POPs) and heavy metals by marine organisms and the environment (Chua et al., 2014; Brennecke et al., 2016), and reduce the feeding activity of invertebrates (Besseling et al., 2013). The exposure and ingestion of MPs can cause physical damage, chemical harm (Au et al., 2015; Von Moos et al., 2012) as well as acute mortality in some cases (Gray & Weinstein, 2017). MPs in marine ecosystem has especially received a lot of attention since 2005 and reported extensively, whereas microplastics in freshwater systems has received more recent attention with studies

Key Issues contributing to pollution of the river Ganga

- **Water Pollution: The Big concerns**

- **Agricultural Runoffs**

High pesticide application has led to the accumulation of these chemicals in the environment, which is considered to be one of the biggest problems linked to agriculture. Pesticides enter and contaminate the nearby water bodies through agricultural surface runoff, leaching, drainage, atmospheric precipitation, soil percolation, erosion or volatilization and could affect the non-target organisms, natural ecosystem and its services.

- **Discharge of sewage and industrial wastes**

Every day, large amounts of toxic pollutants, from municipal and industrial wastes are discharged in Ganga River. It is estimated (CPCB) that **~2900 Million Litres of waste water** from sewage, and industrial sources are discharged directly into the Ganga, **of which over 80% is sewage discharge**, contributing substantially towards the steep decline in its water quality. In the absence of adequate sewerage lines, all the treated and untreated sewage wastewater is discharged into Ganga River through open Drains/Nullahs. 154 open drains and nullahs discharge **9146.09 MLD** of waste-water into main stem of Ganga River with BOD (Biological oxygen Demand Load) of ~ 1000 tons/day and total organic load of 361.2 (Tons Per Day).

- **Change in natural flow:**

Excessive abstraction of water for irrigation, industrial settlements, and urban use had led to failure in maintaining the minimum environmental flow, required to support a healthy ecosystem. Through a cascade of dams and barrages on the Ganga, by the time it reaches the half-way point of its journey (in Uttar Pradesh) to the Bay of Bengal, approximately 80% of the natural flow of the river is reduced. This could lead serious consequences such as deteriorating water quality, reduction of species habitat, diversity and abundance.

- **Threat to biodiversity**

With the incessant flow of contaminants from agricultural runoffs, municipal and industrial effluents, the survival and biodiversity of Ganga River is at high risk. Considering, that the entire stretch of Ganga is also home to rich and diverse fauna including several endangered species, the threat to biodiversity and ecological risks posed by contaminants is quite serious.

now also being conducted on rivers and lakes and recently becoming an intense topic of study (Jiang et al., 2019; Mani et al., 2015; McCormick et al., 2014). In India there are extremely limited studies on microplastic contamination in freshwater ecosystems (Sruthy & Ramasamy, 2017). So far, no study has been conducted on assessing the load of MPs in river Ganga and this is the first attempt to quantify MPs in sediment collected from the Ganga.

Objectives and Approach of Ecotoxicology Component

The Ecotoxicology Component is aimed to investigate the occurrence, spatial-temporal distribution, and ecological risks of persistent and toxic pollutants of immediate concern viz OCPs, PCBs, Heavy Metals and Microplastics along the Ganga River across all the five states.

Previous studies on the Ganga lacked comprehensive assessment of ecological risks from multiple stressors to the aquatic species. Further these studies neither included entire river nor the seasonal aspect. The lack of complete data has affected biodiversity conservation plans and environmental monitoring efforts for Ganga River. Therefore, we adopted a systematic and comprehensive approach to conduct appropriate ecotoxicological risk assessment (Figure 1.8) of target contaminants group along the Ganga. The study is important to identify high risk or vulnerable zones that need immediate attention for biodiversity conservation program and develop effective monitoring and mitigation strategies. The output of this ecotoxicology research will be helpful to policymakers in identifying the trends, current status, especially the effectiveness of the policy to ban persistent pollutants and ecological risks of toxic pollutants usage at the state level. This will ensure that effective measures are implemented at the priority zones to control pollution and conserve the aquatic biodiversity of the Ganga River.

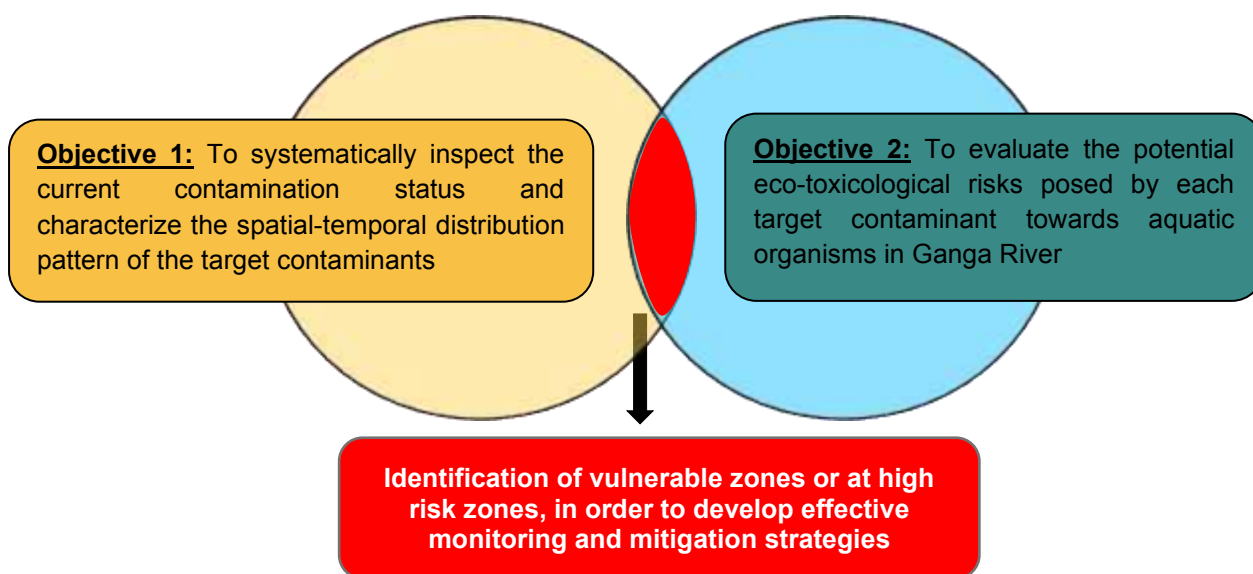


Figure 1.8: Comprehensive Eco-toxicological Risk Assessment approach

Based on the history of pollution, high historic usage, detection frequency reported in previous studies, pollutants included in the CPCB monitoring network, and listed as POP in Stockholm convention and contaminants with high toxicity profiles (**Annexure – I, Table A1**), the following group of pollutants as presented in Table 1.6 were selected for present study:

- (i) 23 Pesticides
- (ii) 9 Heavy metals
- (iii) 11 Highly toxic polychlorinated biphenyls congeners
- (iv) Microplastics

Table 1.6: List of pollutants analysed in the study:

Pesticides	
(i) Organochlorine Pesticides	
HCHs	alpha-hexachlorocyclohexane (α -HCH)
	beta-hexachlorocyclohexane (β -HCH)
	gamma-hexachlorocyclohexane (γ -HCH) or commonly known as lindane
	delta hexachlorocyclohexane (δ -HCH)
DDTs	p,p'-dichlorodiphenyltrichloroethane (p,p'-DDT)
	p,p'-dichlorodiphenyldichloroethane (p,p'-DDD)
	p,p'-dichlorodiphenyldichloroethylene (p,p'-DDE)
Chlordanes (CHLs)	cis-chlordane (c-CHL)
	trans-chlordane (t-CHL)
Heptachlors (HCHLs)	Heptachlor
	Heptachlor Epoxide
Drins	Aldrin
	Dieldrin
	Endrin
	Endrin Aldehyde
	Endrin Ketone
Endosulfan (ES)	α -endosulfan (α -ES)
	β -endosulfan (β -ES)
	endosulfan sulfate (ESS)
Methoxychlor (M-CHLR)	
(ii) Organophosphorous Pesticides	
Methyl Parathion	
Malathion	
Chlorpyrifos	

(iii) Heavy Metals	(iv) Polychlorinated Biphenyls (PCBs) Congeners
Arsenic	28 2,4,4'-Trichlorobiphenyl
Cadmium	44 2,2',3,5'-Tetrachlorobiphenyl
Chromium	52 2,2',5,5'-Tetrachlorobiphenyl
Copper	77 3,3',4,4'-Tetrachlorobiphenyl
Iron	101 2,2',4,5,5'-Pentachlorobiphenyl
Lead	105 2,3,3',4,4'-Pentachlorobiphenyl
Mercury	118 2,3',4,4',5'-Pentachlorobiphenyl
Nickel	126 3,3',4,4',5'-Pentachlorobiphenyl
Zinc	138 2,2',3',4,4',5'-Hexachlorobiphenyl.
Arsenic	153 2,2',4,4',5,5'-Hexachlorobiphenyl
Cadmium	180 2,2',3,4,4',5,5'-Heptachlorobiphenyl
Chromium	

Additionally, physico-chemical parameters were also recorded and analysed for surface water at each site. The parameters selected were: temperature, pH, dissolved solids, dissolved oxygen, compounds of nitrogen (Nitrates and Ammonium), conductivity and were recorded through digital kit **ProDSS and YSI**.

Chapter 3

Sampling Methods

3.1 Zone demarcation and Sampling sites

Prior to sampling, it is important to understand factors affecting water quality thoroughly, and then it is necessary to select specific areas that are representative of the river to sample. The sampling sites are determined based on the objectives of the study and site-specific condition. Keeping the above criteria in account, we conducted a rapid reconnaissance survey for aquatic habitat assessment between May–June 2017 for finalizing the sampling sites. The final sampling sites were selected based on the presence/absence of agricultural and industrial belts, upstream/downstream sites of potential contaminant discharges, and the existing monitoring stations prescribed by the Central Pollution Control Board (CPCB) of India.

Among the five Ganga states, there is a significant difference in environmental flow, demographics, land use pattern, average pesticide consumption rate, industrial settlements, and wastewater generation as presented in Table 1.7. Therefore, to gain a better understanding of the factors influencing the water quality parameters and distribution of contaminants (organic and inorganic) in different stretches of Ganga River, based on key features presented in Table 1.7, we demarcated the 2525 Km stretch into five zones (Figure 1.9 and Figure 1.9 & 1.10).

Table 1.7: Demarcation of zones based on cultivable land, cropping intensity and Industrial settlements in the states of the Ganga

States	Zone	Total cropped Area (000 Thousand Hectares, 2013-2014) ^b	Cropping Intensity [#] (%) (2013-2014) ^b	Total pesticide consumption (%) 2016-2017 ^c	Industrial settlements (Grossly Polluting Industries)
Uttarakhand	UZ	1099	146	0.92	42
Uttar Pradesh	UMZ1 ⁺	25896	145	71.03	687
	UMZ2 ⁺⁺				
Bihar	LMZ	7580	123	5.88	13
Jharkhand		1672	59	3.79	0
West Bengal	LZ	9618	172	18.38	22

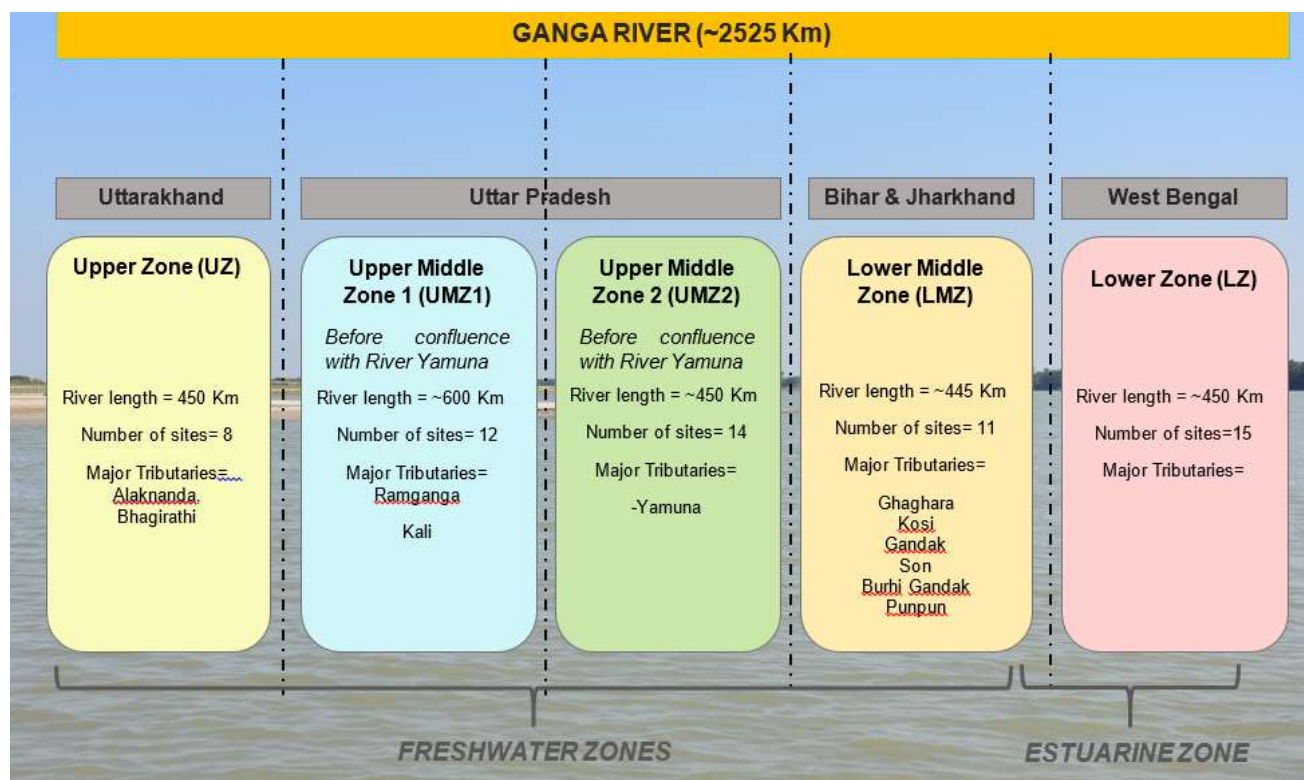


Figure 1.9 Zones Demarcation and characteristics attributes

Within these five-zones, forty-three sampling sites (Table 1.8) were selected. Subsequently, the samples were collected throughout two seasons i.e. Post-Monsoon (October to November 2017) and Post-Winter (April to May 2018) to characterize the influence of seasonal variation on the water quality.

Table 1.8: Sampling sites in each state and zones

No.	Sampling Sites	State	Zones
1	Harshil	Uttarakhand	Upper Zone (UZ)
2	Uttarkashi		
3	Dharasu		
4	Tehri upstream		
5	Devprayag (Alakhnanda)*		
6	Devprayag (Bhagirathi)*		
7	Devprayag (downstream)*		
8	Rishikesh		
9	Bijnor	Uttar Pradesh	Upper Middle Zone 1 (UMZ1)
10	Tigri Ghat (Gajraula)		
11	Brijghat (Gajraula)		
12	Narora		
13	Kachla downstream		
14	Dhai Ghat (Samshabad)		
15	Rajghat (Kannauj)		
16	Fattepur (Kanpur)		
17	Jajmau(Kanpur)		
18	Fatehpur (Rewari)		
19	Dhumanganj (Prayagraj)		
20	Rasoolabad (Prayagraj)		
21	Sangam (Prayagraj)*	Uttar Pradesh	Upper Middle Zone 2 (UMZ2)
22	Tela (Bhadoi)		
23	Mirzapur		
24	Varanasi		
25	Mughal Sarai Sewage drain, Varanasi *		
26	Nagwa Drain, Varanasi *		
27	Assi Ghat, Banaras, Varanasi		
28	Khirkia Drain, Varanasi*		
29	Varuna Sewage drain, Varanasi*		
30	Rajghat, Varanasi*		
31	Manikarnika Ghat, Varanasi*		
32	Harishchandra Ghat, Varanasi*		
33	Ghazipur		
34	Ballia		
35	Sitabdiara to Revelganj	Bihar	

36	Hajipur downstream*		Lower Middle Zone (LMZ)
37	Ramdauli (Patna)		
38	Mokama Upstream*		
39	Mokama downstream*		
40	Simariya Ghat		
41	Munger		
42	Tilakpur (Navagarhi)*		
43	Sultanganj*		
44	Kahalgaon		
45	Sahibganj	Jharkhand	Lower Zone (LZ)
46	Hashimpur	West Bengal	
47	Ajimganj/Jiaganj		
48	Sujapur		
49	Nabadwip		
50	Sukhsagar		
51	Tribeni		
52	Serampur*		
53	Dakshineshwar*		
54	Shibpur*		
55	Garden Reach		
56	Batanagar		
57	Uluberia*		
58	Falta		
59	Diamond Harbour		
60	Haldia*		

**Only water quality parameters are reported at these sites*

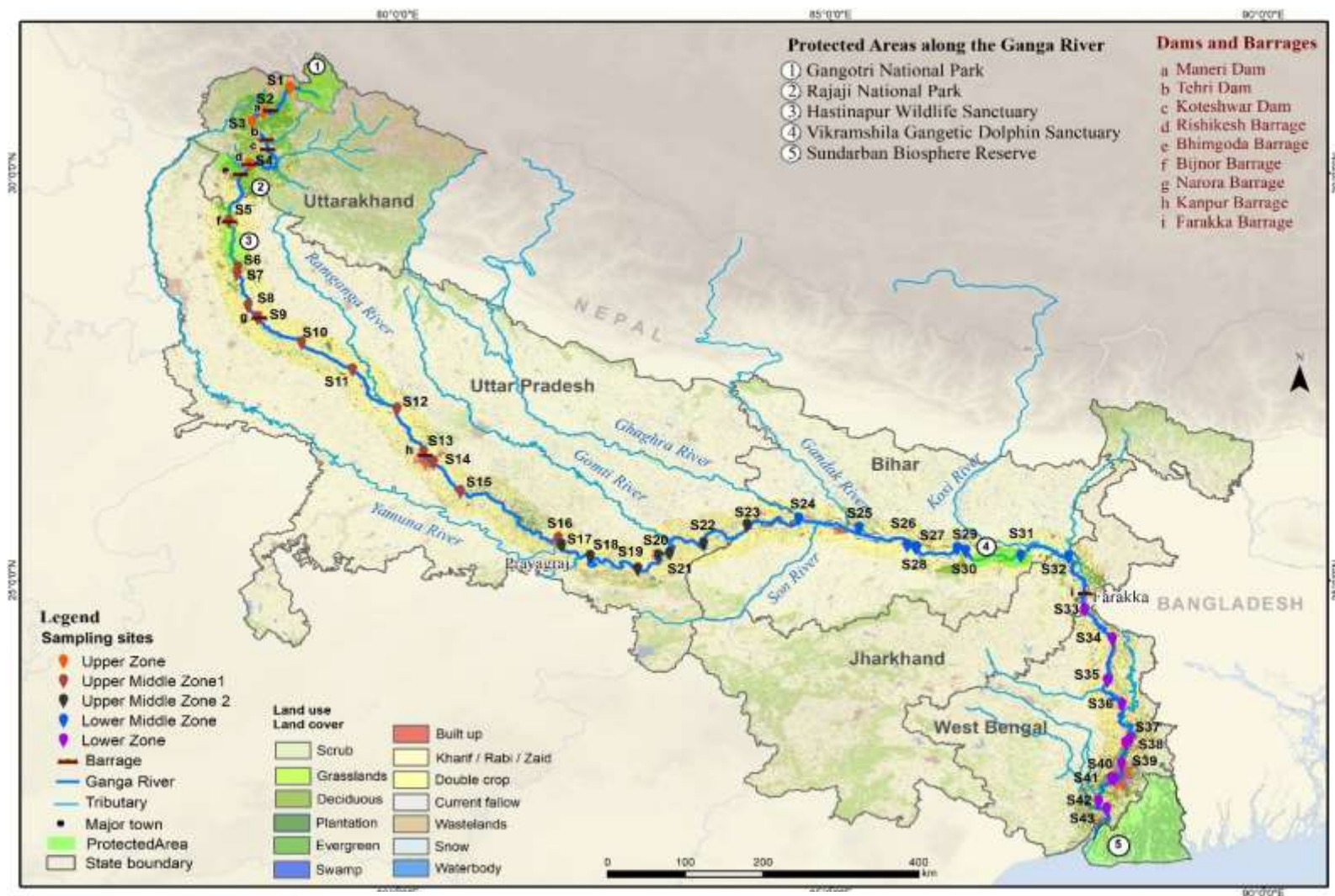


Figure 1.10: Demarcation of zones and sampling sites

3.2 Sample Collection Methodology

The sampling methodology adopted for the present study is designed according to project objectives and according to the international and material guidelines. A detailed manual titled “Technical Guidance for Collection of Abiotic and Biotic Samples” was developed that includes the general and specific procedures, methods and considerations to be followed for the collection of abiotic and biotic samples from River. (Annexure -). At each sampling site a 5 km stretch was selected as representative of that site and physico-chemical parameter were evaluated at an average interval of 1 Km. Along this 5 km stretch, three to five abiotic samples (water and sediment) were collected randomly, and were bulked together to form a composite sample. The biotic samples, mainly fish samples, were collected from the entire 5 km stretch (Figure 1.11).

3.2.1 Water Samples

At each sampling site (n=43) three surface water samples were collected randomly, at an average depth of 30 cm, in amber coloured pre-cleaned high-density polyethylene (HDPE) bottles and were bulked together to form a composite sample. Water samples collected for heavy metal analysis were fixed at pH 2 using 0.5% HNO₃ whereas samples for pesticides analysis were stored without preservatives. After collection, the samples were properly labelled and shipped in cooling stage (icebox) to the laboratory and were kept at 4°C until further analysis.

3.2.2 Sediment Samples

At each sampling site (n=43) three surface sediment samples were collected from beneath an aqueous layer from the depth starting from ~10-15 cm either directly, or using a handheld device such as auger. The sediment samples were collected in a

tightly capped zip lock bag and were adequately labelled. Samples were stored at low temperature to prevent degradation of pesticides.

3.2.3 Fish Samples

To enable statistically sound data, up to 5 to 6 fish per species of nearly uniform size ranges were collected from each site (within ~5Km stretch). As a general guideline, it was ensured that the largest and smallest fish within each group does not exceed the average length of the group by more the 25%. If the fishes were small, more than five individuals were collected so that there is enough tissue per sample for the laboratory analysis. All the physical attributes of fish sample including weight, height, sex deformities, external parasites, etc. were noted in the field notebook of ecotoxicological datasheet. After the dissection, tissue sample of at least 150-200 gm were collected in polypropylene tubes for analysis of both toxicants types (i.e. inorganic/organic). After collection, the samples were properly labelled and shipped in the cooling stage (liquid N₂ can) to the laboratory and were kept at -20°C until further analysis.



Figure 1.11: Sample collection at different sites

4.1. Pesticides

1. Abiotic Matrix

As mentioned earlier, more than 70% of the land along both sides of Ganga River is utilized extensively for agricultural activities, and pesticides run-offs from near-by fields contribute significantly toward the organic contamination and load in the Ganga River. Therefore, we investigated the occurrence, spatial-temporal distribution, potential sources, of banned, as well as restricted OCPs and some OPPs, in the abiotic matrices i.e. surface water and sediments of the Ganga. The results of each class of pesticides are presented below:

4.1.1. Organochlorine Pesticides (OCPs)

Twenty OCPs were investigated in this study which were selected on the basis of criteria mentioned in sec. A list of these pesticides is given in Table 1.6.

(i) Total OCPs in Surface Water

A summary of descriptive analysis of the twenty target OCPs detected in Ganga River is presented in Figure 2.1 & 2.2. The total OCPs (Σ OCPs) concentration in water samples ranged from **0.028 -16.228 $\mu\text{g/L}$** (**Mean: 1.567 $\mu\text{g/L}$** ; median **0.630 $\mu\text{g/L}$**) in post-monsoon season, and **0.018-12.464 $\mu\text{g/L}$** (**Mean: 0.939 $\mu\text{g/L}$** ; median **0.400 $\mu\text{g/L}$**) in post-winter season.

For all the water samples, the mean concentration of Σ OCPs in Ganga River were significantly higher (~2 to 5 times) in the post-monsoon season than those in post-winter season. This could be explained by the high atmospheric precipitation and subsequently higher agricultural surface run-off in monsoon season that facilitates the entry of pesticides to nearby waterbodies. In addition, just before the monsoon, approximately 5 Km land on both sides of the riverbank in all states except Uttarakhand (UZ) is utilized extensively for dry river-bed cultivation of seasonal vegetables with possibly high pesticide application. These pesticides

may eventually end up as surface run-off due to high flooding and precipitation in monsoon season, thus increasing their levels in surface water of the river.

The seasonal variation in zone-wise and site-wise distribution of individual OCPs concentration (mean in $\mu\text{g/L}$) in surface water of the Ganga River is presented in Figure 2.3 a and Figure 2.3b. The zone-wise pollution gradient observed in post-monsoon season was **LZ (Mean: $3.763\mu\text{g/L}$) > UMZ2 (Mean: $1.029\mu\text{g/L}$) > UMZ1 (Mean: $0.906\mu\text{g/L}$) > UZ (Mean: $0.896\mu\text{g/L}$) > LMZ (Mean: $0.481\mu\text{g/L}$).**

The results demonstrate that highly contaminated sites, mostly, prevail in Lower Zone (LZ) representing state of West-Bengal with the highest pesticides contamination recorded at Jiaganj, Diamond Harbour, Farrakka, and Serampore. The high concentration of OCPs in LZ, representing state of West Bengal, could be explained by, high cropping intensities in this catchment (Table 1.7), reduction in river flow due to diversion of river water to Bangladesh and abstraction of water for irrigation at Farakka barrage as well as potential illegal ongoing usage of target OCPs. The state uses 0.679 kg/ha of pesticides, which is higher than its neighboring state Uttar Pradesh (area wise 2.7 times bigger West Bengal) ([Devi et al., 2017](#)). Further a wide range of wet and dry season field crops, vegetables, fruits and spices are being grown with around 185% cropping intensity in the LZ. The LZ is the largest producer of rice, jute, pineapple and vegetables and second largest producer of potatoes and litchis in the country (State Agriculture Report, West Bengal, 2019). Major vegetable growing districts are all located on the Ganga River belt of the state. Unlike other food crops, most of the vegetables and fruits are succulent and attract several insect pests thereby requiring high pesticide input for these crops. Additionally, the kharif crop which is cultivated between December and April, is non-rain fed hence rely a lot on technological and chemical interventions like use of mechanized implements and pesticides.

In case of point source pollution, in LZ, there are 59 priority drains (having equal to or more than 1 MLD of flow) discharging tonnes of treated and untreated municipal and industrial wastes (organic load:190.41 tonnes per day; highest than other zones) into River Ganga.

LZ is the last zone in India and before the Ganga River outfalls in Bay of Bengal, it converts in the estuarine zone. Therefore, we also anticipate the influence of pesticides from point and non-point source pollution, tidal flushes, flood currents and, wind effects in this estuarine zone may result in higher accumulations of OCPs in sediment column which are washed downstream during heavy local precipitation.

The low pesticide pollution gradient in LMZ, representing states of Bihar and Jharkhand, could be explained by high drainage from major tributaries like Ghaghra (94.4 billion cumecs), Gandak (52.2 billion cumecs), and Son (22.42 billion cumecs) contributing significantly to the environment flow (~5) and increase in dilution factor. In addition, the cropping intensity in this catchment is also low as compared to the other zones.

The zone-wise pollution gradient observed in post-winter season was **LZ (Mean: 2.041µg/L) > UZ (Mean: 0.859µg/L) > LMZ (Mean: 0.631µg/L) > UMZ2 (Mean: 0.473µg/L) > UMZ1 (Mean: 0.459µg/L)**. UZ (Uttarakhand) located at high elevation (sites at 883-2000 m above the sea level) and considered as relatively pristine and unpolluted zone/state with relatively low agricultural practices, also recorded significant amount of OCPs (particularly HCHs). This could be explained by long-range atmospheric transfer (LRAT) of HCH followed by condensation in low volatility range, wherein the low temperature delays their photolytic and microbial degradation and maintain their persistence in such areas (Oehme and Manø, 1984; Barrie et al., 1992; Willet et al., 1998). Further, potential fresh inputs of some OCPs for orchards farming could also be the contributing factor towards high concentration of OCPs in this zone.

Individual pesticide concentration in each season is given in Figure 2.4. The group-wise seasonal and spatial distribution of OCP revealed the **predominance of Heptachlors**

(HCHLs) & HCH isomers in all zones for both seasons (Figure 2.2 & 2.4), however, the low dilution in dry season (post-winter) highlights the presence of other OCPs also. The mean concentration of group-wise of OCP, for post-monsoon season, followed the order as **Σ HCHLs (3.799 ug/L) > Σ HCHs(2.266 μ g/L) > Σ Drins (0.785 μ g/L) > Σ CHLs(0.10 μ g/L) > Σ DDTs(0.09 μ g/L) > Σ ESs(0.02 μ g/L) > MCHLR(0.01 μ g/L)** whereas in post-winter season the mean concentrations followed the pattern as: **Σ ES (3.30 μ g/L) > Σ HCHLs (0.497 ug/L) > M-CHLR (0.395 μ g/L) > Σ HCHs(0.138 μ g/L) > Σ Drins(0.072 μ g/L) > Σ DDTs (0.043 μ g/L) > Σ CHLs(0.015 μ g/L).** The detection frequencies (Figure 2.5) of OCPs, in water, were in the range of 12-91% in post-monsoon and 4-98% in post-winter. The results revealed the ubiquitous distribution of *Heptachlor* and its metabolite (belonging to group H-CHLs), *Lindane* (γ -HCH), and, α - & β - HCH (belonging to group HCHs), that reflect their potential fresh and illegal usage.

Figure 2.1: Mean concentrations of OCPs and groups in surface water of Ganga River for post-monsoon (PM) and post-winter (PW)

Figure depicts that the concentration of T-OCPs in Ganga River were higher in the PM season than in PW season.

Among the T-OCPs, the concentrations of major contributing groups (HCH, HCHLs, and Drins) were also higher in PM season.

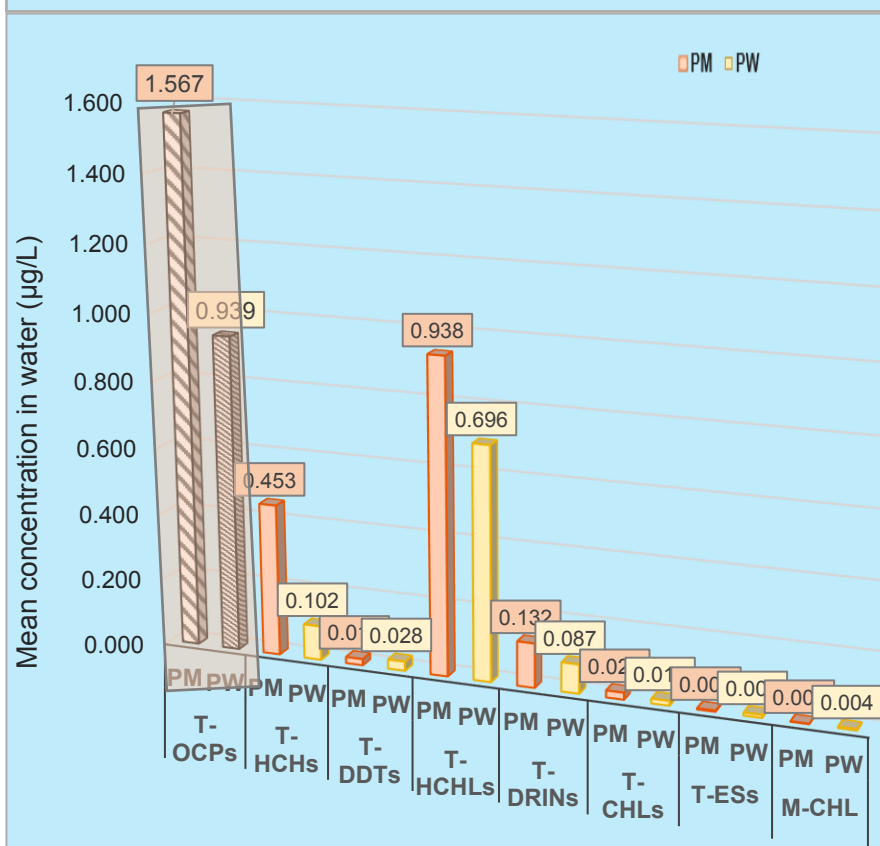
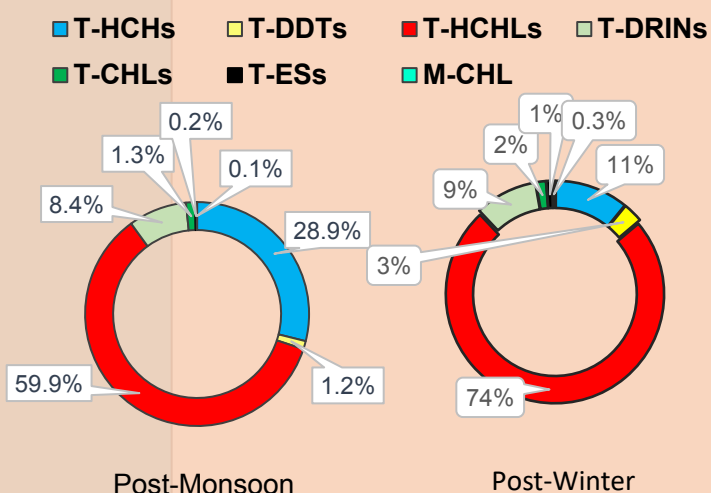


Figure 2.2: % contribution of pesticide groups towards T-OCPs of different groups of OCPs in surface water of Ganga River

Figure depicts the dominance of T-HCHLs > T-HCH > T-Drins for both seasons



SURFACE WATER

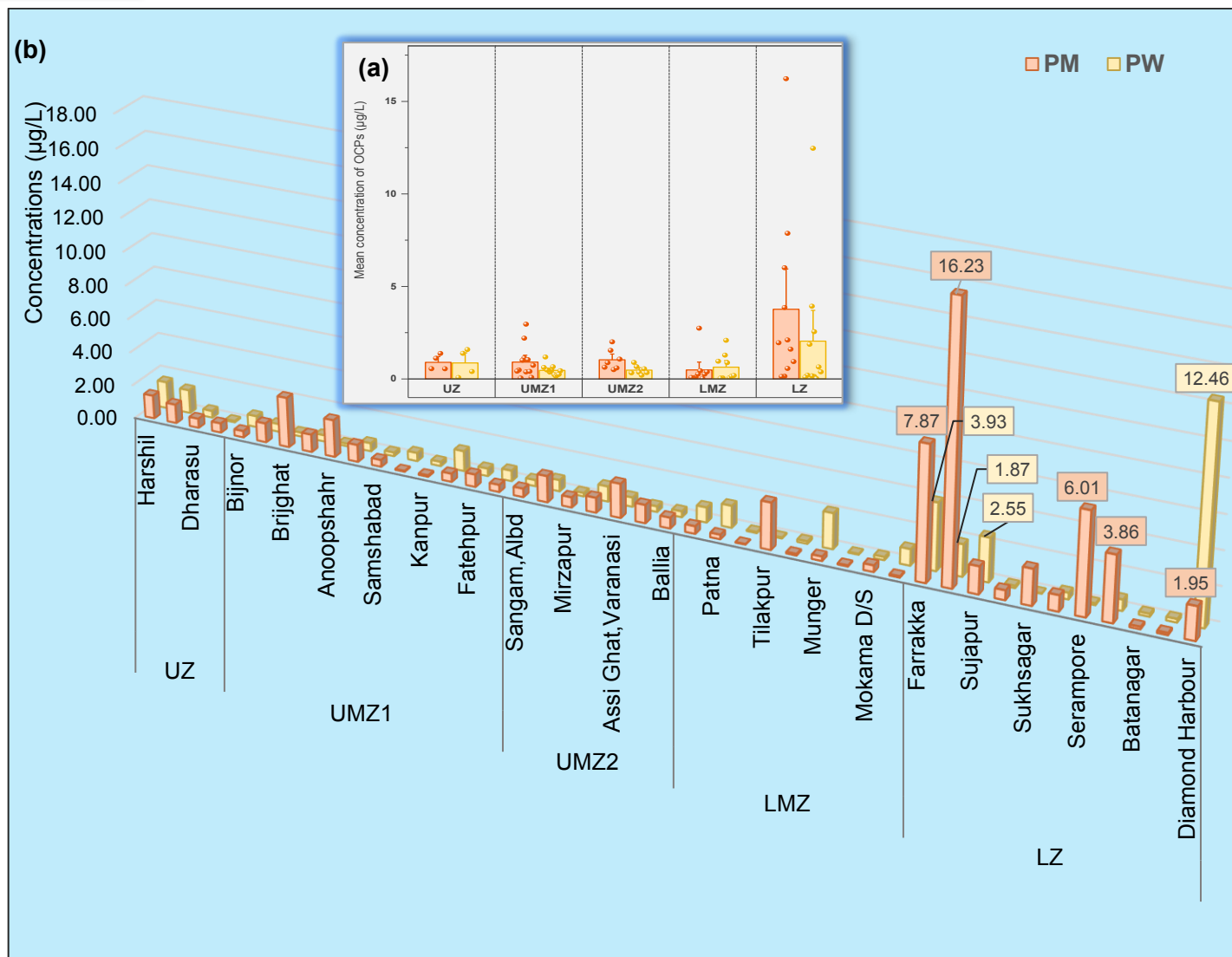


Figure 2.3: (a) Zone-wise distribution of OCP (mean)

(b) Site-wise distribution (Sum) for post-monsoon (PM) and post-winter (PW)

Highly contaminated sites mostly prevails in Lower Zone (LZ) representing state of West-Bengal. The five most pesticides contaminated sites Jiaganj, Diamond Harbour, Farakka, and Serampore

Lowest contamination prevails in Lower Middle Zone (LMZ) representing state of Bihar.

**Graph (Figure a) represents mean bar with data scatter as circles t

SURFACE WATER

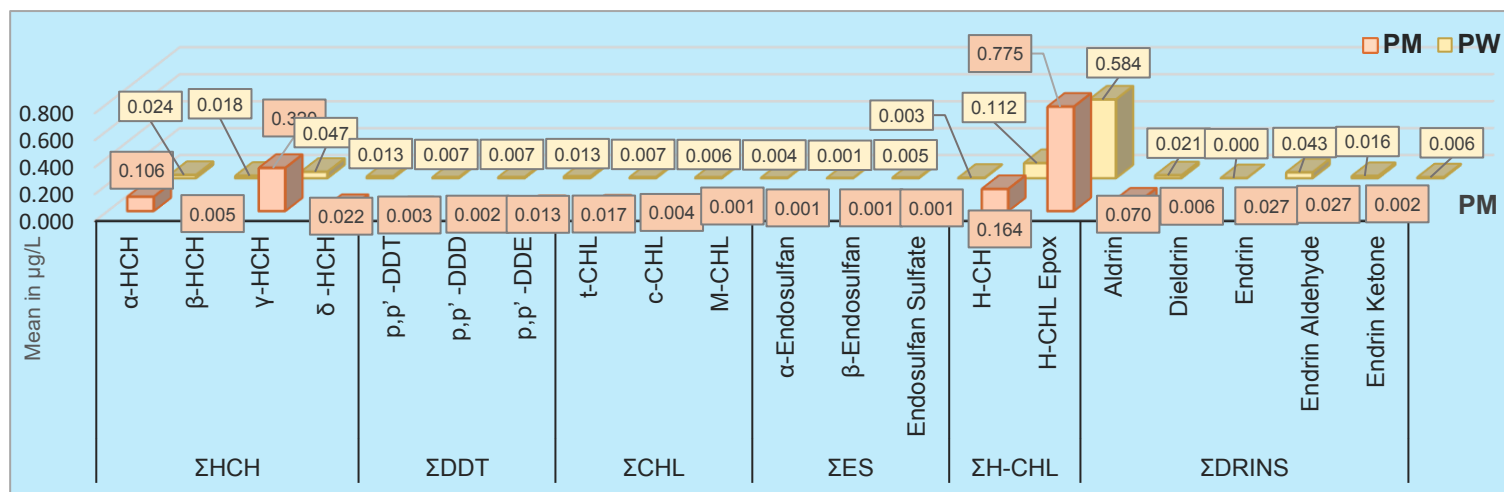


Figure 2.4: Individual OCPs concentration (mean in µg/L) in surface water of Ganga River for post-monsoon (PM) and post-winter (PW)

The highest concentration were observed for **Heptachlor Epoxide** and **Heptachlor** belongs to group H-CHLs, **Lindane (γ-HCH)**, and, **α-HCH** belonging to group HCHs that reflect their predominant uses.

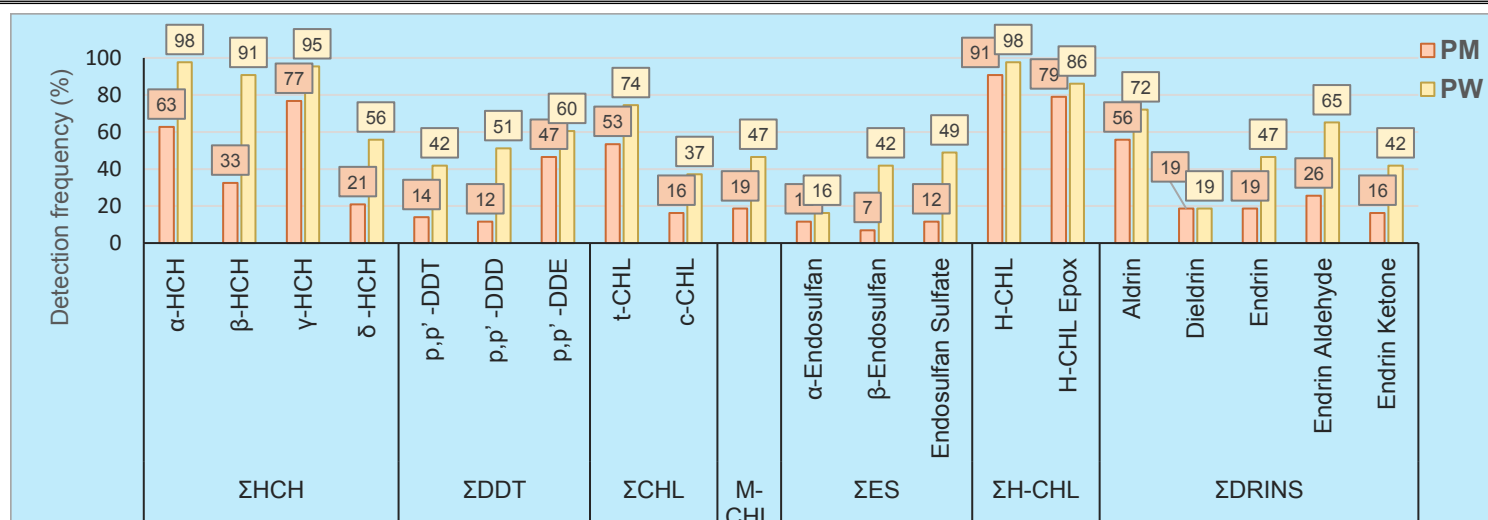


Figure 2.5: Detection frequency (%) of OCPs in surface water of Ganga River

The most frequently detected OCPs, were **Heptachlor Epoxide** and **Heptachlor** belongs to group H-CHLs, **Lindane (γ-HCH)**, and, **α- & β- HCH** belonging to group HCHs, **Aldrin** belonging to Drins

(ii) Total OCPs in Sediment

Uncontrolled discharge of pesticides in environmental matrices has led to the accumulation of these contaminants in river sediments, making them the secondary source of pollution with the potentially detrimental effect on both the human health and ecosystems. In addition to being pollutants sink, sediments are a source of contamination when change in chemical composition of aqueous phase, anthropogenic disturbance, or biological activity remobilize the pollutants. Also, aquatic biota is exposed to the pesticides accumulated within the sediments and may transfer potentially toxic concentrations via food chain to different trophic levels including humans, therefore the assessment of pesticides in sediments becomes equally important. Pesticides and their transformation products (TPs) are mainly hydrophobic, persistent and bio-accumulable wherein they tend to strongly bind to sediment/ soil and biological tissue. Pesticides that exhibit such behaviour include the organochlorines such as DDT, endosulfan, endrin, heptachlor, lindane and their TPs. Most of them are now banned for agriculture but their residues are still present (Vijayan *et al.* 2008, Muralidharan *et al.* 2011).

In present study the total OCPs (Σ OCPs) concentration for sediment samples (Figure 2.6) ranged from **2.753 - 703.413 $\mu\text{g/kg}$ (Mean: 63.93 $\mu\text{g/kg}$; Median: 23.396 $\mu\text{g/kg}$)**, in post-monsoon season and **0.726 – 57.979 $\mu\text{g/kg}$ (Mean: 16.18 $\mu\text{g/kg}$; Median: 12.986 $\mu\text{g/kg}$)** in post-winter season. Similar to water samples, the mean concentration of Σ OCPs, in all the sediment samples from the Ganga River were significantly higher (~4 to 5 times) in the post-monsoon season than those in post-winter season. The pesticides (having high K_{oc}) often have high affinity towards the soil matrix therefore as compared to water samples, the levels and detection frequencies of pesticides were higher in sediment samples compared to water samples.

The zone-wise seasonal variation in individual OCPs concentration (mean in $\mu\text{g/kg}$) in sediments of Ganga River is presented in Figure 2.8a. The zone-wise pollution gradient observed in post-monsoon season was **UZ (Mean: 172.381 $\mu\text{g/kg}$) > UMZ2 (Mean: 161.453**

µg/kg) > LMZ (Mean: 44.418 µg/kg) > UMZ1 (Mean: 32.097 µg/kg) LZ (Mean: 13.136 µg/kg).

For post-winter the trend was **UMZ1 (Mean: 20.539 µg/kg) > LMZ (Mean: 19.418µg/L)>UMZ2 (Mean: 18.124 µg/kg)> LZ (Mean: 11.720 µg/kg) > UZ (Mean: 4.702 µg/kg).**

As compared to water samples, the pattern of OCPs accumulation in sediment samples were different which could be attributed to binding capacity of sediment/soil (soil texture and particle size), and its organic matter content. Unlike water samples, low accumulation was observed in Lower Zone (LZ) and high OCPs concentration were recorded in LMZ. These patterns could be due to lower binding capacity and other physical attributes of its sediment thus making these pesticides bioavailable or releasing in water compartment rather than keeping it in bound form.

Figure 2.8b shows site wise distribution of individual pesticides along the Ganga. Balia in UMZ2 (Uttar Pradesh) recorded highest pesticide accumulation in sediment (703.41 µg/kg).

The group-wise seasonal and spatial distribution of OCP in sediment samples revealed the **predominance of Heptachlors (T-HCHLs) & HCH isomers (T-HCH)** in all zones for both seasons (Figure 2.6 and 2.7), however, the low dilution in dry season (post-winter) highlights the presence of other OCPs also. The group-wise distribution of OCP, for post-monsoon season, followed the mean concentration order as: **ΣHCHLs (32.21 µg/kg)> ΣHCHs (18.74 µg/kg)> ΣCHLs (8.44 µg/kg)> ΣDrins (8.436 µg/kg > M-CHLR (1.39 µg/kg)>), ΣDDTs (1.37 µg/kg)> ΣESs (1.21 µg/kg)> ΣCHLs (0.571µg/kg).** For post-winter, the group-wise distribution of OCP followed the order as: **ΣHCHs (5.99 µg/kg)> ΣHCHLs (4.00 µg/kg)> Drins (3.90 µg/kg)> ΣDDTs (1.05 µg/kg)> ΣESs (0.71 µg/kg) > ΣCHLs (0.37 µg/kg)>M-CHLR (0.19 µg/kg).**

Seasonal variation in individual OCP concentration is given in Figure 2.9. The detection frequencies of OCPs in sediments (Figure 2.10) were in the range of 2-91% in post-monsoon and 9-88% in post-winter.

The results revealed the widespread distribution of **Heptachlor Epoxide** and **Heptachlor** belonging to group H-CHLs, **Lindane (γ -HCH)**, and, α - & β - HCH belonging to group HCHs, and **Methoxychlor (M-CHL)**.

Figure 2.6: Mean concentrations of total OCPs (T-OCPs) and its groups in sediments of Ganga River for post-monsoon (PM) and post-winter (PW) season

Similar to surface water, the concentration of T-OCPs in sediments of Ganga River were higher in the PM season than in PW season. Among the T-OCPs, the concentrations of major contributing groups (HCHLs, HCHs and CHLs) were also higher in PM season.

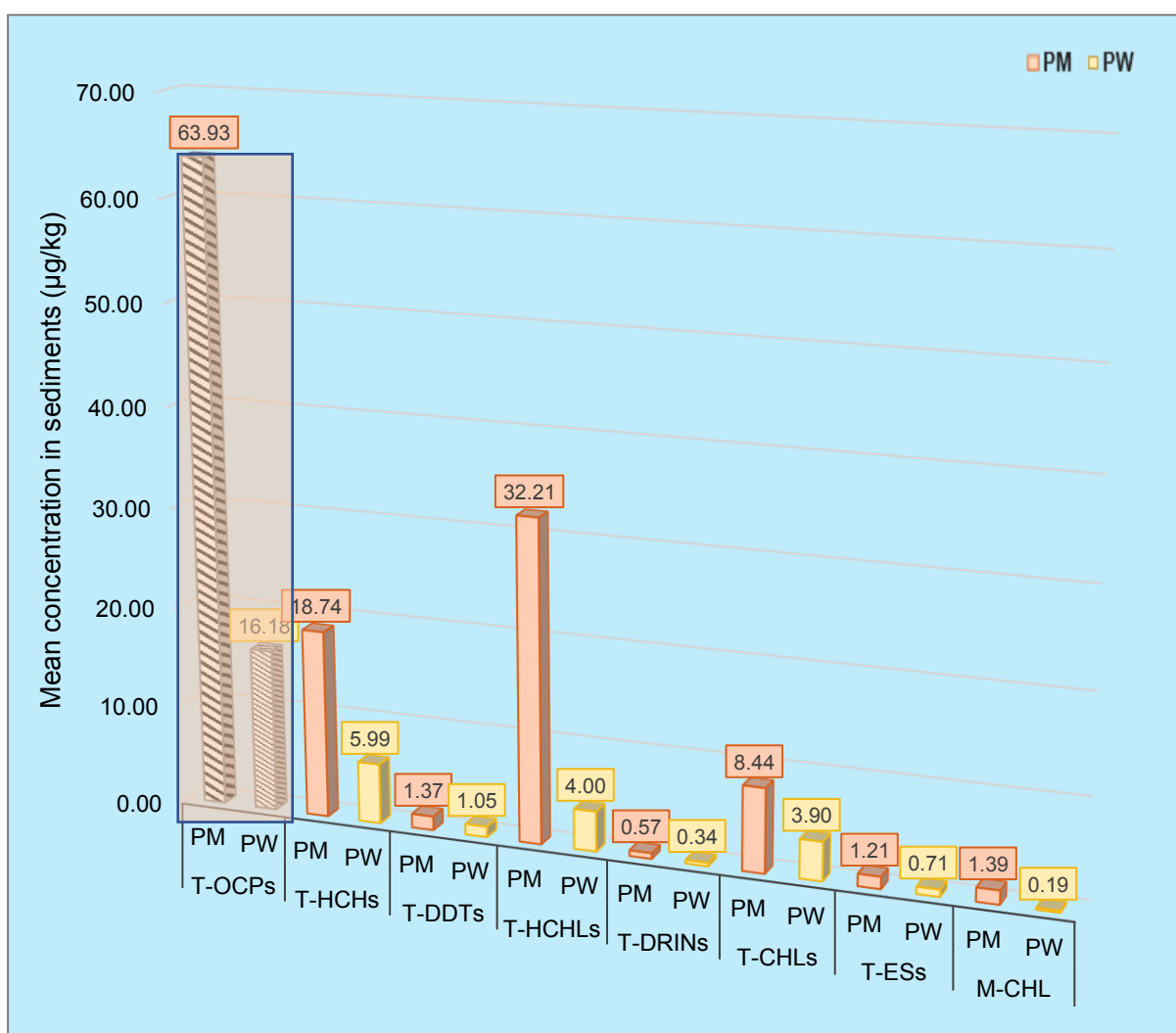
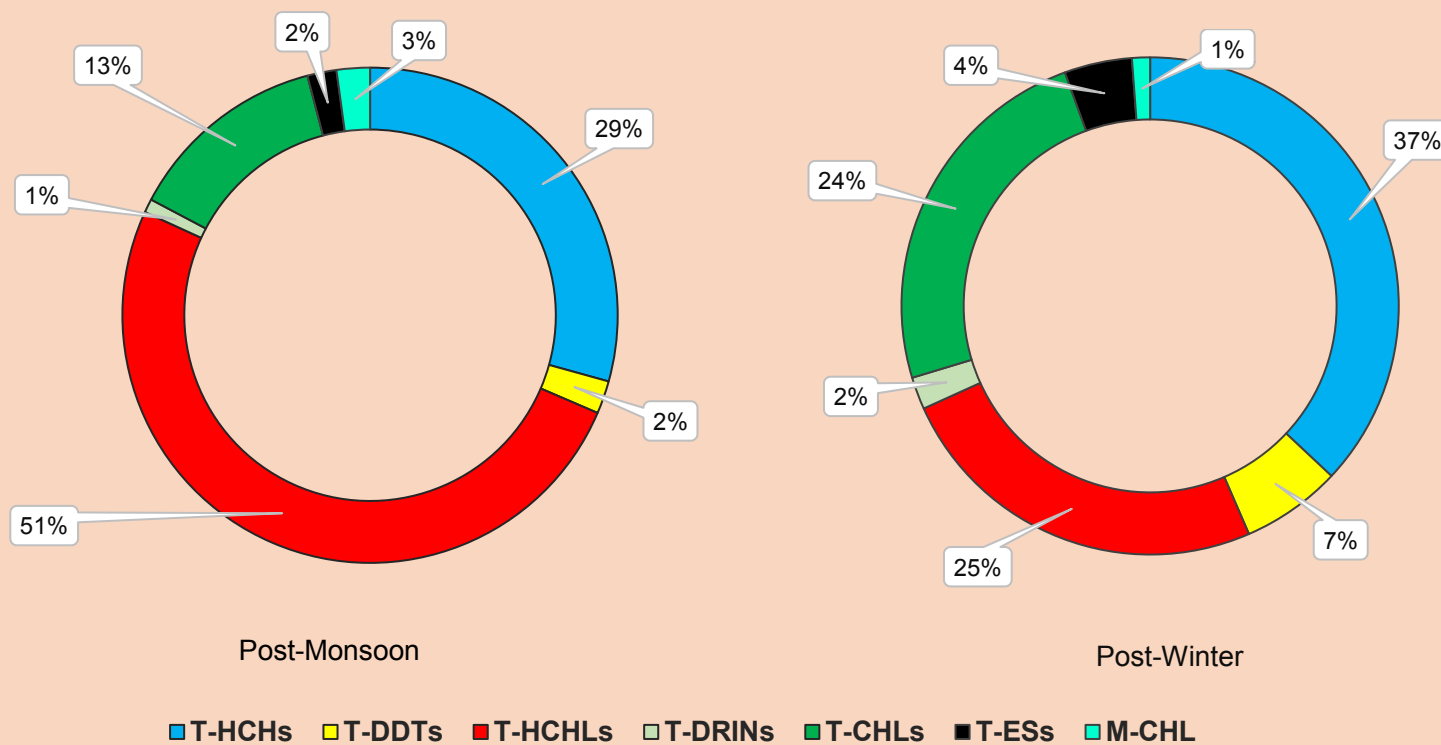


Figure 2.7: % contribution of pesticide groups towards T- OCPs of different groups of OCPs in sediment of Ganga River

Figure depicts the dominance of T-HCHLs and T-HCH. Unlike surface water (wherein T-Drins were third contributing group towards T-OCPs), in surface sediments T-CHLs emerged at third position.



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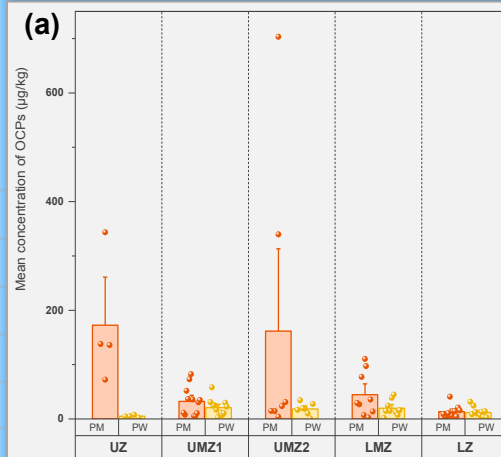
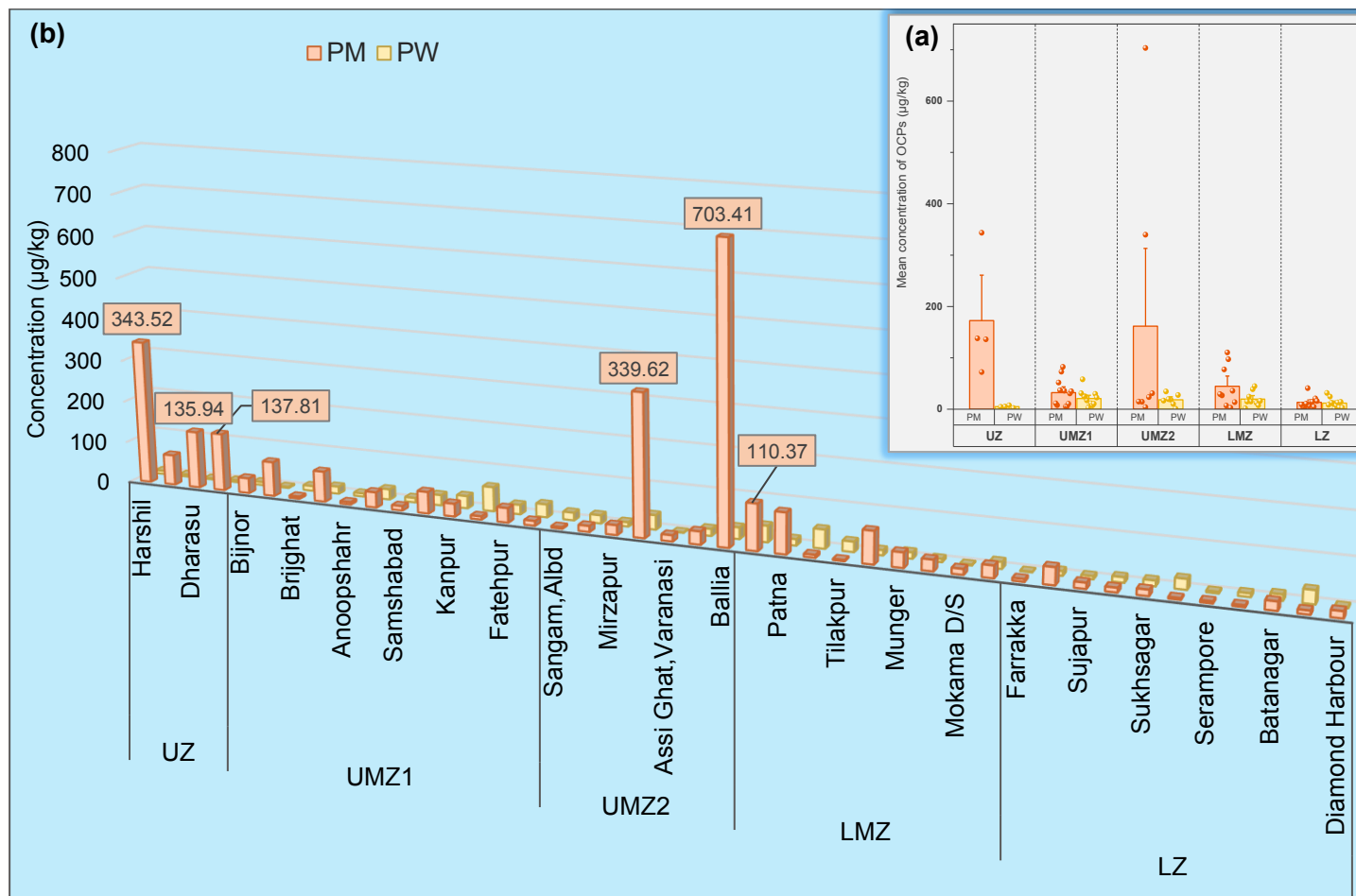


Figure 2.8: a) Zone-wise distribution of OCP (mean)

(b) Site-wise distribution (Sum) for post-monsoon (PM) and post-winter (PW)

Highly contaminated sites prevails in UZ and UMZ2. The five most pesticides contaminated sites are Ballia, Harshil, Varanasi, Rishikesh and Dharasu.

Unlike surface water, the lowest contamination prevails in Lower Zone (LZ) representing state of West Bengal. This observed trend in LZ could be attributed to the soil texture and particle size. The more sand and silt a sediment has, the less attractive it is to organic (carbon-based) contaminants such as OCPs

****Graph (Figure a) represents mean bar with data scatter as circles in the right**

Figure 2.9: Individual OCPs concentration (mean in $\mu\text{g/kg}$) in sediments of Ganga River

The highest concentration was observed for **Heptachlor Epoxide and, Lindane (γ -HCH)**.

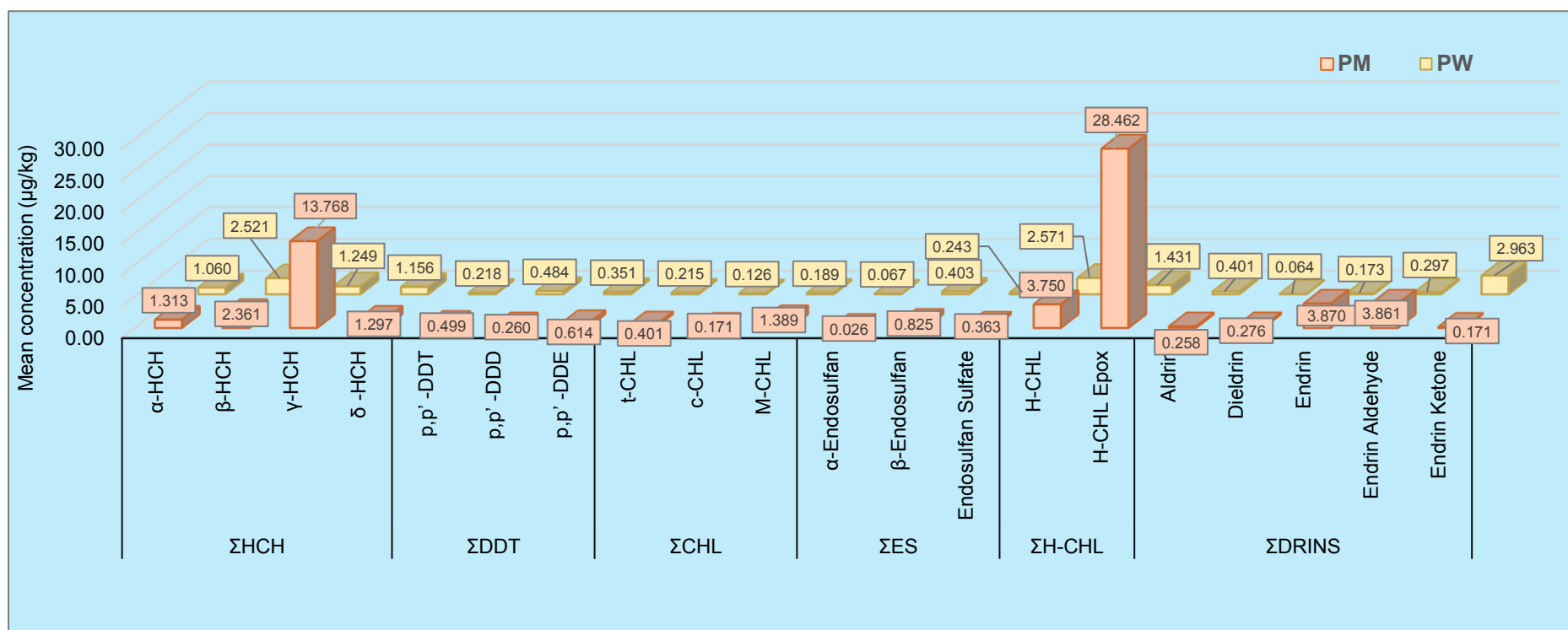
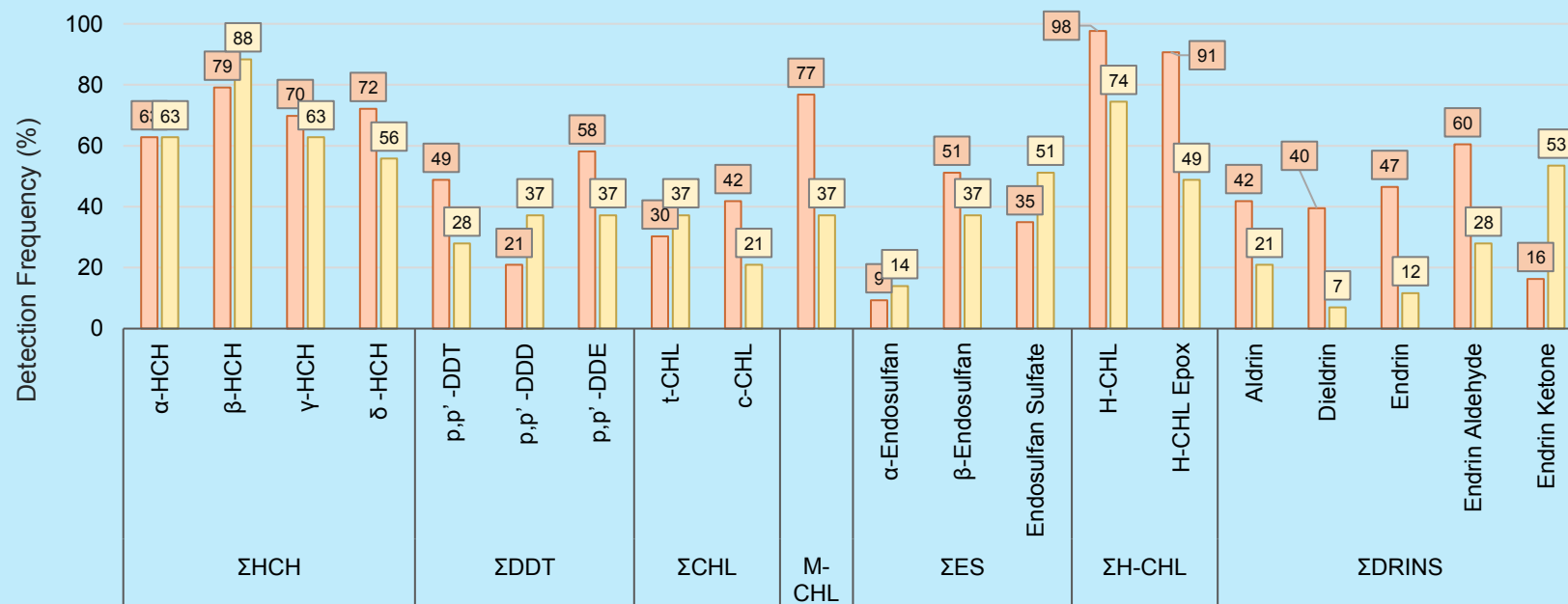


Figure 2.10: Detection frequency (%) of OCPs in surface sediments of Ganga River

The most frequently detected OCPs, were **Heptachlor Epoxide and Heptachlor** belongings to group H-CHLs, **Lindane (γ -HCH)**, and, **α - & β - HCH** belonging to group HCHs, and **Methoxychlor (M-CHL)**



(iii) Discussion on dominant pesticide groups

1. Heptachlors (HCHLs)

It is a pesticide which was used predominantly for soil-borne pests for agricultural crops and also use to kill soil insects and termites. It has been used more widely to kill cotton insects, grasshoppers, other crop pests and malaria carrying mosquitos. It's use is banned in the India since 1996, and most of the other countries of the world because of the persistence of its two break-down products viz. heptachlor epoxide and photoheptachlor in the environment. All these compounds are lipophilic and particularly heptachlor epoxide and photoheptachlor tend to accumulate in the food chain.

In this study, the distribution of Σ HCHLs (Figure 2.11a), in surface water, across zones showed the order as LZ(2.81 μ g/L)> UMZ1 (0.46 Ug/L) > LMZ(0.26) μ g/L> UMZ2(0.23 μ g/L)> UZ(0.06 μ g/L), in post-monsoon and LZ (1.65 μ g/L) >UZ (0.65 μ g/L)> LMZ (0.50 μ g/L) > UMZ2 (0.27 μ g/L)>LMZ1 (0.24 μ g/L) in post-winter. The percentage composition (Figure 2.11b) of Σ HCHLs in water samples revealed predominance of Heptachlor Epoxide (H-CHL Epo) with 83% and 62% contribution towards Σ HCHLs in post-monsoon and post-winter respectively.

The distribution of T-HCHLs (Figure2.12a), in sediments across zones showed the order as UMZ2 (143.85ug/kg) >UMZ1 (19.07 ug/kg)> UZ (12.16ug/kg)> LMZ (7.62 ug/kg)> LZ (2.92 ug/kg) in post monsoon. In post winter season the trend observed was UMZ1 (9.19 ug/kg)> UMZ2 (5.04 ug/kg) > LZ (1.39 ug/kg)> LMZ (1.24 ug/kg)> UZ (0.03 ug/kg). The percentage composition (Figure 2.12b) of Σ HCHLs in sediment samples revealed predominance of parent compound Heptachlor (H-CHL) with 64% and 88% contribution towards Σ HCHLs in post-monsoon and post-winter respectively.

The site-wise seasonal variation of H-CHLs in surface water and sediments of Ganga River is presented in Figure 2.13a and 2.13b respectively. In post-monsoon season, the Σ H-CHLs concentration ranged from **0.009-11.518 μ g/L (Mean: 0.938 μ g/L; Median: 0.144 μ g/L)** in

water and **0.264 -679.091 µg/kg (Mean: 32.213 µg/kg; Median: 4.810 µg/kg)** in sediment. In post-winter season, the ΣH-CHLs concentration ranged from **0.006-11.651 µg/L (Mean: 0.696 µg/L; Median: 0.149 µg/L)** and **BDL-48.903 µg/kg (Mean: 4.003 µg/kg; Median: 1.850 µg/kg)** in water and sediment respectively. Most contaminated site for water was Diamond Harbor (UZ) and for sediment was Balia and Varanasi (UMZ)

Sources of H-CHL- Historic or fresh inputs

When the ratio of heptachlor epoxide/heptachlor is > 1, the heptachlor contamination most likely originates from older uses of heptachlor (Jiang et al., 2009). In present study, in almost 60% of the sampling sites heptachlor contamination was >1 indicating historic or older usage of this banned pesticide.

SURFACE WATER

Figure 2.11a: Seasonal variation and zone-wise distribution of total HCHLs (ΣH-CHLs) in water

High contamination prevails in LZ (West Bengal) whereas lowest recorded for UMZ2 (Uttar Pradesh, after confluence with Yamuna)

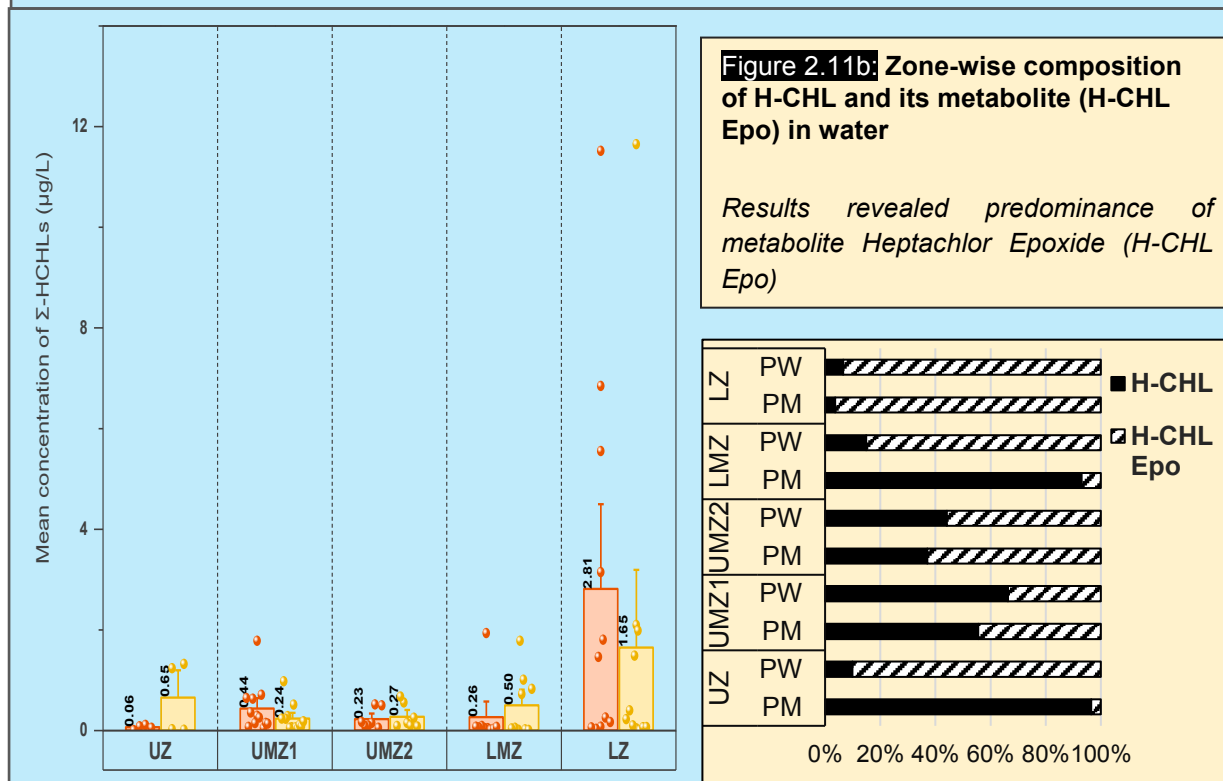
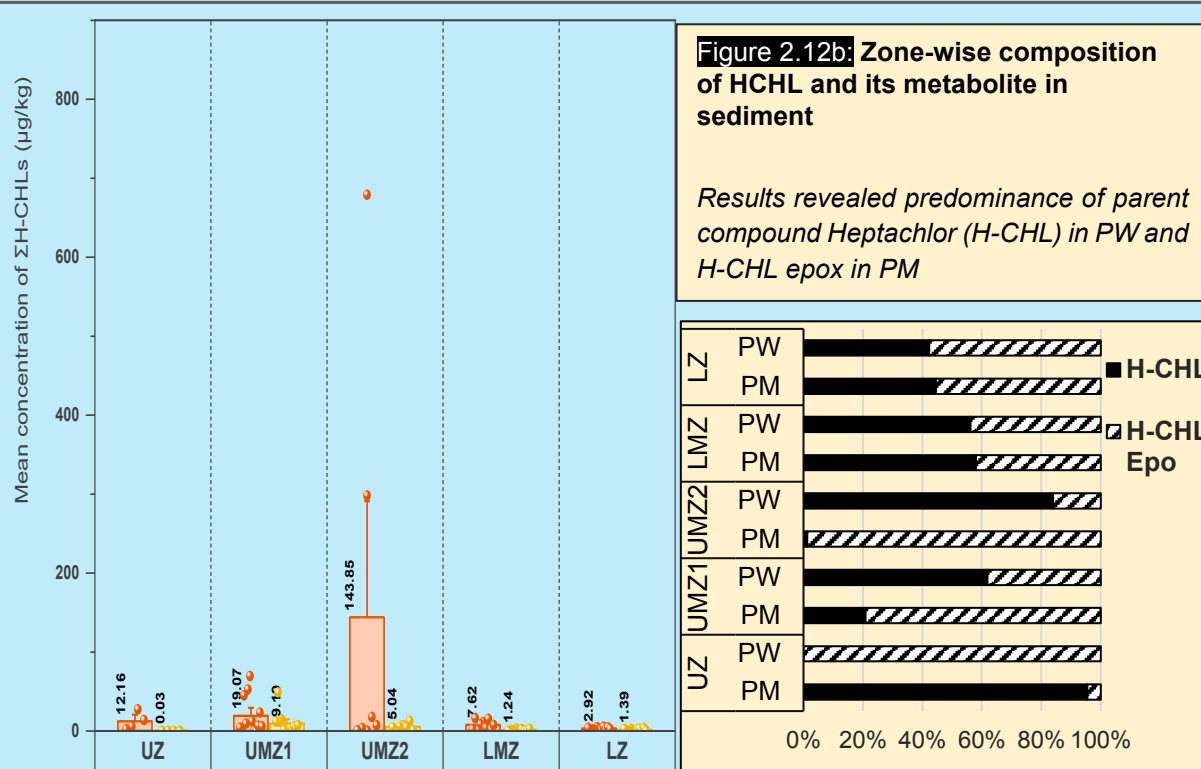
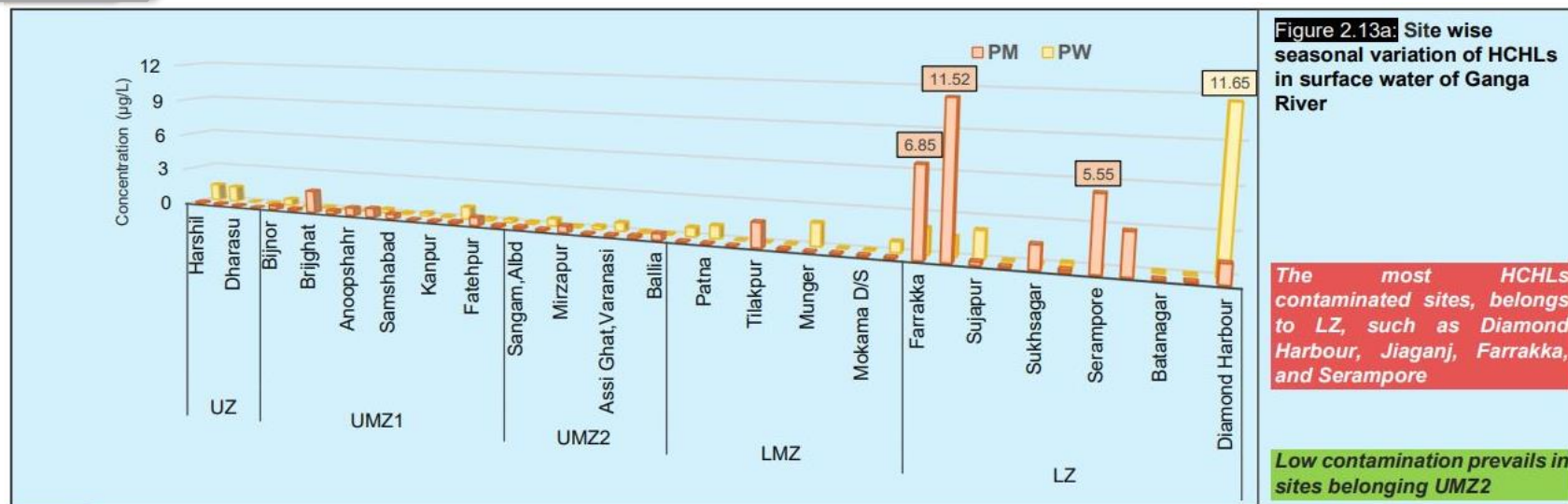


Figure 2.12a: Seasonal variation and zone-wise distribution of total HCHLs (Σ H-CHLs) in sediments

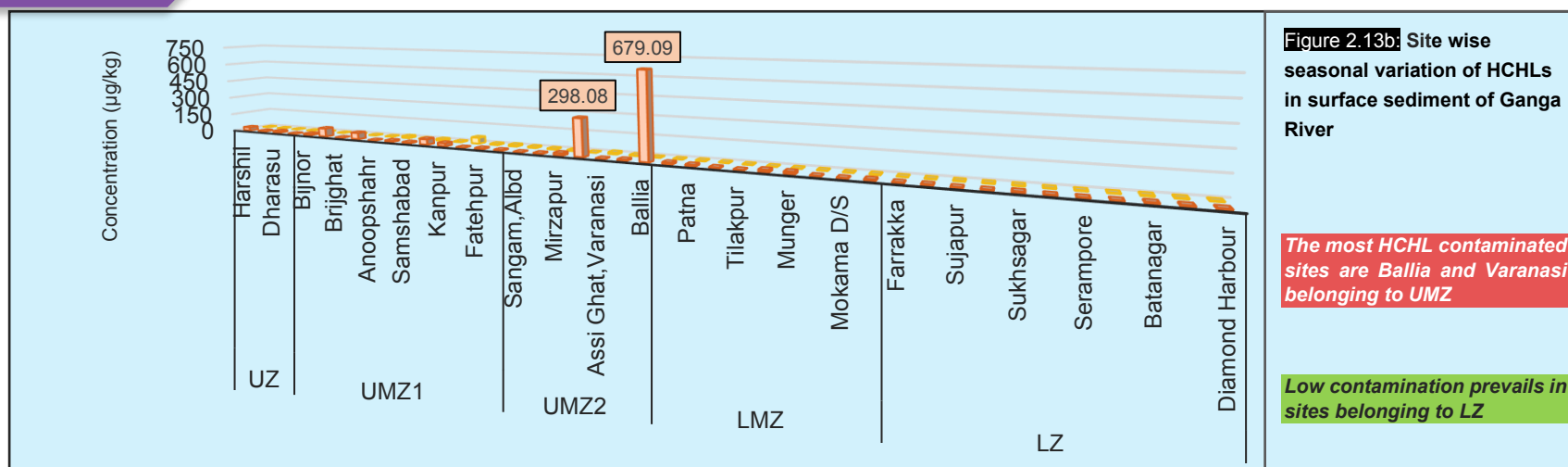
High contamination prevails in UMZ2 in post monsoon whereas lowest recorded for UZ (West Bengal) in post winter



SURFACE WATER



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2. Hexachlorocyclohexanes (HCH)

Technical HCH or Hexachlorocyclohexane is a broad spectrum organochlorine insecticide that was available for decades and used throughout the world for agricultural and non-agricultural purposes because of its effectiveness and low cost (Li *et al.* 1998; Raina *et al.*, 2008; Carvalho *et al.* 2009b). It has more than five isomeric forms (α , β , γ , δ and ϵ etc), which are all toxic, recalcitrant and exhibits both acute and chronic toxicity, particularly β isomer, acts as an environmental estrogen (Walker *et al.* 1999). Its use continued unabated until HCH was also banned in 1997 in India, but restricted use was allowed for lindane (99% γ HCH) till 2011. It is still used illegally for control of mosquitoes and other insect pests (Raina *et al.*, 2008 and Lal *et al.*, 2010).

The distribution of Σ HCHs (Figure 2.14a), in surface water, across zones showed the order as LZ(0.773 μ g/L)> UMZ2(0.566 μ g/L)>UZ(0.468 μ g/L)>UMZ1(0.336 μ g/L)> LMZ(0.122 μ g/L) in post-monsoon and UMZ1(0.144 μ g/L)>UMZ2(0.111 μ g/L)>LZ(0.105 μ g/L)> UZ(0.099)> LMZ(0.039 μ g/L) in post-winter. The mean concentration of Σ HCHs in all five zones was ~4x higher in post-monsoon than post-winter. Further, UZ recorded significant amount of HCHs and this could be explained by their long-range atmospheric transfer and their possible fresh and illegal input for orchards and vegetable/pulses farming (Oehme and Manø, 1984; Barrie *et al.*, 1992; Willet *et al.*, 1998).

The compositional profile of HCHs (Figure 2.14b) revealed the dominance of the γ -HCH isomer with 71% in the post-monsoon and 43% in the post-winter season, followed by α -HCH (~23% for both seasons). The contribution (%) of two other HCH isomers, namely β -HCH and δ -HCH, toward Σ HCHs was found to be in the range of 1.03%–5% (post-monsoon) and 13%–17% (post-winter).

Figure 2.14a: Zone-wise distribution and seasonal Variation of total HCHs (Σ HCHs) in water in PM and PW

Σ HCHs concentrations were higher in post-monsoon than in post-winter.

High contamination prevails in LZ (West Bengal) and UMZ (Uttar Pradesh) whereas lowest recorded for LMZ (Bihar Jharkhand)

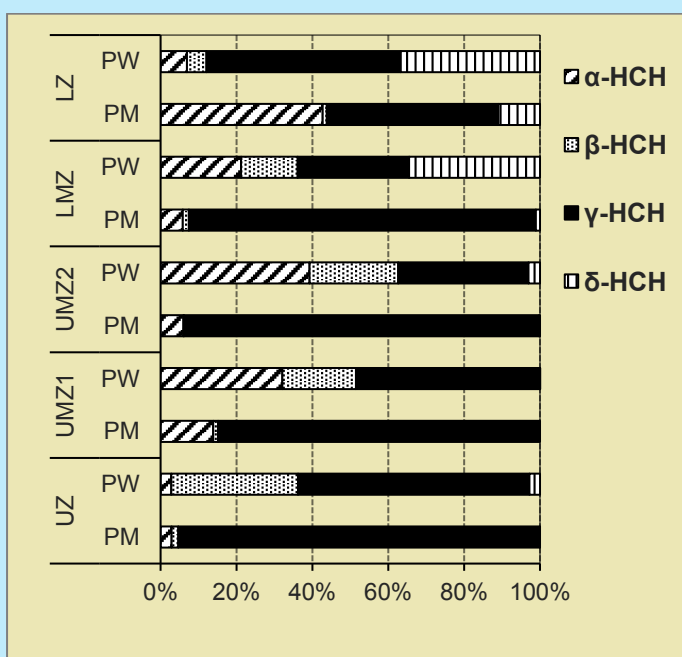
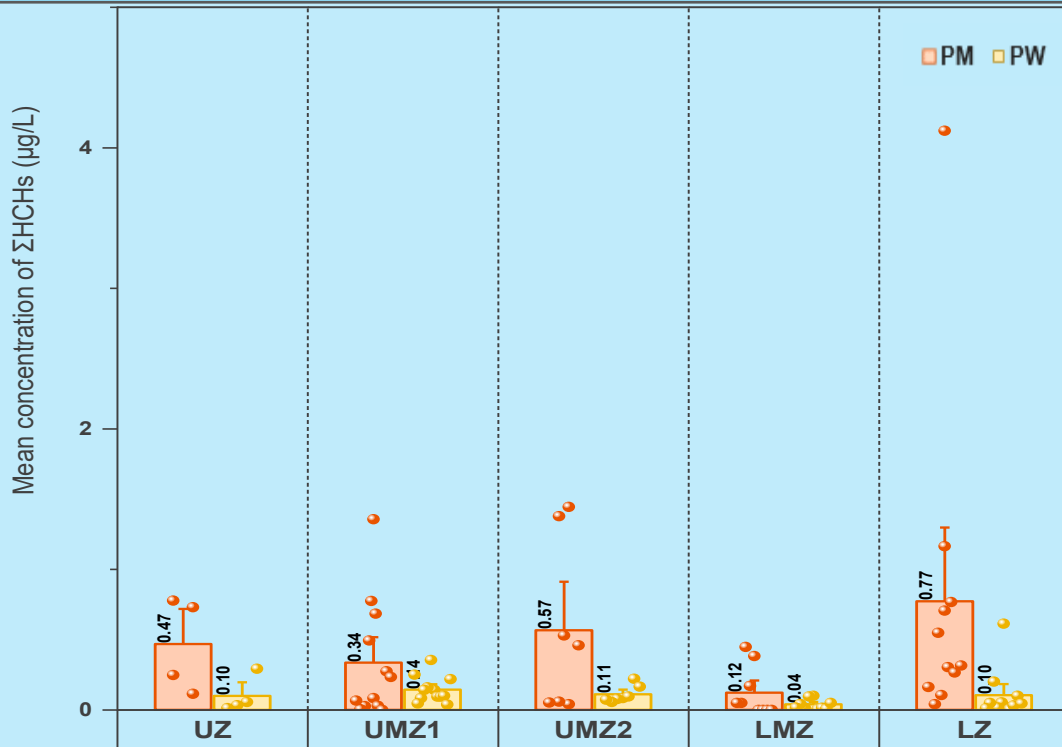


Figure 2.14b: Zone-wise composition of HCH isomer in water.

*The most dominant isomer **Lindane (γ -HCH)**, followed by α -, β -, and δ -HCHs*

Figure 2.15a: Zone-wise distribution and seasonal variation of total HCHs (Σ HCHs) in sediments

Σ HCHs concentrations were higher in post-monsoon than in post-winter.

High contamination was observed for UZ (Uttarakhand), and LMZ in PM season

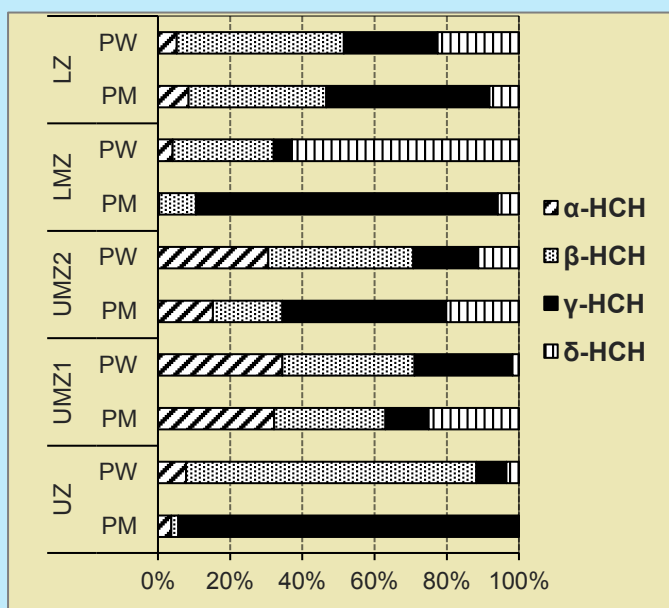
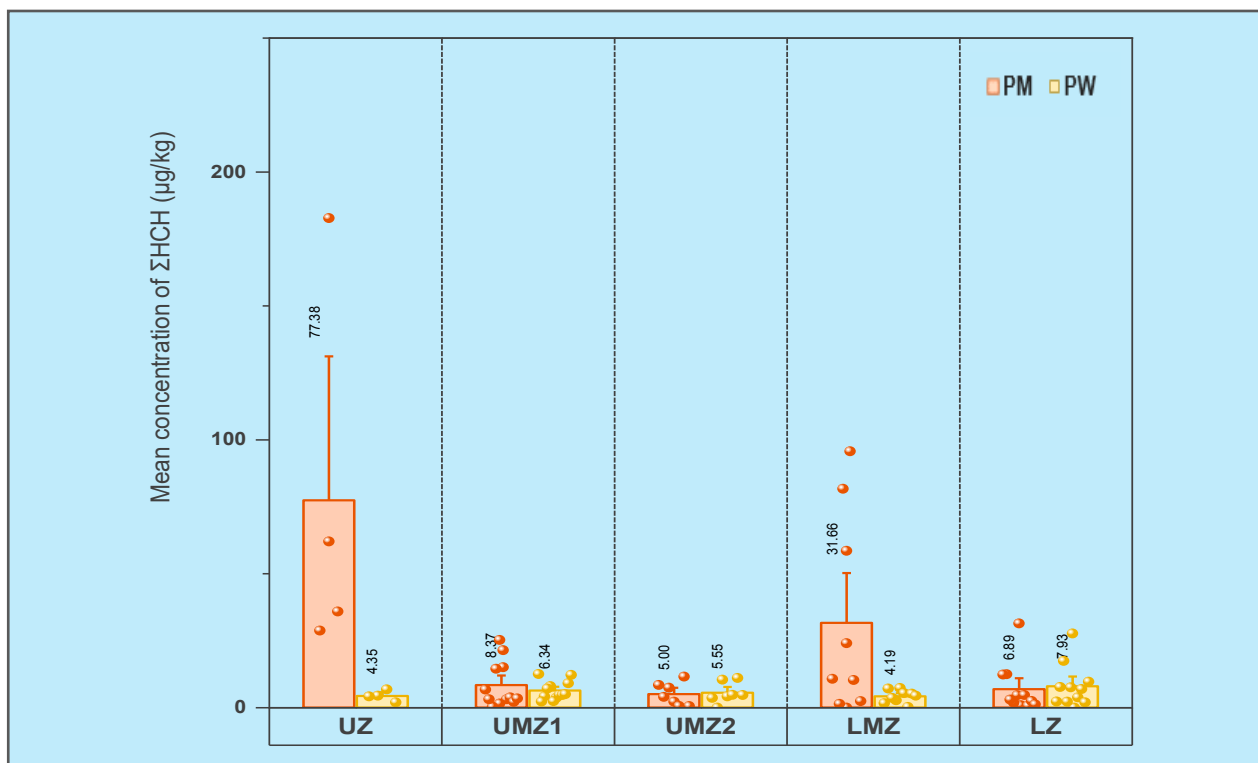


Figure 2.15b: Zone-wise composition of HCH isomer in sediment

The most dominant isomer **Lindane (γ -HCH)**, followed by β -, α -, and δ -HCHs

The distribution of Σ HCHs (Figure 2.15a), in surface sediments, across zones showed the order as **UZ(77.38 μ g/kg)> LMZ(31.66 μ g/kg)>UMZ1(8.37 μ g/kg)>LZ(6.89 μ g/kg)> UMZ2(5 μ g/kg) in post-monsoon and **LZ(7.93 μ g/kg)>UMZ1(6.34 μ g/kg)> UMZ2(5.55 μ g/kg)> UZ(4.35 μ g/kg)> LMZ(4.19 μ g/kg) in post-winter.****

The compositional profile of HCHs (Figure 2.15b), in sediments, revealed the dominance of the γ -HCH isomer with 73% in the post-monsoon and 21% in the post-winter season, followed by β -HCH (~13% & 42 % in post-monsoon and post-winter respectively). Despite the ban, the widespread occurrence and elevated concentrations of γ -HCH residues, in water and soil samples, could be attributed to their high historic usage (because of their low cost and broad spectrum insecticidal property), strong persistence, and potential fresh inputs (possibly through illegal sources) to the river. In addition, compared to other target OCPs that were banned years ago, γ -HCH was banned relatively recently in 2013. The contribution (%) of two other HCH isomers, namely α -HCH and δ -HCH, toward Σ HCHs was found <20% for both the seasons. Amongst the four isomers of HCHs, β -HCH is the most persistent owing to its low vapor pressure and resistance to degradation resulting in its prevalence in sediments matrix, as compared to water (Law et al., 2001; Tan et al., 2009).

The site-wise seasonal variation of HCHs in surface water and sediments of Ganga River is presented in Figure 2.16a and 2.16b respectively. In post-monsoon season, the Σ HCHs concentration ranged from **BDL-4.122 μ g/L (Mean: 0.453 μ g/L; median 0.248 μ g/L)** and **BDL-182.786 μ g/kg (Mean: 18.739 μ g/kg; median 4.702 μ g/kg)** in water and sediment respectively. In post-winter season, the Σ HCHs concentration ranged from **0.006-0.614 μ g/L (Mean: 0.102 μ g/L; median 0.073 μ g/L)** and **BDL-27.678 μ g/kg (Mean: 5.986 μ g/kg; Median: 4.733 μ g/kg)** in water and sediment respectively. For water samples, highest contamination from T-HCH was observed at Jiaganj (LZ) whereas for sediment, the highest conc. of T-HCH was recorded at Anoopshahar (UMZ).

SURFACE WATER

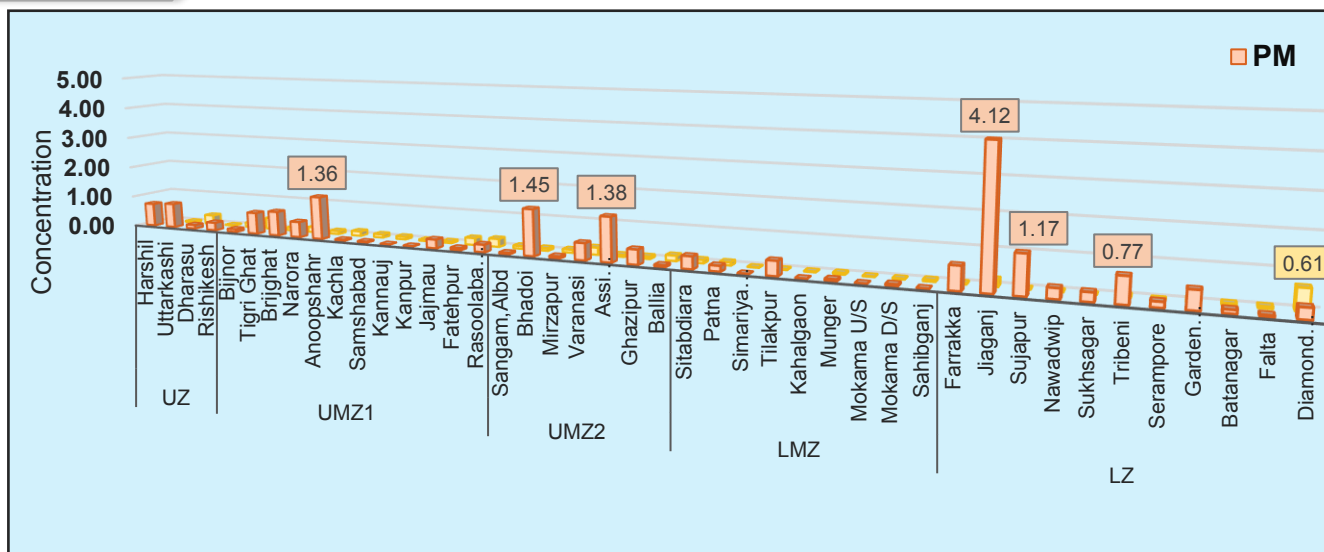


Figure 2.16a: Site-wise and zone-wise seasonal variation of HCHs in surface water of Ganga River

The five most T-HCH contaminated sites are Jiaganj, Bhadoi, Assi Ghat, Varanasi, Anoopshahr, Sujapur, and Tribeni

Lowest HCH contamination found at sites in Lower Middle Zone (LMZ)

SEDIMENTS

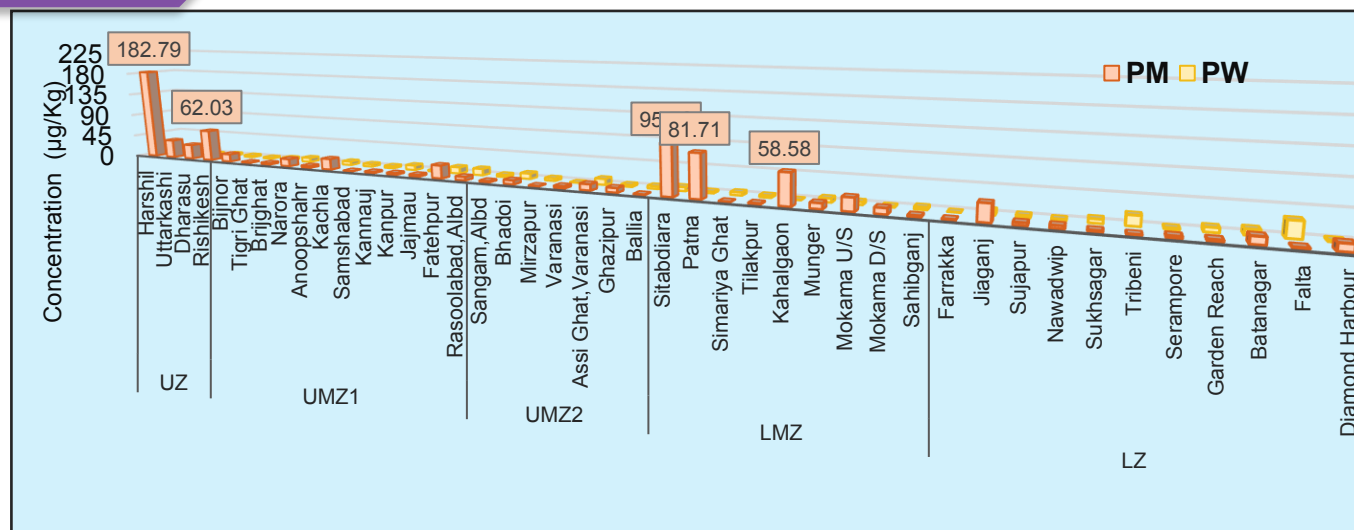


Figure 2.16b: Site-wise and zone-wise seasonal variation of HCHs in surface sediments of Ganga River

The five most HCHs contaminated sites are Harshil, Sitabdiara, Patna, Rishikesh, and Kahalgaoon

Lowest HCH contamination found in Lower Zone (LZ) sites

2.1 Sources of HCH- Historic or fresh inputs

The ratio analysis of α -HCH/ γ -HCH, in all the five zones for both seasons, indicated the **possible illegal ongoing usage** of HCH in the study area. Further the % of β -HCH (most persistent isomer) ranged from 1.04 to 17.28% for both the seasons at all sites and this relatively low % indicates the fresh inputs of HCH. We anticipate that the reason for detection of fresh inputs of technical HCH (particularly lindane) could be link to their application in paddy fields. In the UMZ1, UMZ2, LMZ, and LZ, under rainfed conditions, rice is generally grown along the Ganga basin and these zones (and corresponding states) are top cultivators/producers of rice in the country (NFSM). The elevated concentrations of HCH detected during wet season, in the present study, indicates that this insecticide is largely applied during the flowering season of paddy (Ramesh et al., 1991).

3. Drins

Drins, for this study, represents five OCPs namely aldrin, dieldrin, endrin, endrin aldehyde, and Endrin ketone. Aldrin was largely used as a pesticide and also in soil to kill termites, grasshoppers, corn rootworm, and other insect pests. It is banned from manufacturing, use, export and import in India from 17th July 2001. Dieldrin is an oxidation product of Aldrin, which is used primarily to control locust, termites, textile pests and to control insect-borne diseases and insects living in agricultural soils. It was banned from manufacture, use, export and import from 17th July 2001 but marketing and restricted use (locust control) of Dieldrin was permitted for a period of two years from the date of the ban, or up to the date of expiry, whichever was earlier. Another Drin, Endrin is a pesticide, primarily used as an insecticide in cotton, rice, sugarcane and other crops and is also used as a rodenticide for mice and voles. Endrin aldehyde, is an impurity and breakdown product of endrin, and endrin ketone, is a product of endrin when it is exposed to light. Endrin import, export, manufacturing and production has been completely banned in India from 15th May 1990 by the Government of India.

In current study, the distribution of Σ Drins (Figure 2.17a), in surface water samples, across zones showed the order as UZ (0.32 μ g/L)>UMZ2 (0.17 μ g/L)>LZ (0.12 μ g/L)>UMZ1 (0.11 μ g/L)>LMZ (0.07 μ g/L) in post-monsoon and LZ (0.22 μ g/L)> UZ (0.05 μ g/L)> UMZ2 (0.045) (μ g/L)> UMZ1 (0.042 μ g/L)> LMZ (0.03 μ g/L) in post-winter. *Except for LZ, Σ Drins were higher in post-monsoon season.* The percentage composition of Drins in water samples was observed as Aldrin (53.5%)>Endrin (20.3%) \cong Endrin Aldehyde (20.3%) >Dieldrin(4.4%)> Endrin Ketone (1.9%) in post-monsoon and Endrin (49.8%)>Aldrin (24.4%)>Endrin Aldehyde (18.4%) > Endrin Ketone (7.2%)> Dieldrin (0.2%) in post-winter. The zone-wise composition of Drins in water samples is presented in Figure 2.17b.

The distribution of Σ Drins (Figure 2.18a), in surface sediments, across zones showed the order as UZ (73.30 μ g/kg)>UMZ2 (3.3 μ g/kg)> UMZ2 (3.38 μ g/kg)> LMZ (2.56 μ g/kg)> UMZ1 (1.33 μ g/kg)>LZ (0.63 μ g/kg)in post-monsoon and LMZ(11.21 μ g/kg) >UMZ1 (2.16 μ g/kg)>LZ (0.92 μ g/kg)> UZ (0.10 μ g/kg). The percentage composition of Drins in sediment samples was observed as Endrin \cong Endrin Aldehyde (46%) > Aldrin \cong Dieldrin(3%)> Endrin Ketone (2%) in post-monsoon and Endrin Ketone (82.1%) >Endrin Aldehyde (15.2%)> Endrin (1.5%)> Dieldrin(0.9%)>Aldrin (0.3%) in post-winter. The zone-wise composition of Drins in sediments samples is presented in Figure 2.18b. *Σ Drins were usually higher in post-winter season, whereas unexpected high levels were observed in UZ in post-monsoon season.*

The site-wise seasonal variation of Drins in surface water and sediments of Ganga River is presented in Figure 2.19a and 2.19b respectively. In post-monsoon season, the Σ Drins concentration ranged from **BDL-0.514 μ g/L (Mean: 0.132 μ g/L; Median: 0.082 μ g/L)** and **BDL-128.018 μ g/kg (Mean: 8.436 μ g/kg; Median: 0.586 μ g/kg)** in water and sediment respectively. In post-winter season, the Σ Drins concentration ranged from **BDL-1.759 μ g/L (Mean: 0.087 μ g/L; Median: 0.036 μ g/L)** and **BDL-34.065 μ g/kg (Mean: 3.898 μ g/kg;**

Median: 0.881 $\mu\text{g/kg}$) in water and sediment respectively. The sites having highest Drin contamination were located in LZ for water and UZ in sediments.

SURFACE WATER

Figure 2.17a: Seasonal variation and zone-wise distribution of total Drins (ΣDrins) in surface water

ΣDrins were usually higher in post-monsoon season. Highest contamination prevails in UZ and lowest in LMZ.

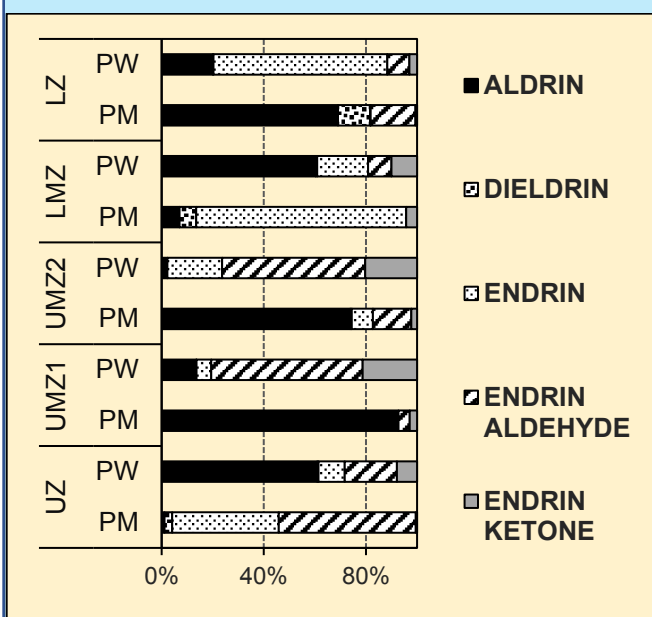
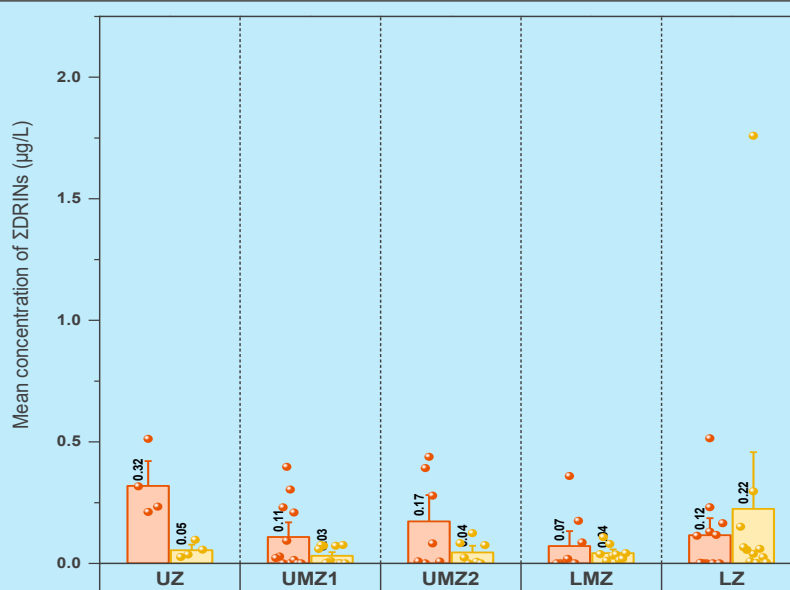


Figure 2.17b: Zone-wise composition of Drins in water

The most dominant among Drins is Aldrin followed by Endrin and its metabolites

Figure 2.18 a: Seasonal variation and zone-wise distribution of total Drins (Σ Drins) in surface sediment

Σ Drins were usually higher in post-winter season. Highest contamination prevails in UZ and lowest in UMZ1

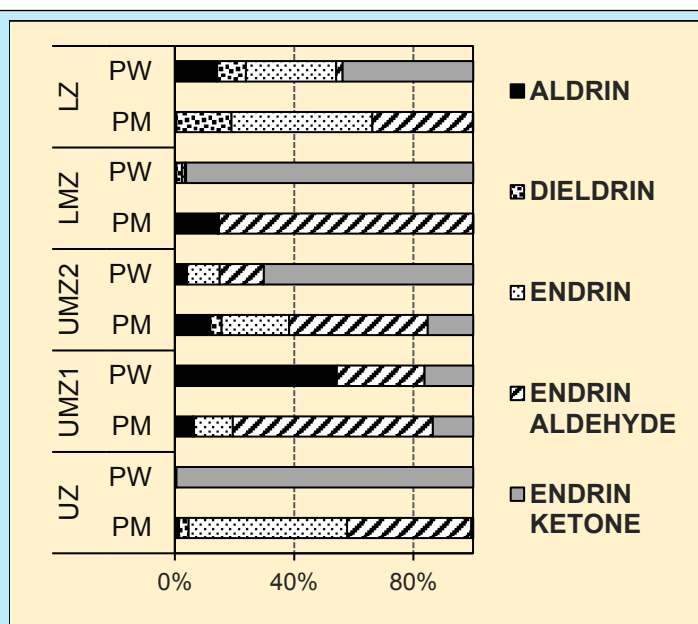
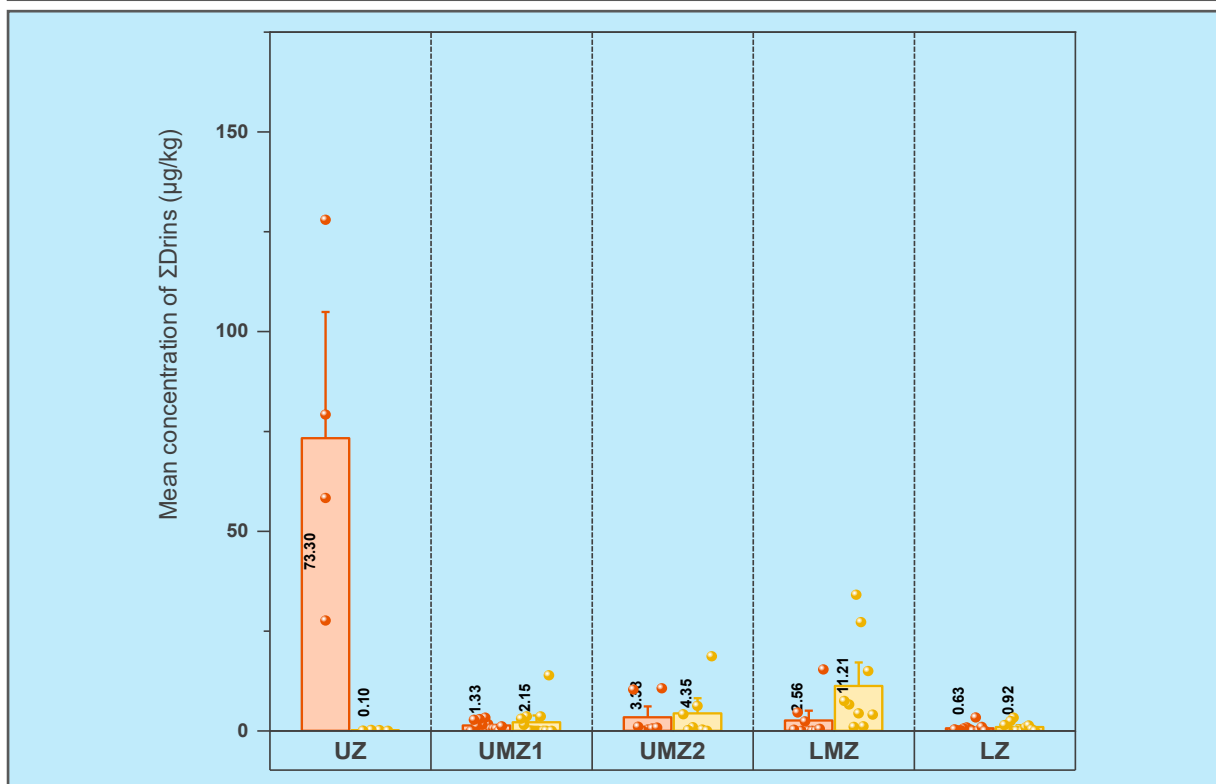


Figure 2.18b: Zone-wise frequency of Drins metabolites in sediment

The most dominant among Drins are Endrin and its metabolites

SURFACE WATER

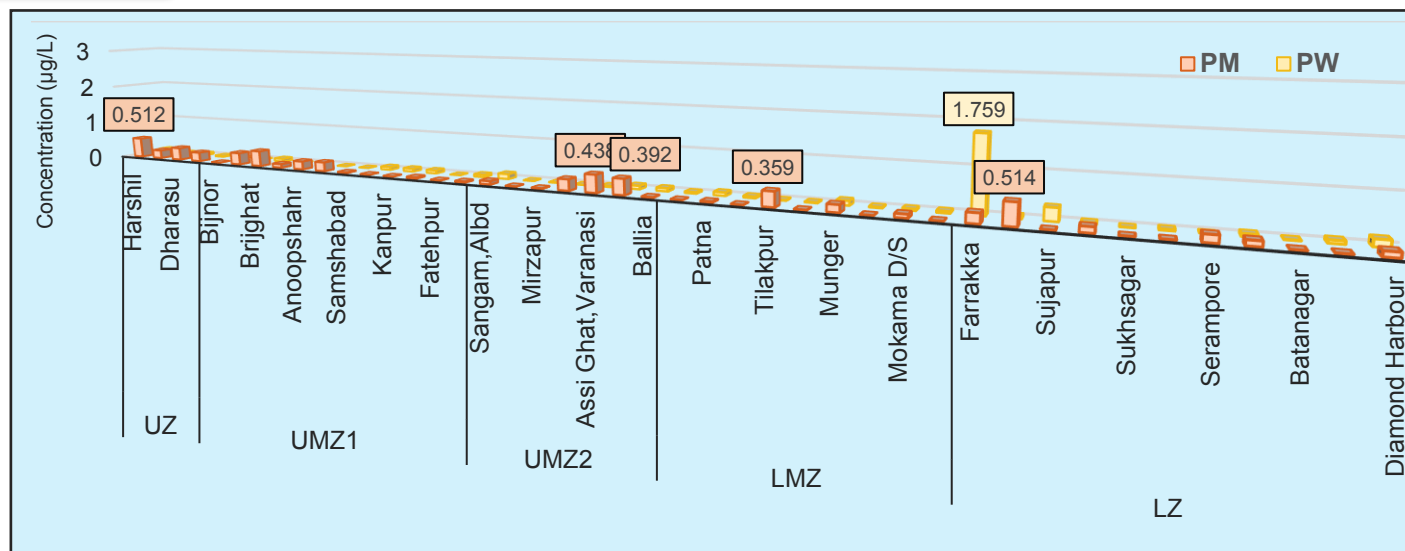


Figure 2.19a: Seasonal variation and site-specific distribution of Drins in surface water

The most Drins contaminated sites are Farrakka (PM), Jiaganj, Harshil and Assi Ghat Varanasi (PW)

Relatively, low contamination prevails in sites belonging to LMZ

SEDIMENTS

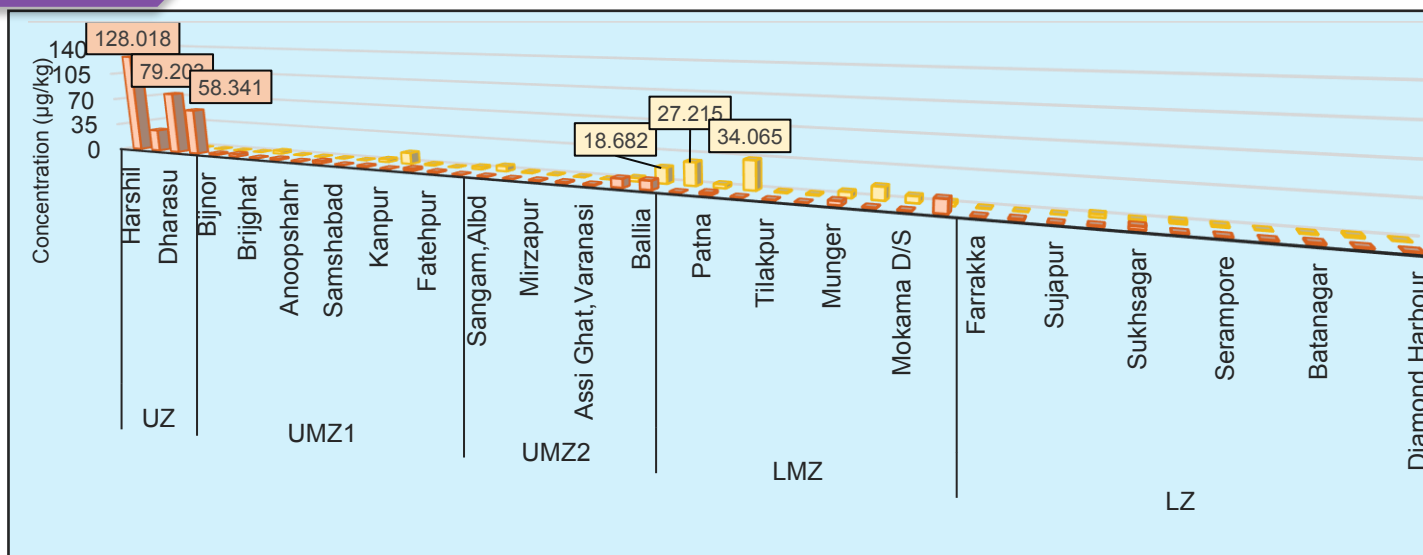


Figure 2.19b: Seasonal variation and site-specific distribution of Drins in surface sediments

The most Drins contaminated sites prevails in UZ and in PW season

Relatively, low contamination prevails in sites belonging to LZ and, UMZ1 in both the seasons

4. Chlordanes (CHLs)

Chlordane (CHLs) is a pesticide used extensively on grains, sugarcane, vegetables, maize, potatoes, sugar beets, nuts, fruits, jute, cotton, other oilseeds, and cotton, etc. to control termites as a broad-spectrum insecticide and it remains in the soil for a long time. The technical grade chlordane mixture consists of major components, trans-CHL(13%), and cis-CHL (11%), trans-nonachlor (5%), and heptachlor (5%), and over thirty less abundant chlordanes, nonachlors, and, chlordenes (Bidleman et al., 2002).

In the present investigation, the spatial distribution of Σ CHLs (t-CHL & c-CHL) in surface water (Figure 2.20a), across zones revealed the sequence as **UMZ2 (0.029 μ g/L) > LZ (0.025 μ g/L) > UZ (0.021 μ g/L) > UMZ1 (0.019 μ g/L) > LMZ (0.010 μ g/L) in post-monsoon and LMZ (0.020 μ g/L) > LZ (0.016) (μ g/L) > UZ(0.016 μ g/L) > UMZ2(0.011 μ g/L) > UMZ1(0.009 μ g/L) in post-winter.**

The mean concentration of CHLs in all five zones was higher in post-monsoon than post-winter.

The distribution of Σ CHLs (Figure 2.21a), in surface sediments, across zones showed the order as in **UZ (3.64 μ g/kg) > LMZ(0.74 μ g/kg) > UMZ1 (0.24 μ g/kg) > UMZ2 (0.05 μ g/kg) > LZ (BDL) post-monsoon and UMZ1 (0.48 μ g/kg) > LMZ (0.41 μ g/kg) > LZ (0.30 μ g/kg) > UMZ2 (0.026 μ g/kg) > UZ (0.03 μ g/kg) in post-winter. Σ CHLs were usually higher in post-winter season, whereas unexpected high levels were observed in UZ in post-monsoon season.**

Among the isomers of chlordane, t-CHL was dominant isomer, during both seasons, in water (post-monsoon: 81%; post-winter: 58%) as well as sediment samples (post-monsoon: 70%; post-winter: 63%) (Figure 2.20b & 2.21b).

The site-wise seasonal variation of CHLs in surface water and sediments of Ganga River is presented in Figure 2.22a and 2.22b respectively. In post-monsoon season, the Σ CHLs concentration ranged from **BDL-0.155 μ g/L (Mean: 0.021 μ g/L; Median: 0.009 μ g/L)** and **BDL-6.360 μ g/kg (Mean: 0.571 μ g/kg; Median: 0.001 μ g/kg)** in water and sediment

respectively. In post-winter season, the Σ CHLs concentration ranged from **BDL-0.072 $\mu\text{g/L}$** (Mean: 0.014 $\mu\text{g/L}$; Median: 0.005 $\mu\text{g/L}$) and **BDL 1.926 $\mu\text{g/kg}$** (Mean: 0.341 $\mu\text{g/kg}$; Median: BDL) in water and sediment respectively.

SURFACE WATER

Figure 2.20a: Seasonal variation and zone-wise distribution of total CHLs (Σ CHLs) in water
Levels were higher in post-monsoon than post-winter. Highest contamination prevails in UMZ2 and lowest in UMZ1

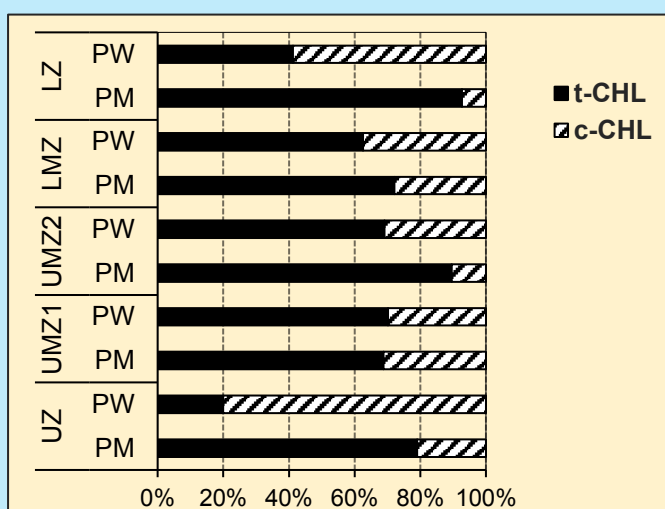
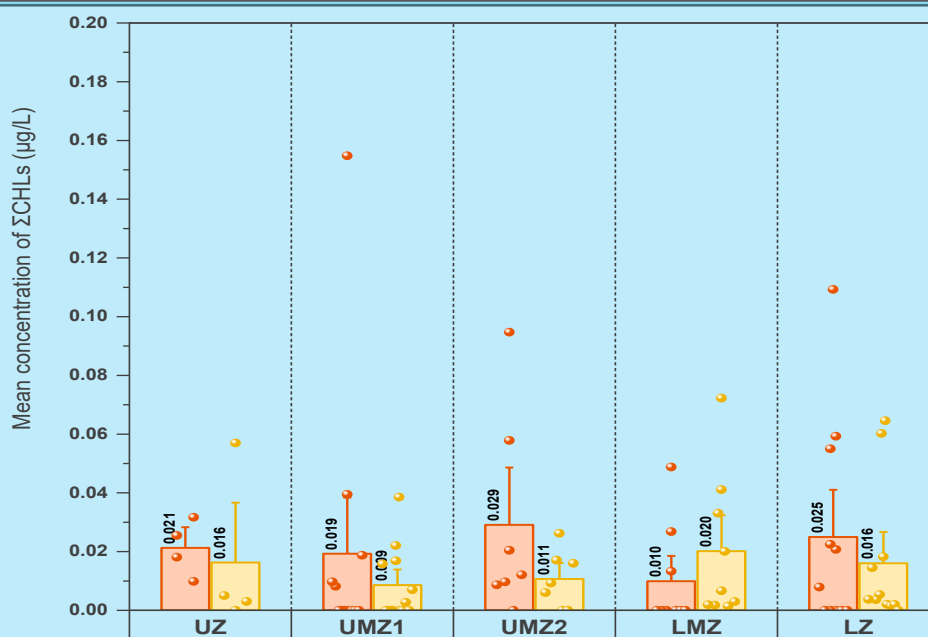


Figure 2.20b: Zone-wise composition of CHL in water

t-chlordane is dominant isomer in all zones in both seasons

Figure 2.21a: Seasonal variation and zone-wise distribution of total CHLs (Σ CHLs) in sediments

Levels were, generally, higher in post-winter than post-monsoon. Highest contamination prevails in UZ and lowest in LZ

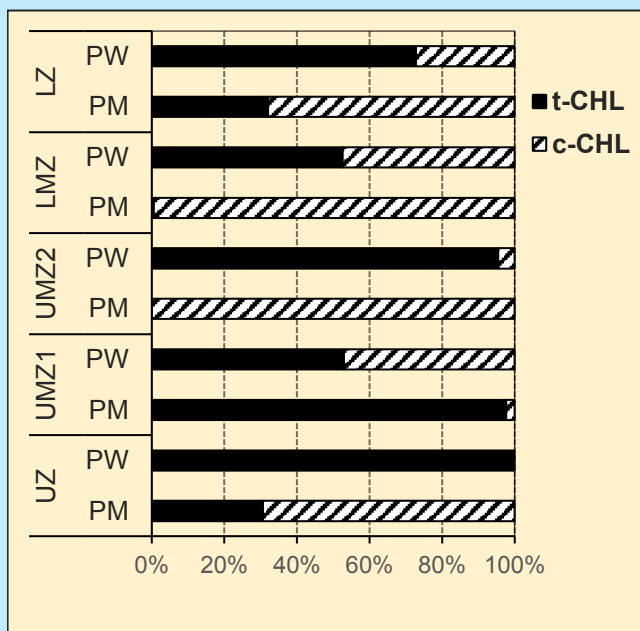
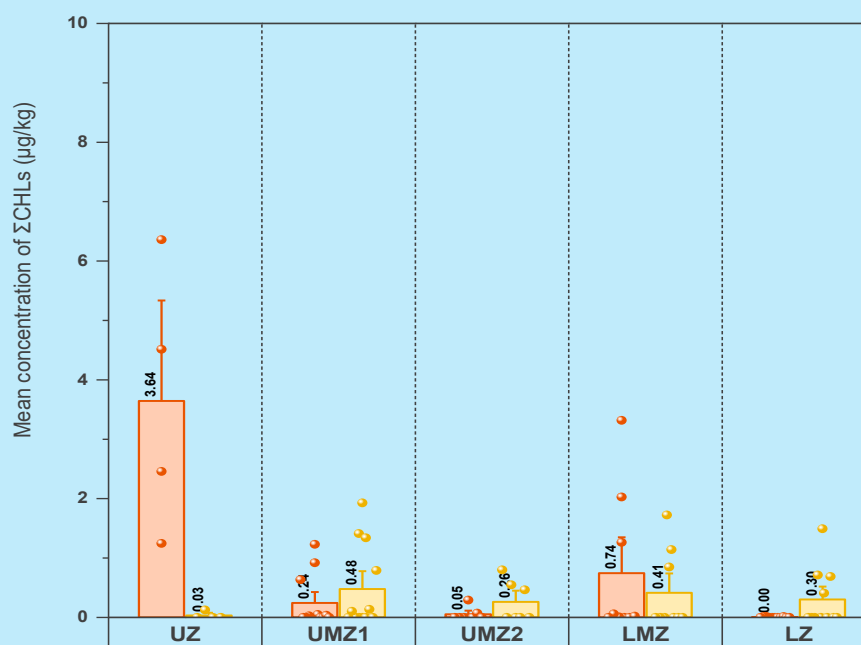


Figure 2.21b: Zone-wise composition of CHL in sediments

t-chlordanes is dominant isomer in all zones

SURFACE WATER

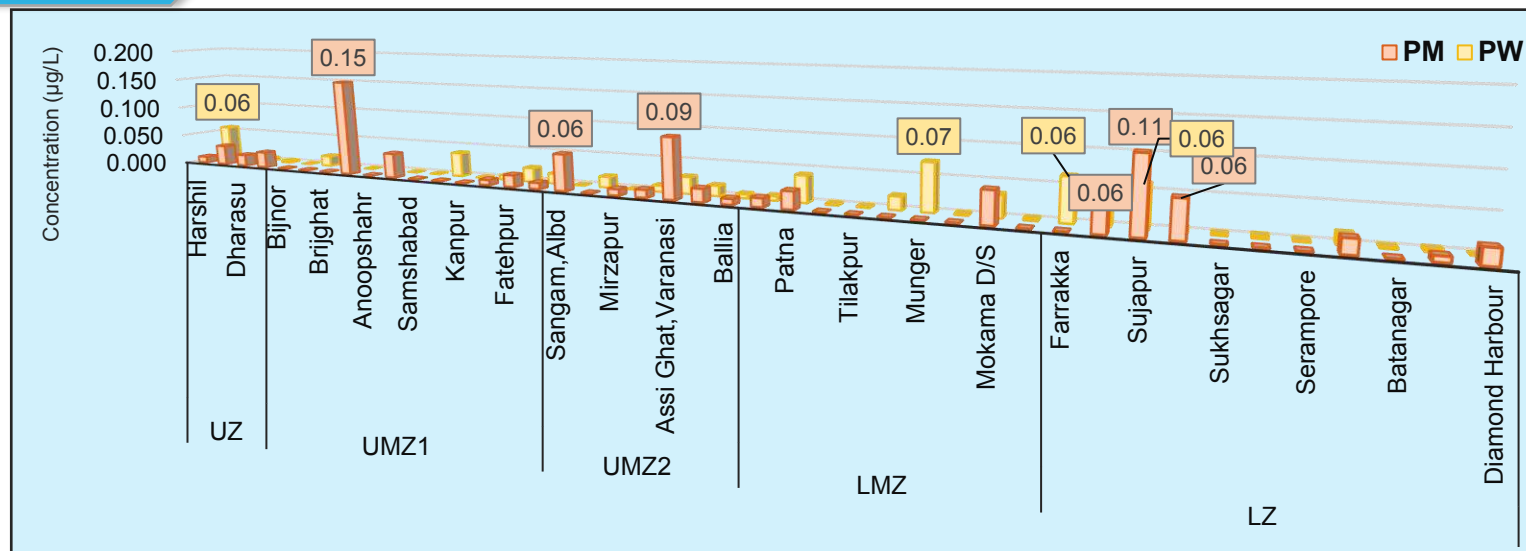


Figure 2.22a: Site wise seasonal variation of CHLs in surface water of Ganga River

The most CHLs contaminated sites are Narora and Sujapur in PM season

Low contamination prevails in sites belonging to LZ in both the seasons

SEDIMENTS

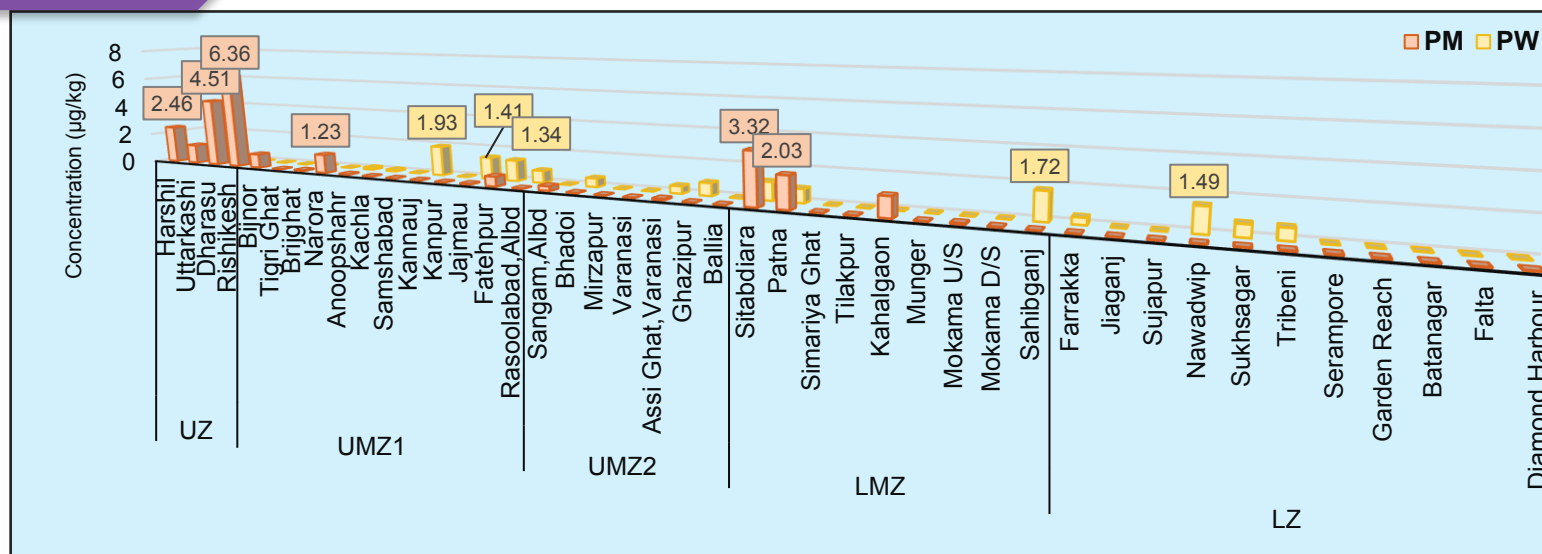


Figure 2.22b: Site wise seasonal variation of CHLs in surface sediment of Ganga River

The most CHLs contaminated sites belongs to UZ, and Sitabdiara and Patna in LMZ in PM

Low contamination prevails in sites belonging to LZ and UMZ2 in both the seasons

4.1 Sources of CHLs- Historic or fresh inputs

The ratio diagnostic method was used to identify the potential sources of CHLs contamination in Ganga River. Among CHLs isomers, the trans-chlordane, owing to its lower half-life, degrades relatively much faster in the environment than its cis counterpart (Yamada et al., 2008). Therefore, the ratio of cis-chlordane to trans-chlordane <1 specifies the fresh usage of chlordane (Bidleman et al., 2002; Yu et al., 2014). In the current study, the ratio calculated for cis/trans chlordane at all the sampling zones were <1 thereby indicating the ongoing and illegal usage of chlordane in the study area.

5. Dichlorodiphenyltrichloroethanes (DDTs)

DDT (1,1'-(2,2,2-Trichloroethane-1,1-diyl) bis(4-chlorobenzene)) has two metabolites DDD (1,1-Dichloro-2,2-bis(p-chlorophenyl)ethane) and DDE (1,1-Dichloro-2,2-bis(p-chlorophenyl)ethylene). In India, the use of DDT in agriculture was banned in 1989 with a mandate to use a maximum of 10,000 tons of DDT per annum for the control of malaria and Kala-azar. Due to their long environmental half-life, atmospheric depositions from distant sources and the continued use of DDT in public health programmes, concentrations of this pesticide will remain at measurable levels in the environment for the years to come. DDE is the primary metabolite found in the environment and is more persistent than DDT.

The distribution of Σ DDTs (Figure 2.23a), in surface water, across zones showed the order as **LZ(0.034 μ g/L)>UMZ2(0.030 μ g/L)> UZ(0.013) (μ g/L)>UMZ(0.013 μ g/L)> LMZ (0.11 μ g/L)> UMZ1 (0.005) (μ g/L) in post-monsoon and **LZ(0.039 μ g/L)> UZ(0.032(μ g/L)> UMZ2(0.027 μ g/L)> UMZ1(0.026 μ g/L)> LMZ(0.015) (μ g/L) in post-winter. However, the mean concentration of DDTs was found to be higher (1.5x) in post-winter than post-monsoon. The relative higher detection frequency of *p,p'* DDT in post-winter could be due to the application of DDT sprays as the climate gets warmer. As a result, during the sprays, the air turbulence and favourable temperature conditions could facilitate the insecticide drift towards the nearby water bodies thus increasing the risk of contamination. Additionally low dilution****

during post-winter seasons could also results in their high concentration. The percentage composition (Figure 2.23b) of DDTs revealed dominance of *p,p'* DDE (post-monsoon: 72%; post-winter: 53%), a break-down product of *p,p'* DDT, in surface water of Ganga River that could be attributed to their slow degradation in water.

The distribution of Σ DDTs (Figure 2.24a), in sediments, across zones showed the order as **UMZ2 (4.77 μ g/kg)> UZ(2.81 μ g/kg)> LMZ (0.054 μ g/kg)>LZ (0.53 μ g/kg)> UMZ1(0.30 μ g/kg) in post-monsoon and **UMZ2 (1.80 μ g/kg)> UMZ1 (1.41 μ g/kg)> LMZ (1.15 μ g/kg)> LZ (0.45 μ g/kg)> UZ(0.10 μ g/kg) in post-winter. The percentage composition (Figure 2.24b) of DDT and its metabolites in sediment samples revealed following seasonal compositional trends as follows:****

DDT Metabolite	PM	PW
<i>p,p'</i> DDE	45%	33%
<i>p,p'</i> DDD	19%	46%
<i>p,p'</i> DDT	21%	36%
<i>TOTAL</i>	100%	100%

The site-wise variation of DDTs in surface water and sediments of Ganga River is presented in Figure 2.25a and 2.25b respectively. In post-monsoon season, the Σ DDTs concentration ranged from **BDL-0.143 μ g/L (Mean: 0.019 μ g/L; median 0.004 μ g/L)** and **BDL-19.887 μ g/kg (Mean: 1.372 μ g/kg; median 0.431 μ g/kg)** in water and sediment respectively. In post-winter season, the Σ DDTs concentration ranged from **BDL-0.144 μ g/L (Mean: 0.028 μ g/L; median 0.012 μ g/L)** and **BDL-7.184 μ g/kg (Mean: 1.052 μ g/kg; Median: 0.318 μ g/kg)** in water and sediment respectively. For water samples highest contamination for T-DDT was recorded at Sangam and Narora in UMZ while for sediment highest contamination was recorded at Varanasi and Ballia also from UMZ.

1.1. Sources of DDT- Historic or fresh inputs

Further, we invested the potential sources of DDT contamination in Ganga River through source apportionment. The calculated ratio of DDT/(DDD+DDE) at majority of sites (in all the zones) for both the season indicated that DDT contamination in the Ganga River was mainly

from its metabolites and ***high historic usage***. However, during the post-winter season the ratio analysis revealed fresh inputs of DDTs at some sampling points in UZ, UMZ1, LMZ and LZ. As already stated, this could be due to current use of DDT in indoor residual spraying, for control of malaria vector, under public health program.

SURFACE WATER

Figure 2.23a: Seasonal variation and zone-wise distribution of total DDT (Σ DDTs) in water

High contamination prevails in LZ (West Bengal) whereas lowest recorded for LMZ (Bihar-Jharkhand) in post-winter and UZ (Uttarakhand) for post-monsoon

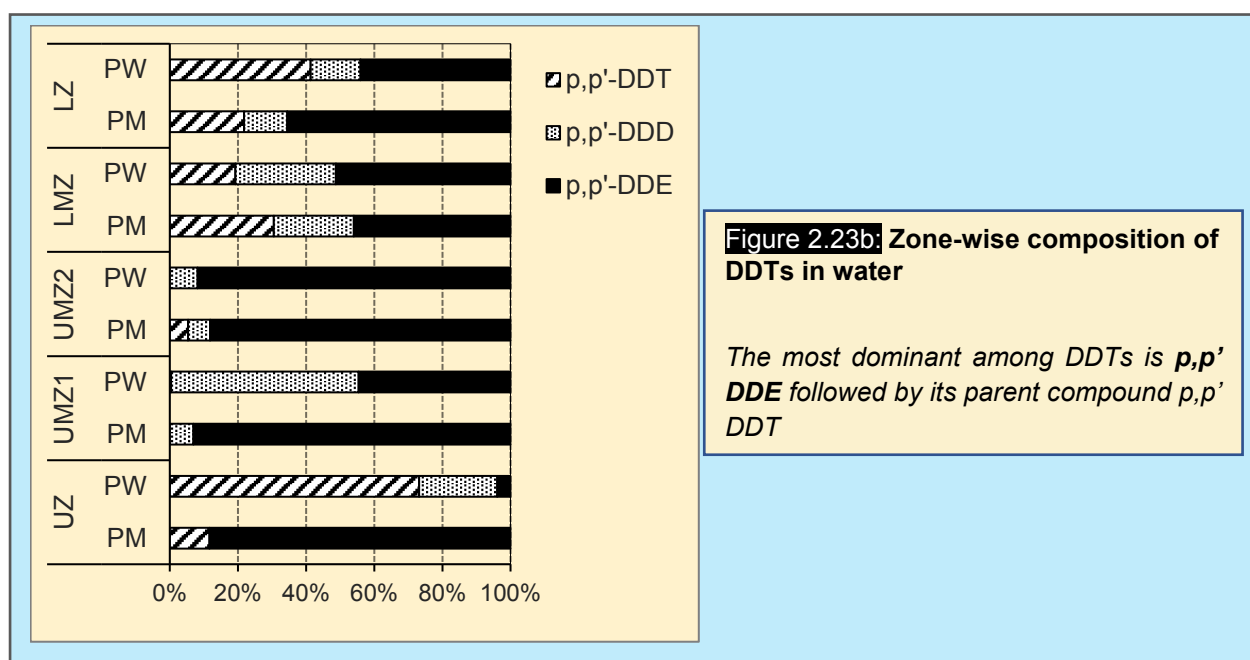
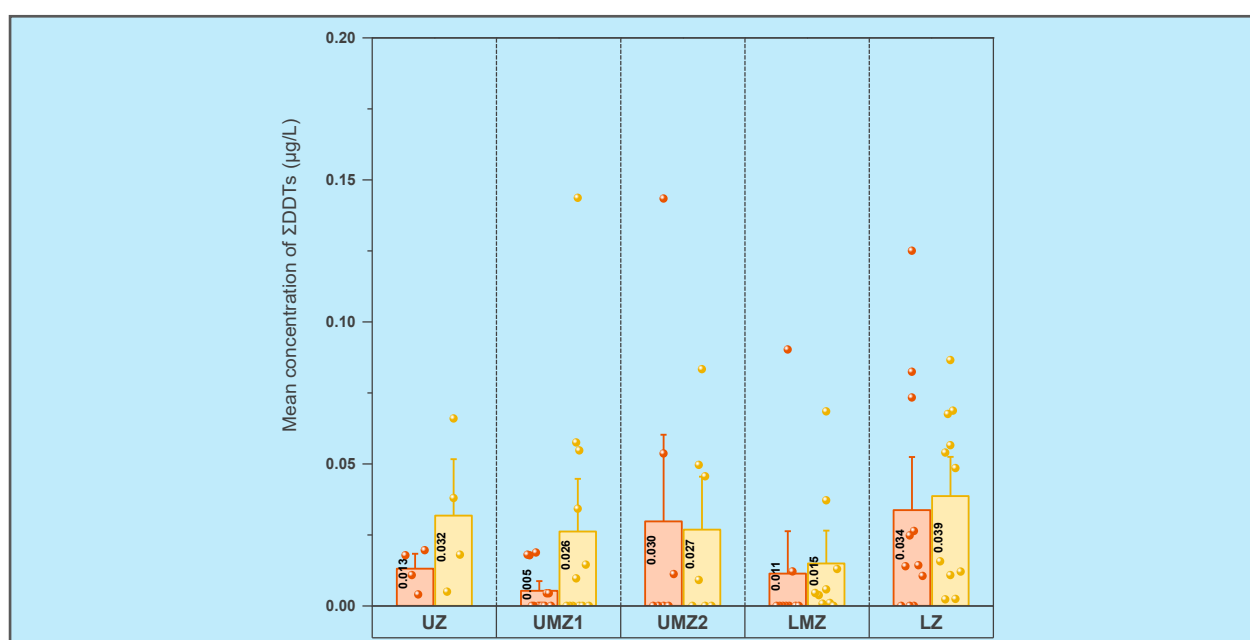


Figure 2.23b: Zone-wise composition of DDTs in water

*The most dominant among DDTs is **p,p'** DDE followed by its parent compound p,p' DDT*

Figure 2.24a: Seasonal variation and zone-wise distribution of total DDT (Σ DDTs) in sediment

High contamination prevails in UMZ2, whereas lowest recorded for UMZ1 (post-monsoon) and UZ (post-winter)

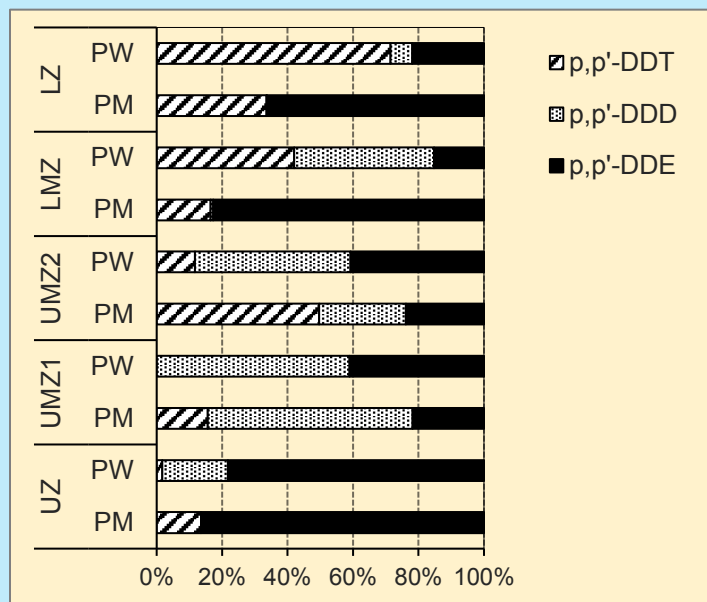
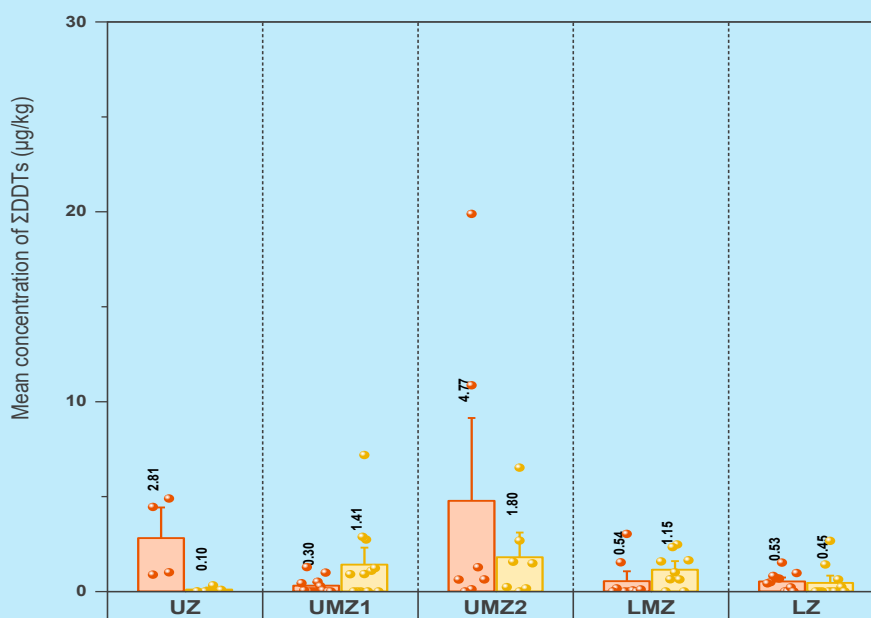


Figure 2.24b: Zone-wise composition of DDTs in sediments

The most dominant among DDTs is **p,p'-DDE** followed by its parent compound **p,p'-DDT**

SURFACE WATER

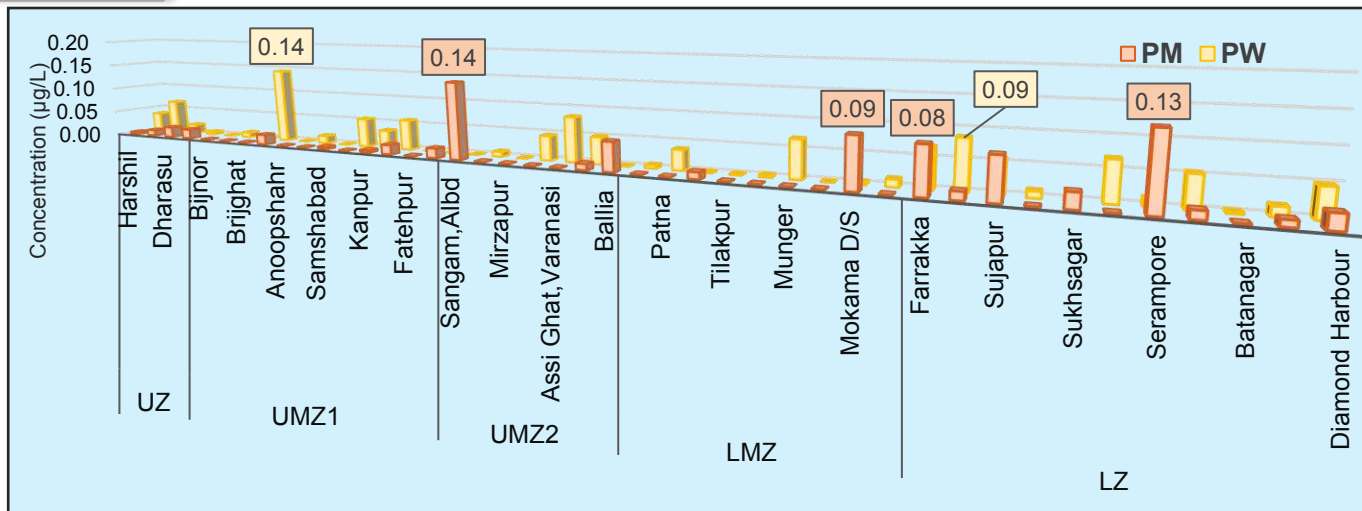


Figure 2.25a: Site-wise seasonal variation of DDTs in surface water of Ganga River

The five most DDT contaminated sites are Sangam, Narora Serampore, Jiaganj, and Mokama D/S

Lowest contamination prevails in sites belonging to LMZ and UMZ1

SEDIMENTS

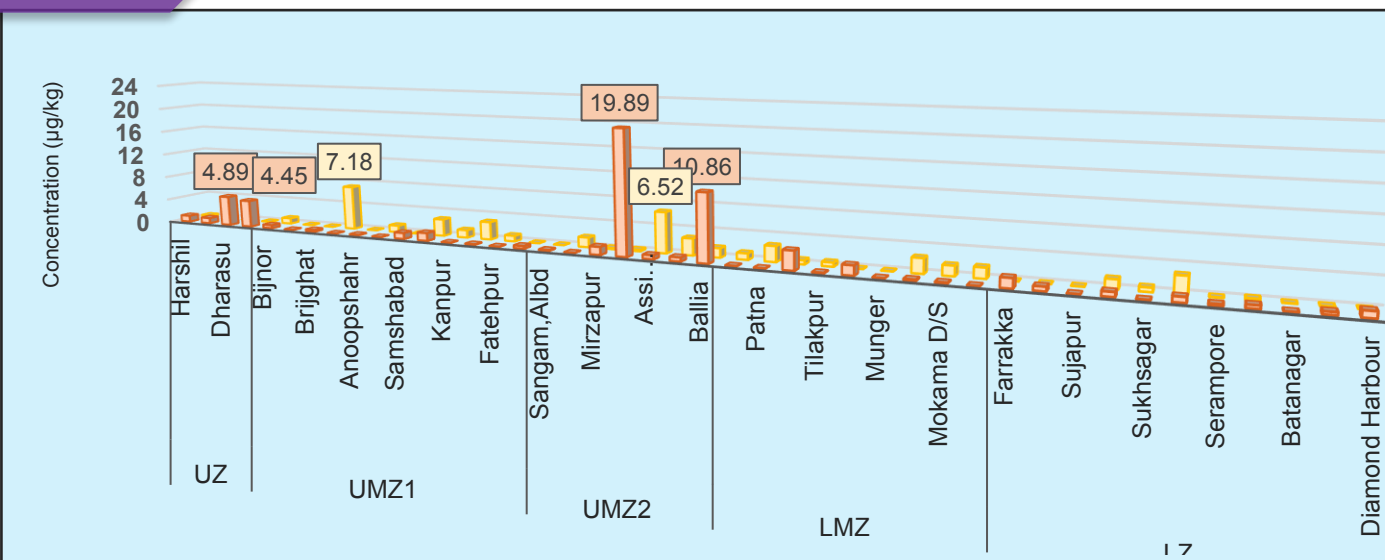


Figure 2.25b: Site wise seasonal variation of DDTs in surface sediments of Ganga River

The five most DDT contaminated sites are Varanasi, Ballia, Assi Ghat, Anoopshahr, Dharasu, and Rishikesh

Lowest contaminated sites prevails in UMZ1 and LZ

6. Endosulfans (ESs)

Endosulfan was registered as an Insecticide/Pesticide under Section 9(3) of the Insecticides Act, 1968. It was used as an insecticide for control of aphids, beetles, foliar feeding larvae, mites, borers, cutworms, bollworms, whiteflies, and leaf hoppers. It is used on cotton, tobacco, cantaloupe, tomatoes, squash, eggplant, sweet potato, broccoli, pears, pumpkins, corn, cereals, oilseeds, potatoes, tea, coffee, cacao, soybean, and other vegetables. The endosulfan isomers, α -endosulfan, and β -endosulfan constitutes up to 70% and 30%, composition of the technical endosulfan mixture, with α -isomer being relatively more degradable in the environment than the β -endosulfan (Jiang et al., 2009). Both the isomers can be metabolized to endosulfan sulfate and endosulfan diol.

In the present investigation, the mean concentration of ESs, in the entire stretch, in water samples was found to be higher ($\sim 3x$) in post-winter than post-monsoon. The spatio-temporal distribution of ESs (Figure 2.26a) in surface water, across zones revealed the sequence as UZ (0.008 $\mu\text{g/L}$) > UMZ 2 (0.005 $\mu\text{g/L}$) > LMZ=LZ (0.003 $\mu\text{g/L}$) > UMZ1 (0.001 $\mu\text{g/L}$) in post-monsoon and LMZ (0.015 $\mu\text{g/L}$) > UZ=LZ (0.008 $\mu\text{g/L}$) > UMZ1 (0.007 $\mu\text{g/L}$) > UMZ2 (0.006 $\mu\text{g/L}$) in post-winter. The zone-wise composition of ESs in water samples is presented in Figure 2.26b.

Among the sediment samples, the distribution of ESs (Figure 2.27a), was found to be higher in post-monsoon than post-winter. The spatio-temporal distribution across zones showed the trend as UMZ2 (2.71 $\mu\text{g/kg}$) > UZ (2.17 $\mu\text{g/kg}$) > UMZ1 (0.98 $\mu\text{g/kg}$) > LZ (0.80 $\mu\text{g/kg}$) > LMZ (0.43 $\mu\text{g/kg}$) in post-monsoon and LMZ (1.02 $\mu\text{g/kg}$) > UMZ2 (0.91 $\mu\text{g/kg}$) > LZ (0.65 $\mu\text{g/kg}$) > UMZ1 (0.63 $\mu\text{g/kg}$) > UZ (0.09 $\mu\text{g/kg}$) in post-winter. The zone-wise composition of ESs in sediments is presented in Figure 2.27b

The site-wise seasonal variation of ESs in surface water and sediments of Ganga River is presented in Figure 2.28a and 2.28b respectively. In post-monsoon season, the ESs concentration ranged from **BDL-0.026 $\mu\text{g/L}$ (Mean: 0.003 $\mu\text{g/L}$; Median: BDL)** and **BDL-**

13.423 µg/kg (Mean: 1.214 µg/kg; Median: 0.554 µg/kg) in water and sediment respectively.

In post-winter season, the ESs concentration ranged from **BDL-0.054 µg/L (Mean: 0.009 µg/L; Median: 0.005)** and **BDL- 3.560 µg/kg (Mean: 0.713 µg/kg; Median: 0.361µg/kg)** in water and sediment respectively. For water samples, highest ESs contamination was recorded at sites such as Diamond Harbour, Jiaganj, Farrakka, and Serampore whereas for sediment samples highest pesticides contamination recorded at sites Ballia and Varanasi belonging to UMZ.

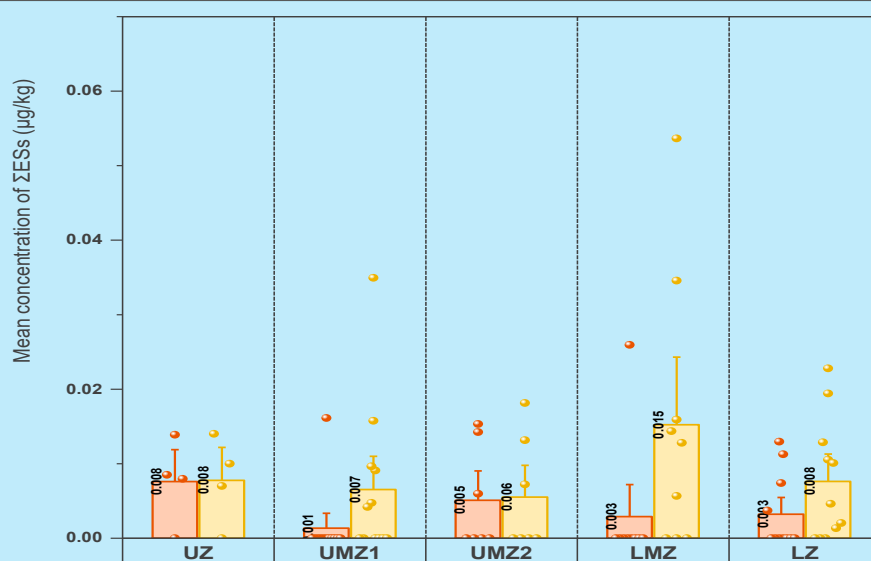
6.1 Sources of ESs- Historic or fresh inputs

The ratio diagnostic method was used to identify the potential sources of ESs contamination in Ganga River. The ratio of α -endosulfan/ β -endosulfan is used to calculate the age and source of endosulfan in the environment. In general, the value < 1 indicates the past usage (Yu et al., 2014). In our study, the ratios of α -endosulfan/ β -endosulfan at almost all zones for both seasons is found to be < 1 indicating the past usage in these areas. However, at some sampling sites in UMZ2 (post-winter) and LZ (post-monsoon), the ratios was >1 thus indicating towards fresh inputs of technical endosulfan.

SURFACE WATER

Figure 2.26a: Seasonal variation and zone-wise distribution of total ESs (Σ ESs) in surface water

High contamination prevails in UZ (Uttarakhand) and in LMZ (post-winter)



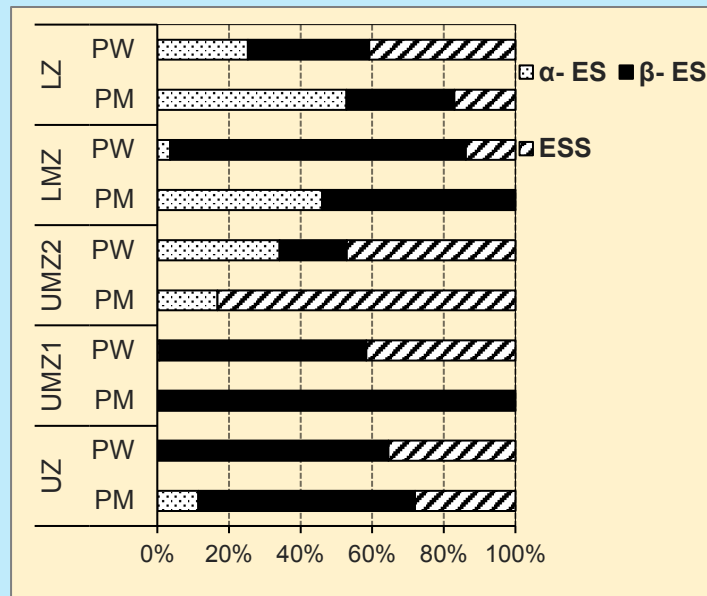


Figure 2.26b: Zone-wise composition of ESs in water

β-Endosulfan is dominant isomer in both seasons

SEDIMENT

Figure 2.27a: Seasonal variation and zone-wise distribution of total ESs (Σ ESs) in surface sediments

High contamination prevails in UZ (post-monsoon) and in UMZ2

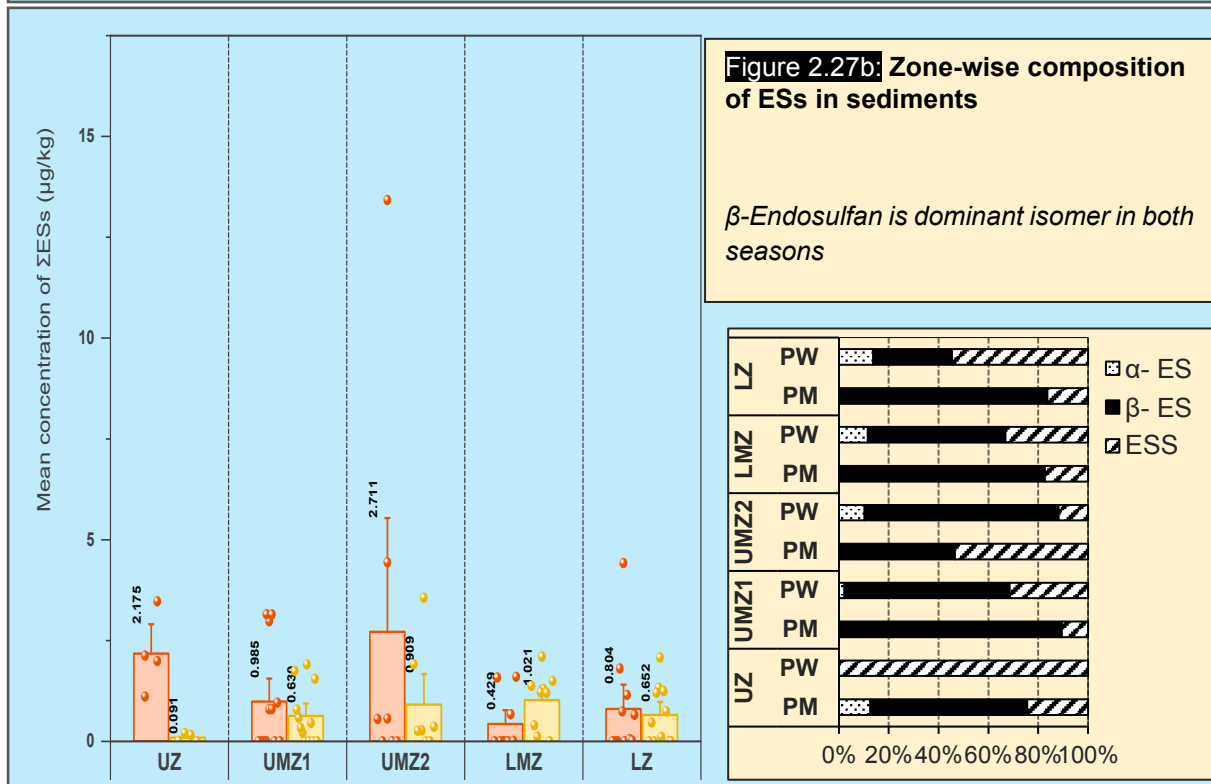
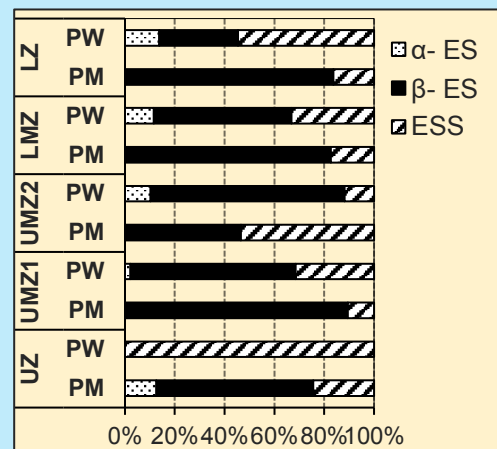


Figure 2.27b: Zone-wise composition of ESs in sediments

β-Endosulfan is dominant isomer in both seasons



SURFACE WATER

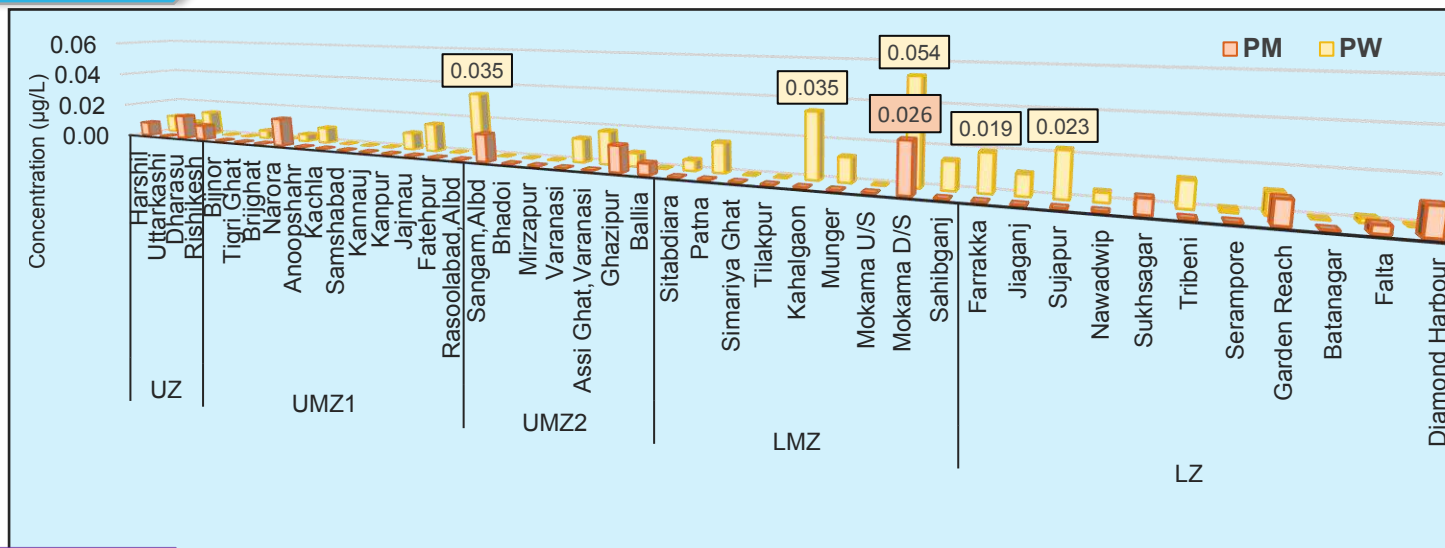


Figure 2.28a: Seasonal variation and site-specific distribution of ESs in surface water

The most ESs contaminated sites are Mokama D/S, Rasoolabad Allahabad, Kahalgaon, Sujapur, and Farrakka

Relatively low contamination prevails in sites belonging to LZ and UMZ1

SEDIMENTS

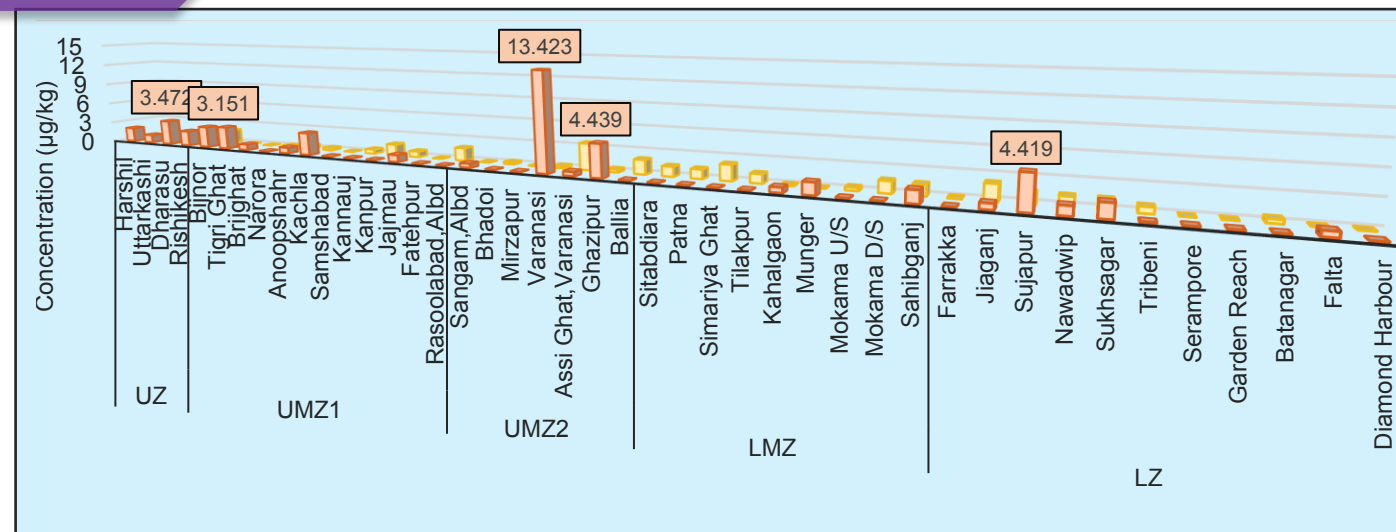


Figure 2.28b: Seasonal variation and site-specific distribution of ESs in surface sediments

The most ESs contaminated sites are Varanasi, Sujapur, Rishikesh and Tigri Ghat

Relatively low contamination prevails in sites belonging to LZ

7. Methoxychlor (M-CHLs)

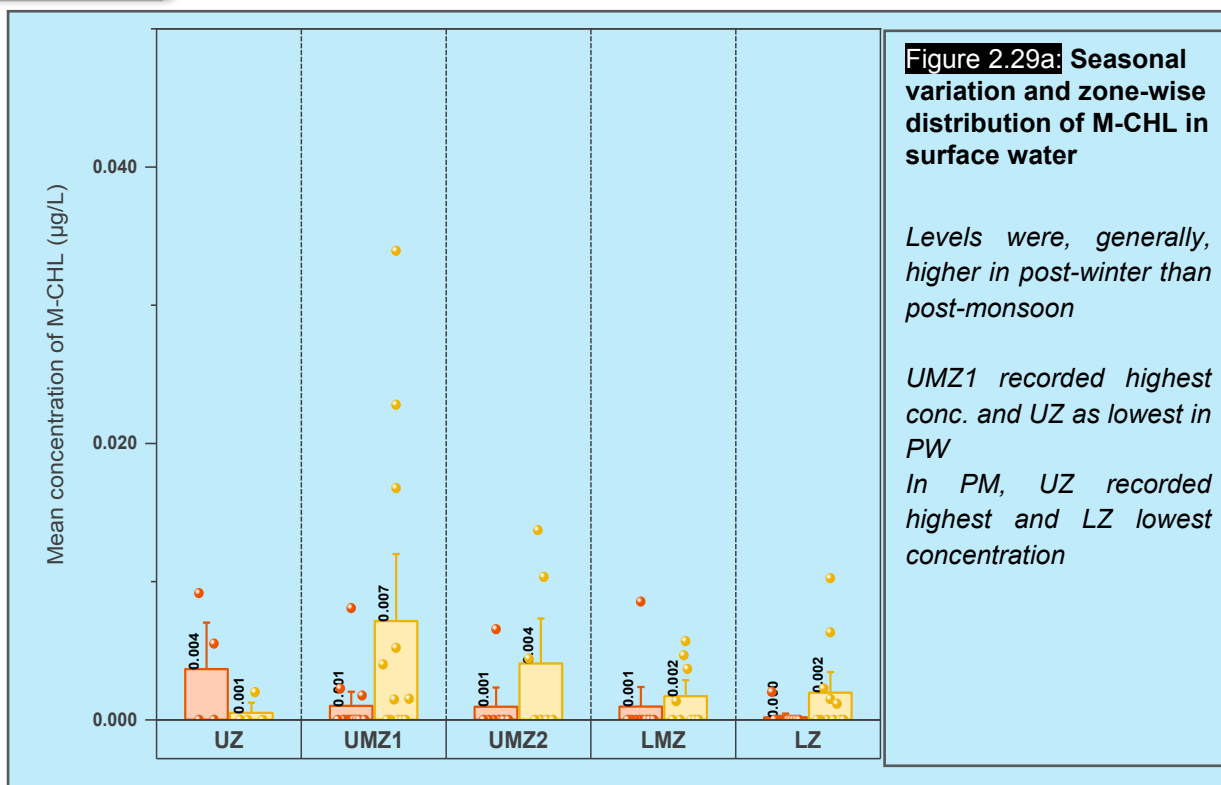
Methoxychlor (M-CHLs) is an organochlorine pesticide originally developed as a replacement for DDT (US EPA, 2011). It has been used as an insecticide combating a wide range of pests including biting flies, houseflies, mosquito larvae and cockroaches. It has commonly been used in both agricultural and veterinary practices, for example for treating field crops, vegetables, fruits, stored grains, livestock, pets, homes, gardens, lakes, and marshes (US Department of Health, 2002).

In present investigation, the mean concentration of M-CHLR in the entire stretch was found to be higher ($\sim 2.5 \times$) in post-winter than post-monsoon and the higher concentration levels in the surface water during post-winter season may be attributed to high evaporation (low water level), and lower flow volume conditions. The spatio-temporal distribution of M-CHLs (Figure 2.29a) in surface water, across zones revealed the sequence as **UZ (0.004 μ g/L) > UMZ1 \cong UMZ2 \cong LMZ (0.001 μ g/L) > LZ (BDL) in post-monsoon and UMZ1 (0.007 μ g/L) > LMZ (0.004 μ g/L) > UMZ 2= LZ (0.002 μ g/L) >UZ (0.001 μ g/L) in post-winter.**

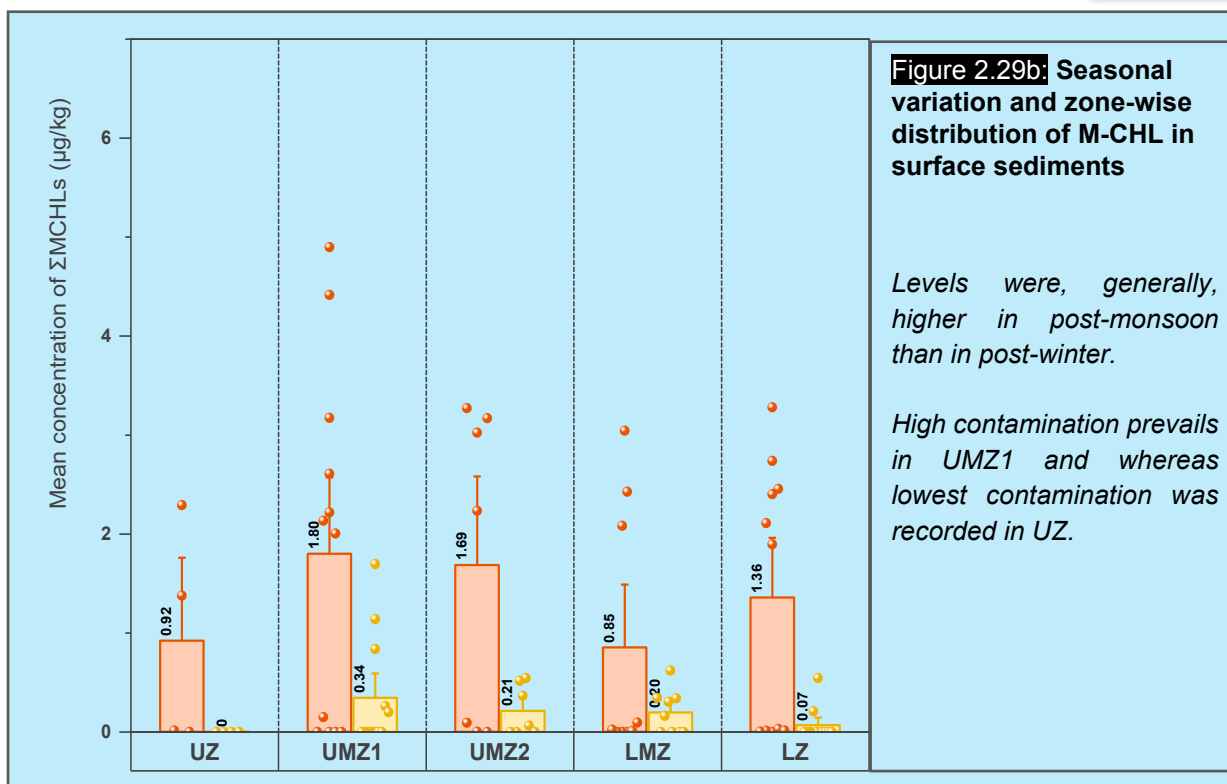
In the sediment compartment, the distribution of M-CHLs (Figure 2.29b) was found to be higher in post-monsoon than post-winter. The spatio-temporal distribution across zones showed the trend as UMZ1 (1.80 μ g/kg)> UMZ2 (1.69 μ g/kg)> LZ (1.36 μ g/kg)>UZ (0.92 μ g/kg)> LMZ (0.85 μ g/kg) in post-monsoon and UMZ1 (0.34 μ g/kg)> UMZ2 (0.21 μ g/kg)>LMZ (0.20 μ g/kg)>LZ (0.07 μ g/kg)>UZ (0.00 μ g/kg) in post-winter.

The site-wise seasonal variation of M-CHLs in surface water and sediments of Ganga River is presented in Figure 2.30a and 2.30b respectively. In post-monsoon season, the M-CHLs concentration ranged from **BDL-0.009 μ g/L (Mean: 0.001 μ g/L; Median: BDL)** and **BDL-4.899 μ g/kg (Mean: 1.389 μ g/kg; Median: 1.378 μ g/kg)** in water and sediment respectively. In post-winter season, the M-CHLs concentration ranged from **BDL-0.034 μ g/L (Mean: 0.004 μ g/L; Median: BDL)** and **BDL-1.697 μ g/kg (Mean: 0.189 μ g/kg; Median: BDL)** in water and sediment respectively.

SURFACE WATER



SEDIMENT



SURFACE WATER

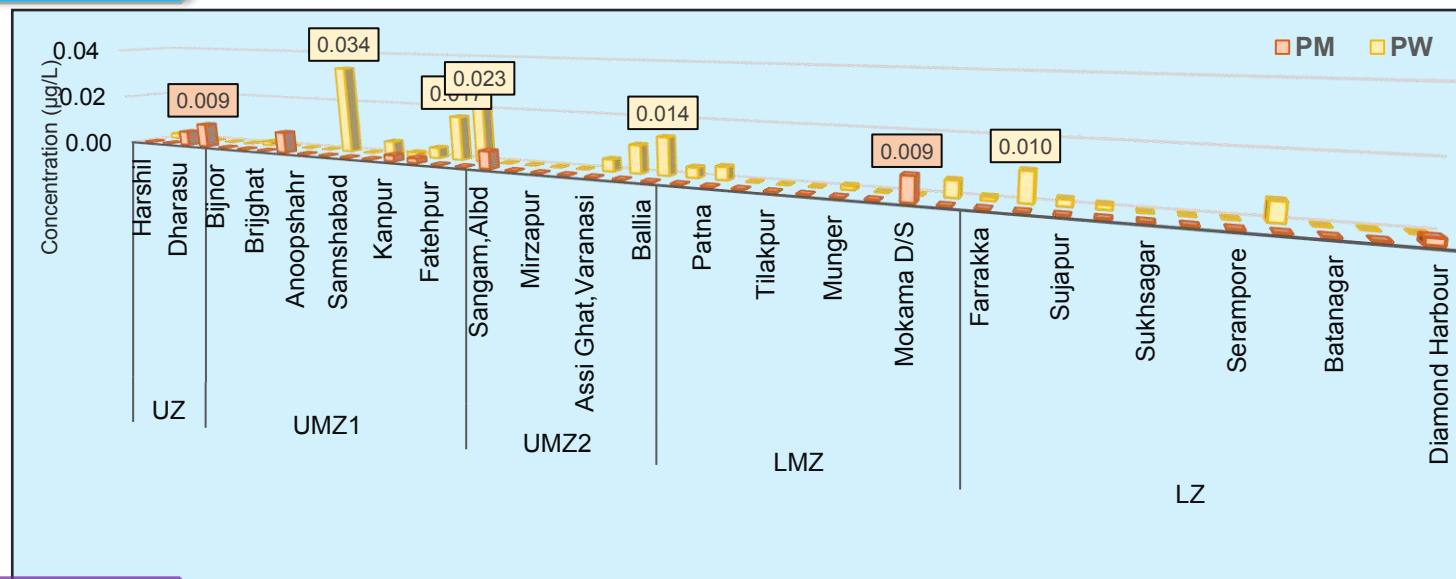


Figure 2.30a: Seasonal variation and site-specific distribution of M-CHL in surface water

The most M-CHLs contaminated sites are Kachla, Rasoolabad-Allahabad, Fatehpur and, Ballia – All from PW season

Relatively low contamination prevails in sites belonging to LZ and LMZ

SEDIMENTS

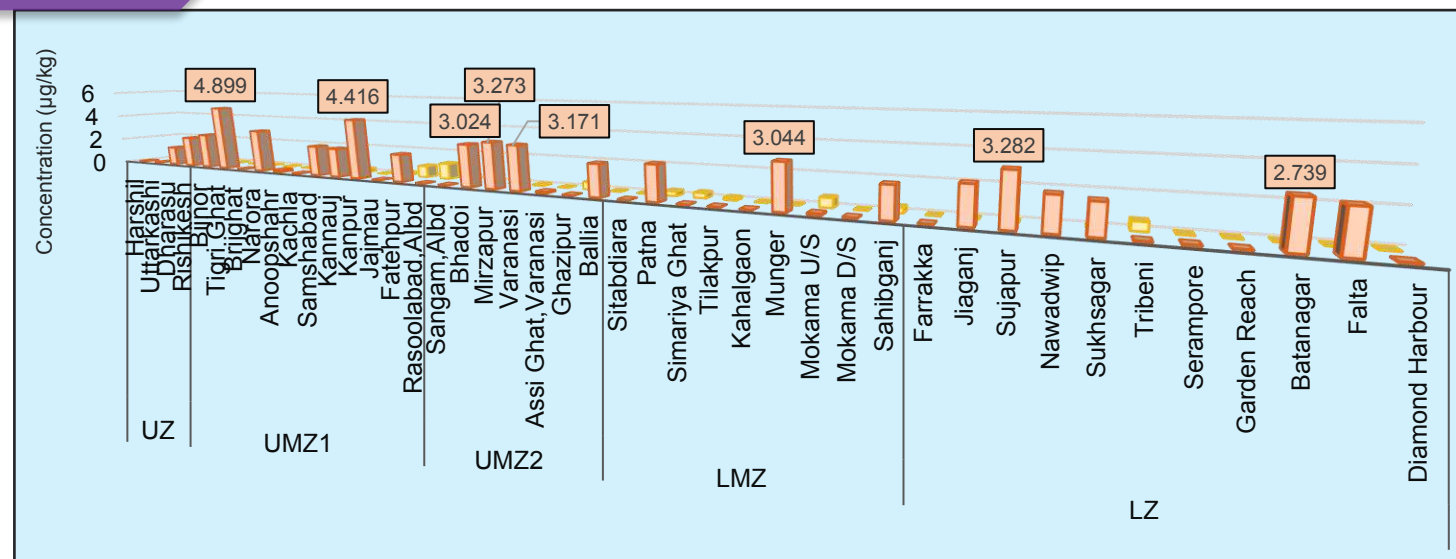


Figure 2.30b: Seasonal variation and site-specific distribution of M-CHL in surface sediments

The most M-CHLs contaminated sites are Tigri ghat, Kanpur, Sujapur, Mirzapur, Narora, and Assi Ghat-Varanasi

Relatively low contamination prevails in sites belonging to LZ in PW and LMZ and LZ in PM

4.1.2 Organophosphorous Pesticides (OPPs)

Three OPPs were investigated in this study that are selected on the basis of their high historic usage, detection frequency reported in previous studies, pesticides included in the CPCB, India monitoring network (CPCB, 2013), and the ones reported to pose high toxicity to wildlife. The studied OPPs are: **Malathion, Chlorpyrifos and Methyl Parathion,**

Contamination status of OPPs in Ganga River and five zones

A summary of descriptive analysis of the three target OPPs detected in Ganga River is presented in Figure 2.31 a, and Figure 2.32.

The total OPPs (Σ OPPs) concentration in water samples ranged from **0.007-3.238 $\mu\text{g/L}$** (Mean: **0.385 $\mu\text{g/L}$** ; Median: **0.087 $\mu\text{g/L}$**) in post-monsoon season and **BDL-1.523 $\mu\text{g/L}$** (Mean: **0.149 $\mu\text{g/L}$** ; Median: **0.086 $\mu\text{g/L}$**) in post-winter season. The *levels were generally higher in post-monsoon than in post-winter.*

For all the water samples, the mean concentration of Σ OPPs in Ganga River were higher in the post-monsoon season than those in post-winter season. The distribution of mean concentration of Σ OPP (Figure 2.31a), in surface water, across zones showed the order as **LZ (0.889 $\mu\text{g/L}$) > UMZ1 (0.404 $\mu\text{g/L}$) > UMZ2 (0.187 $\mu\text{g/L}$) > LMZ (0.062 $\mu\text{g/L}$) > UZ (0.014 $\mu\text{g/L}$) in post-monsoon and **UMZ1 (0.321 $\mu\text{g/L}$) > UMZ2 (0.218 $\mu\text{g/L}$) > LZ (0.078 $\mu\text{g/L}$) > LMZ (0.019 $\mu\text{g/L}$) > UZ (0.002 $\mu\text{g/L}$)** in post-winter. The group-wise seasonal and spatial distribution of OPP revealed the predominance of Malathion and Chlorpyrifos in all the zones for both seasons (Figure 2.31 b), that could be attributed to their current usage in agricultural activities and public health programmes. For water samples highest concentration was recorded at Brijghat, garden Reach, Falta, Diamond Harbour and Kanpur.**

Figure 2.31 a: Seasonal variation and zone specific distribution of total OPPs (Σ OPPs) in water

Levels were higher in post-monsoon than in post-winter

High contamination prevails in LZ (post-monsoon) and in UMZ1 in post-winter

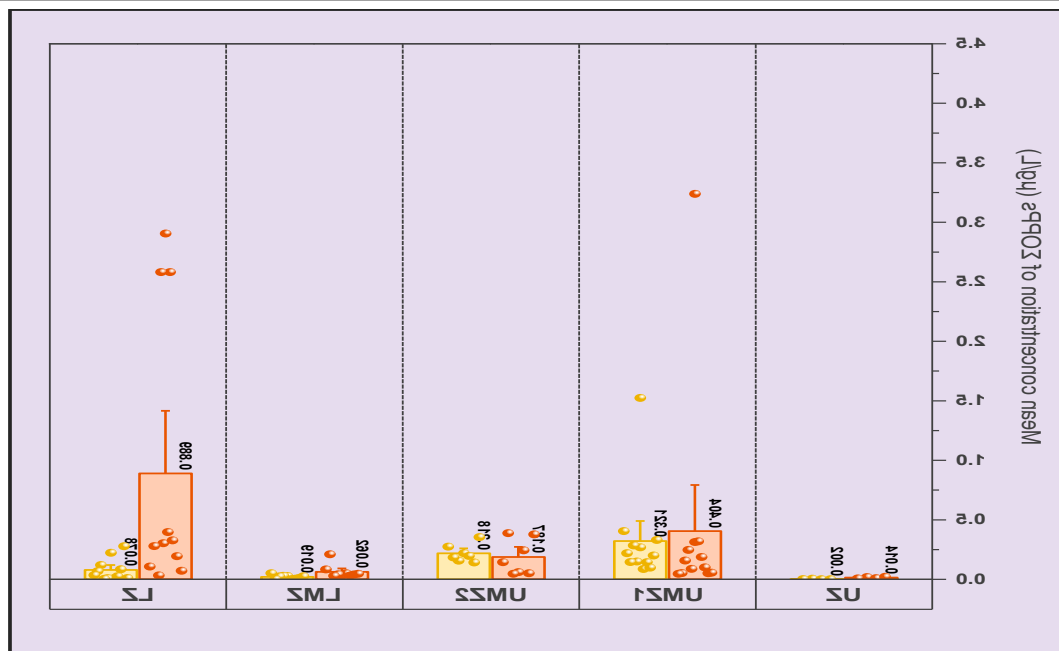
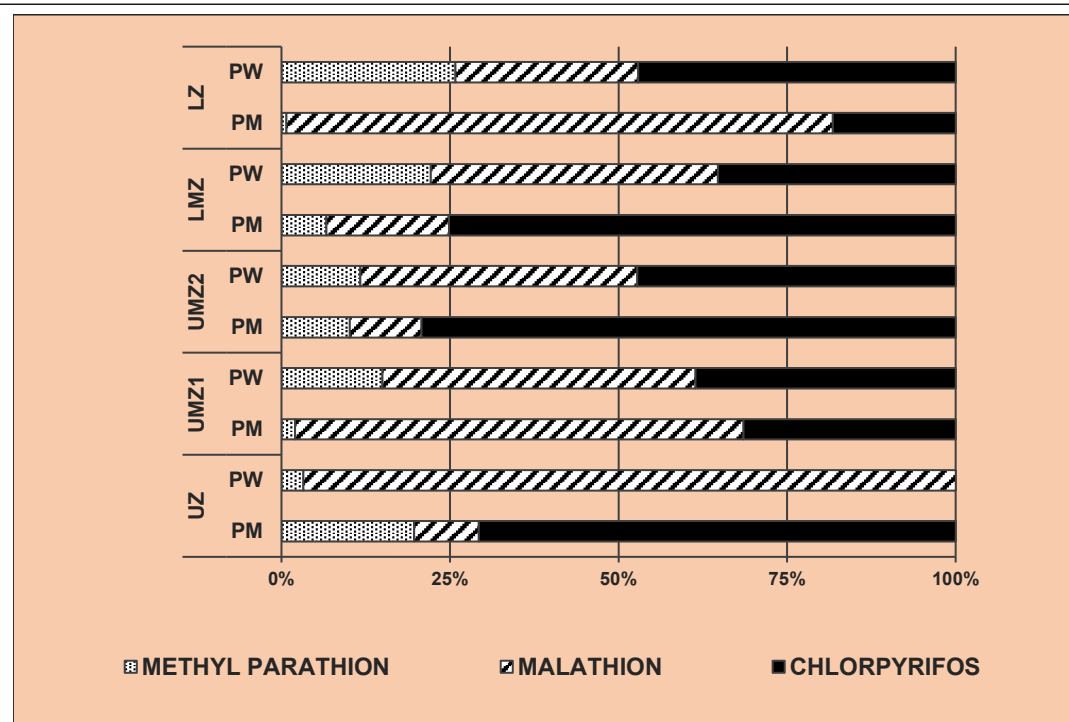
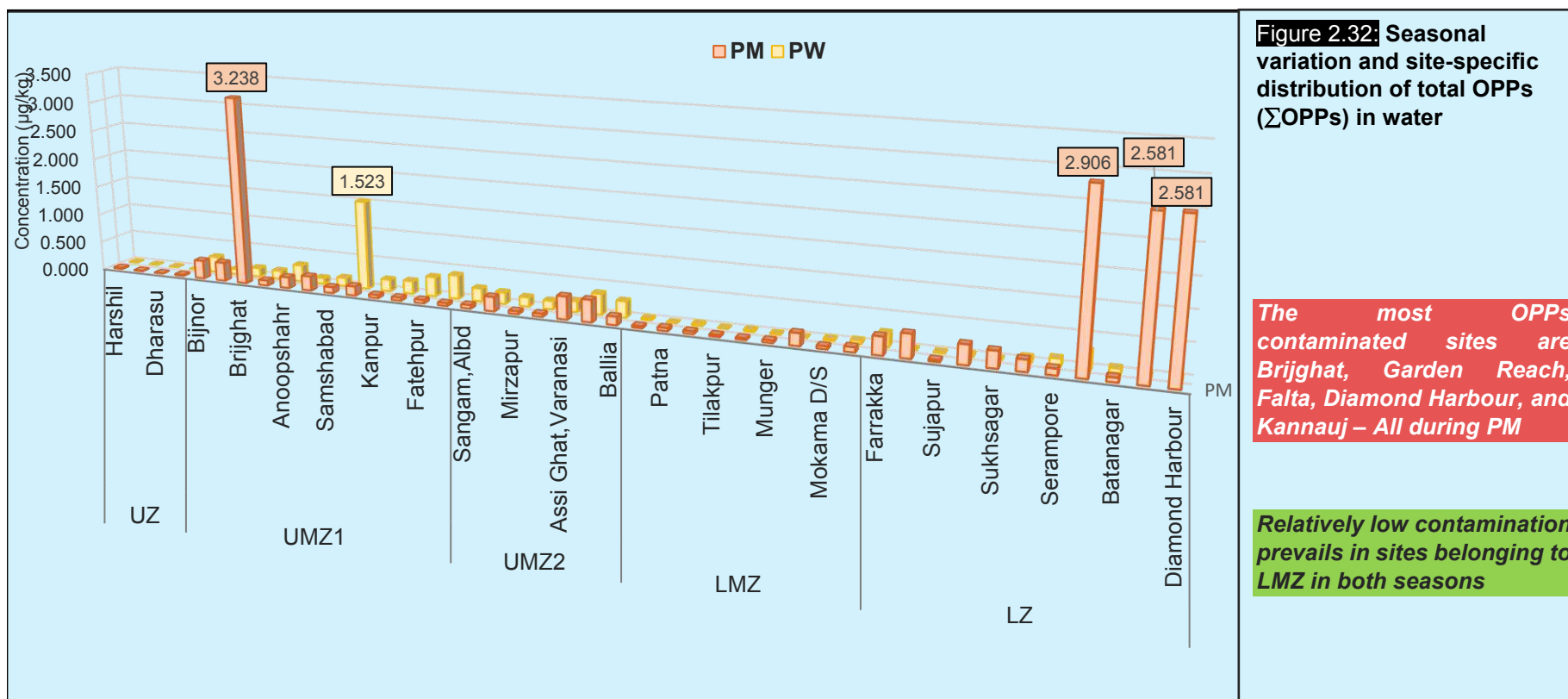


Figure 2.31b: Seasonal variation and zone specific distribution of total OPPs (%) in water

Most prevalent OPPs are Chlorpyrifos, and Malathion





The zone-wise and site-wise seasonal variation of Σ OPPs in surface sediments of Ganga River is presented in Figure 2.33 a and 2.34 respectively. In post-monsoon season, the Σ OPPs concentration ranged from **2.322-52.100 $\mu\text{g/kg}$ (Mean: 11.496 $\mu\text{g/kg}$; Median: 8.616 $\mu\text{g/kg}$)** whereas in post-winter season, the Σ OPPs concentration ranged from **BDL-95.622 $\mu\text{g/kg}$ (Mean: 10.900 $\mu\text{g/kg}$; Median: 2.955 $\mu\text{g/kg}$)**.

A mixed trend was observed for seasonal distribution of OPPs in sediment. The levels were higher in post-monsoon for zones UMZ1 and LZ whereas in post-winter for UMZ1 and UMZ2 recorded high concentrations. UZ had lowest OPP contamination in both the seasons.

The distribution of mean concentration of Σ OPP (Figure 2.33a), in surface sediments, across zones showed the order as **UMZ1 (15.74 $\mu\text{g/kg}$) >UMZ2 (13.71 $\mu\text{g/kg}$) >LMZ (10.41 $\mu\text{g/kg}$) >UZ (9.41 $\mu\text{g/kg}$) > LZ (7.10 $\mu\text{g/kg}$) in post-monsoon and LMZ (27.79 $\mu\text{g/kg}$) >LZ (13.58 $\mu\text{g/kg}$) > UMZ1 (4.18 $\mu\text{g/kg}$) >UMZ2 (2.60 $\mu\text{g/kg}$) >UZ (0.20 $\mu\text{g/kg}$) in post-winter. The sites with highest OPP contamination were Anoopshahar, Mirzapur, Patna, Samshabad, Narora in post-monsoon and Tilakpur, Falta, Simariya ghat, Munger and Sujapur in post-winter season.**

The seasonal and zone-wise composition of Σ OPPs (%) in sediments is presented in Figure 2.33b.

Figure 2.33a: Seasonal variation and zone specific distribution of total OPPs (Σ OPPs) in sediments

High contamination prevails in UMZ (post-monsoon) and, unlike OCPs in LMZ

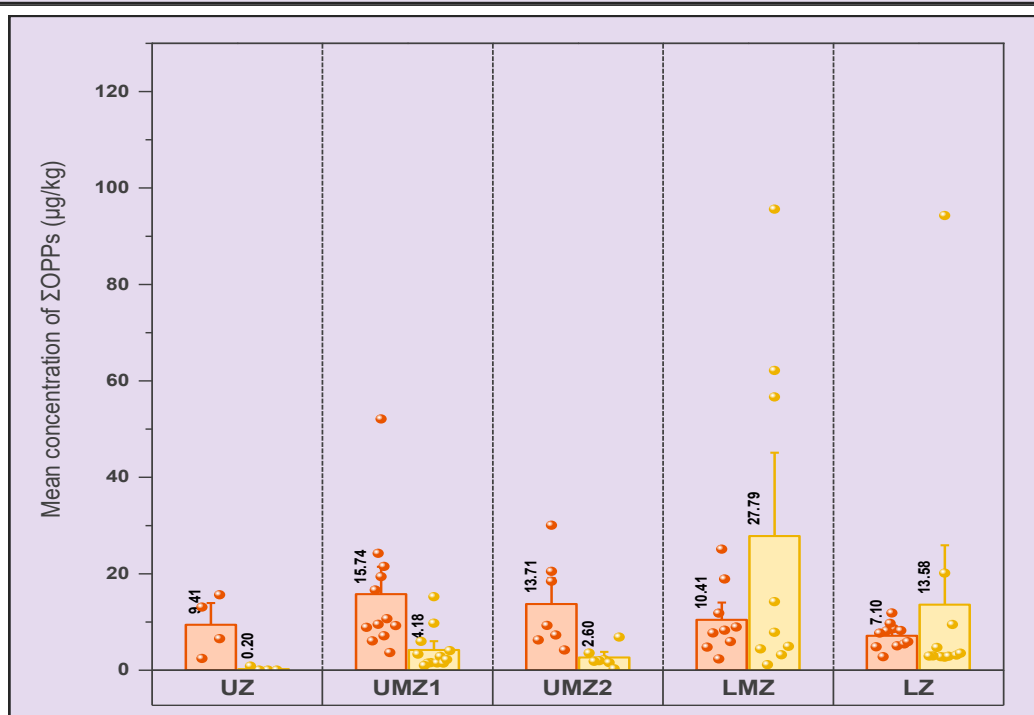
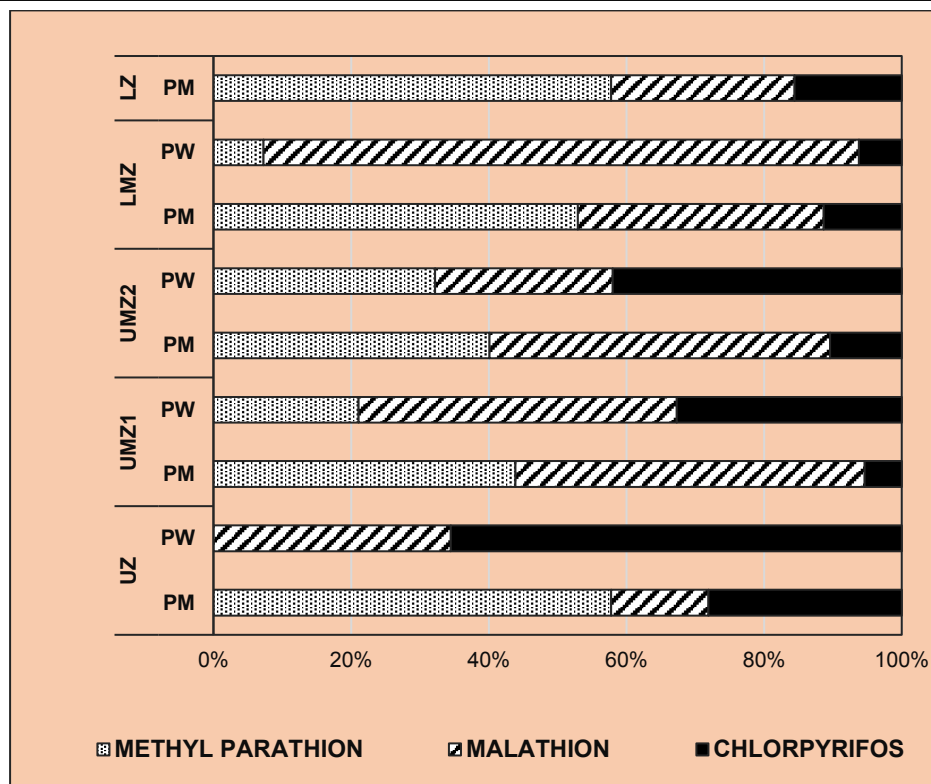
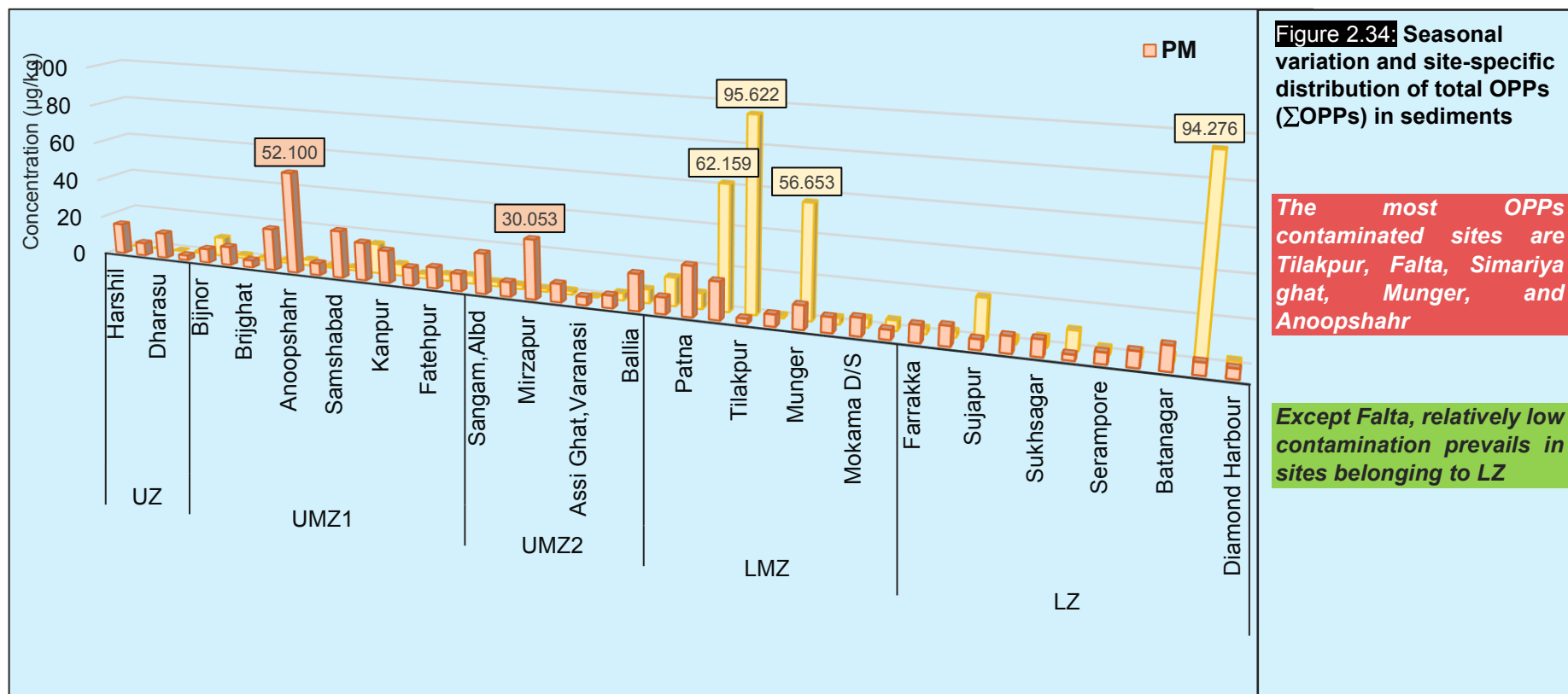


Figure 2.33b: Seasonal and Zone-wise composition of Σ OPPs (%) in sediments

OPPs composition is evenly distributed in sediment





8. Malathion

Malathion is a broad-spectrum insecticide used to control a variety of outdoor insects in both agricultural and residential settings. It is registered for use on food, feed, and ornamental crops and in mosquito and fruit fly eradication programs.

In present investigation, the sum total of malathion across the sites ranged from BDL-2.889 ug/l in post-monsoon and BDL-1.156 ug/l in post-winter season. Zonewise distribution in surface water (Figure 2.35a) revealed pattern as **LZ (0.720 µg/L) > UMZ1 (0.269 µg/L) > UMZ2 (0.020 µg/L) > LMZ (0.011 µg/L) > UZ (0.001 µg/L)** in post-monsoon and **UMZ1 (0.149 µg/L) > UMZ2 (0.089 µg/L) > LZ (0.021 µg/L) > LMZ (0.009 µg/L) > UZ (0.003 µg/L)** in post-winter.

Except for UMZ1 and LZ in post-monsoon, a homogenous seasonal distribution of Malathion was observed.

The distribution of Malathion (Figure 2.35b), in sediments, was found to be higher in post-winter than post-monsoon. The spatio-temporal distribution across zones showed the trend as **UMZ1 (7.992µg/kg) > UMZ2 (6.783µg/kg) > LMZ (3.717µg/kg) > LZ (1.893µg/kg) > UZ (1.331µg/kg)** in post-monsoon and **LMZ (24.046µg/kg) > LZ (9.237µg/kg) > UMZ1 (1.933µg/kg) > UMZ2 (0.670µg/kg) > UZ (0.070µg/kg)** in post-winter. *A mixed trend was observed for seasonal distribution of OPPs in sediment. The levels were higher in post-monsoon for zones UMZ1 and UMZ2 whereas the levels were higher in post-winter for zones LMZ and LZ.*

The sitewise seasonal variation of Malathion in surface water and sediments of Ganga River is presented in Figure 2.36a and 2.36b respectively. In post-monsoon season, the Malathion concentration ranged from **BDL-2.889 µg/L (Mean 0.265 µg/L; Median 0.016 µg/L)** and **BDL-49.434 µg/kg (Mean 4.721 µg/kg; Median 0.0165 µg/kg)** in water and sediment respectively. In post-winter season, the Malathion concentration ranged from **BDL-1.156 µg/L (Mean 0.068**

$\mu\text{g/L}$; Median $0.022 \mu\text{g/L}$) and **BDL-92.280 $\mu\text{g/kg}$** ((Mean $8.051 \mu\text{g/kg}$; Median $0.336 \mu\text{g/kg}$) in water and sediment respectively.

For water samples, highest contamination was recorded at sites such as *Brijghat, Garden Reach, Diamond Harbour and Falta* in post-monsoon season whereas for sediment samples highest pesticides contamination was recorded at *Tilakpur, Falta, Simariya Ghat, Munger (PW)*, mostly belonging to LMZ, except Falta (LZ).

SURFACE WATER

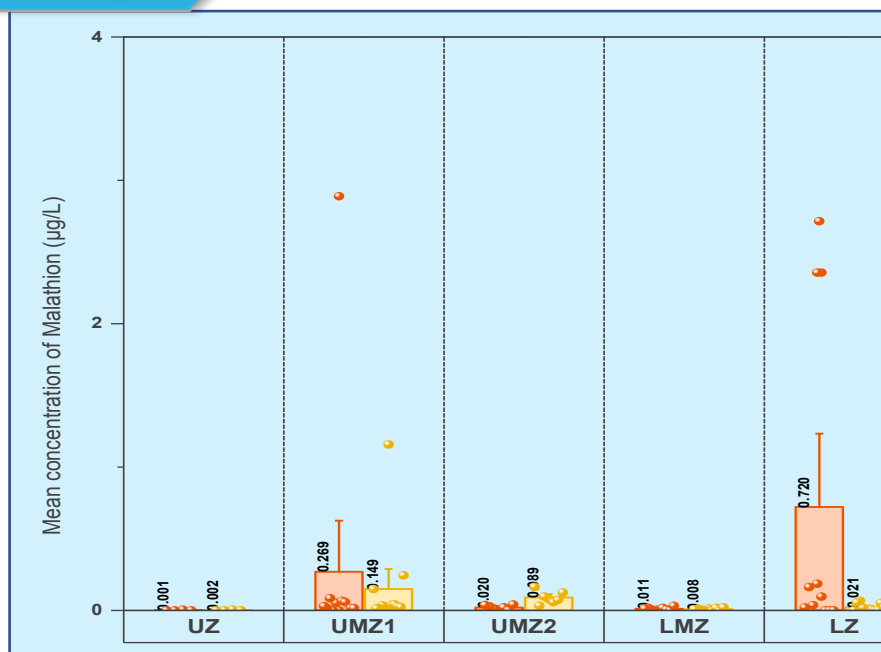


Figure 2.35a: Seasonal variation and site-specific distribution of Malathion in surface water

Highest contamination prevails in LZ whereas lowest contamination was observed at UZ

SEDIMENT

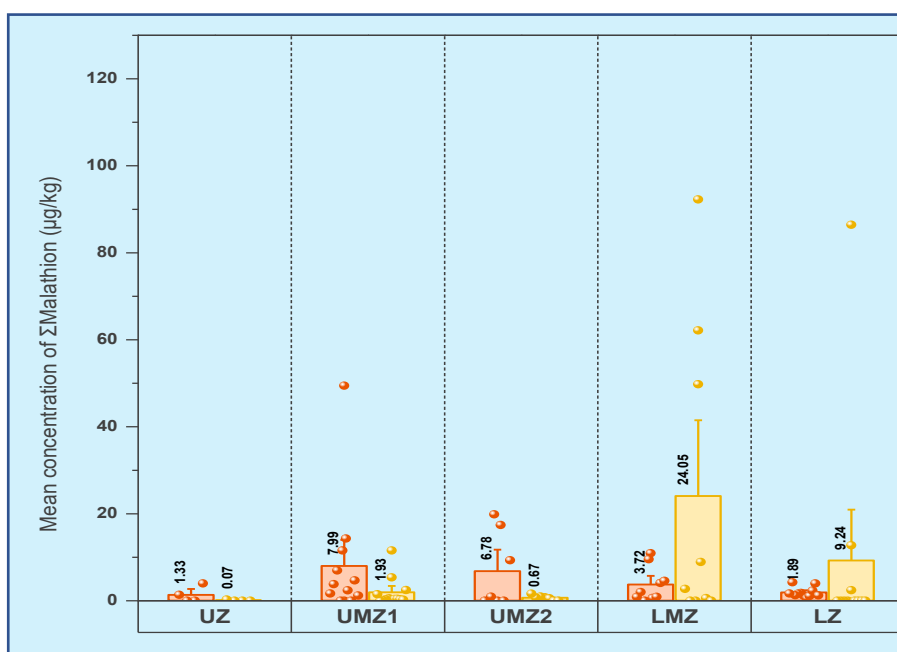


Figure 2.35b: Seasonal variation and site-specific distribution of Malathion in surface sediments

Highest contamination prevails in LMZ whereas lowest contamination was observed at UZ

SURFACE WATER

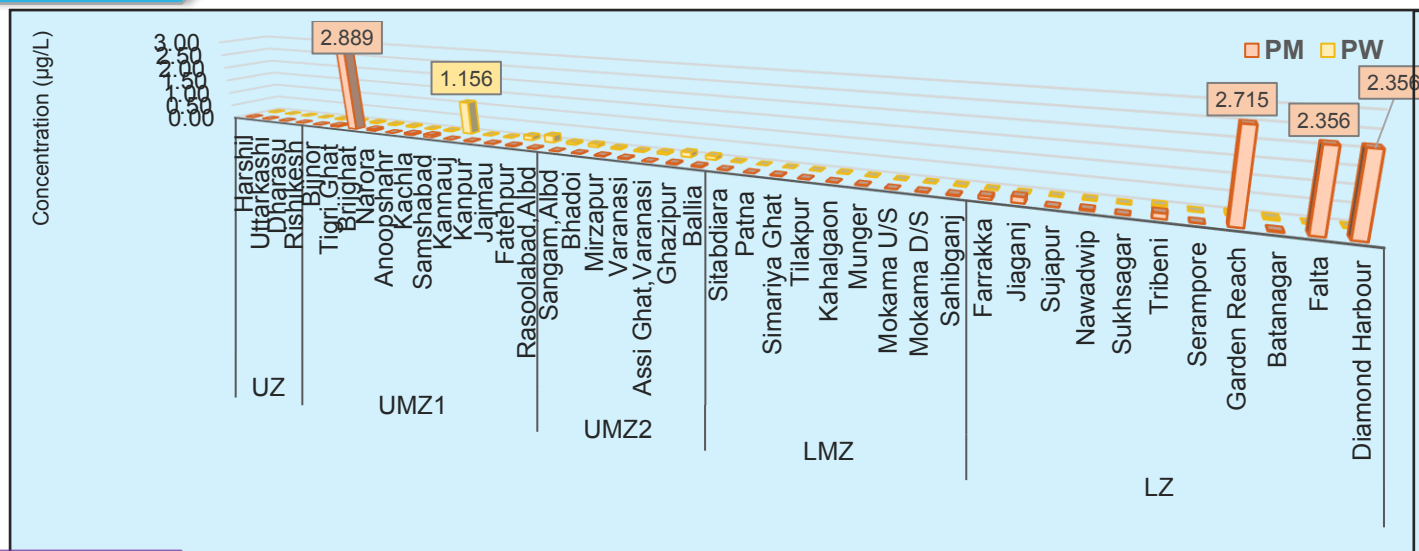


Figure 2.36a: Seasonal variation and site-specific distribution of Malathion in surface water

Highest contamination was recorded at sites such as Brijghat, Garden Reach, Diamond Harbour, Falta (PM) and Kannauj (PW)

Relatively low contamination prevails in sites belonging to LMZ, UMZ, and UZ

SEDIMENTS

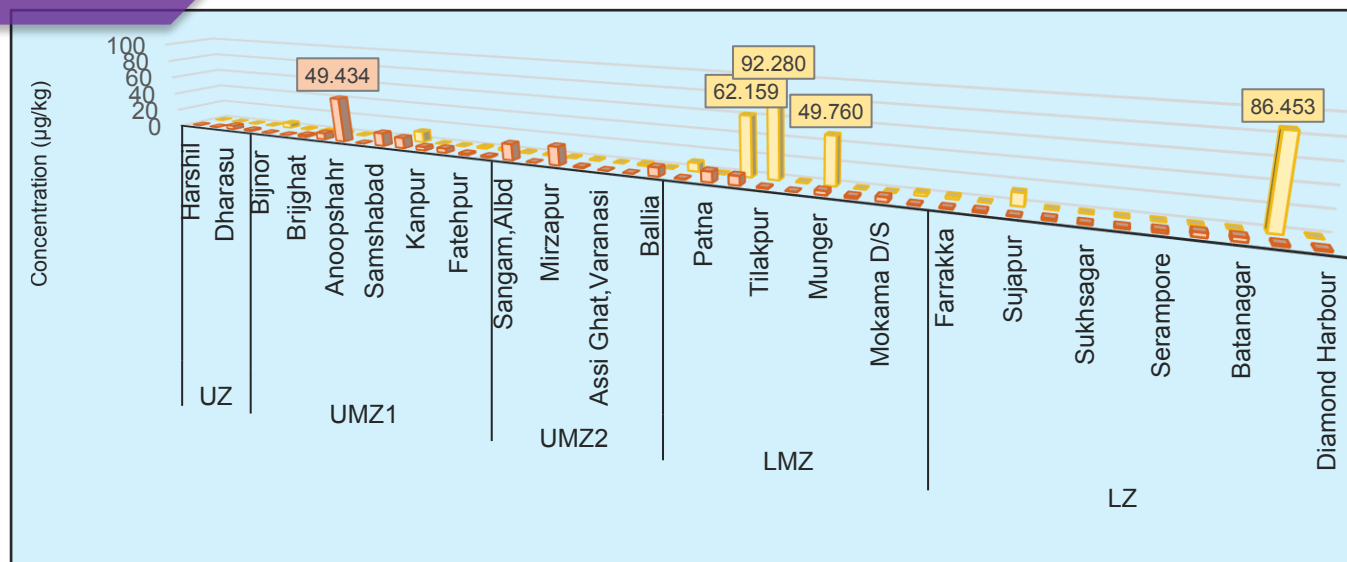


Figure 2.36b: Seasonal variation and site-specific distribution of Malathion in surface sediments

Highest contamination was recorded at sites such as Tilakpur, Falta, Simariya Ghat, Munger (PW) and Anoopshahr (PM)

Relatively low contamination prevails in sites belonging to UZ, and, LZ (Except Falta), UMZ2

9. Chlorpyrifos

Chlorpyrifos is a broad spectrum organophosphate pesticide widely used in agriculture and residential pest control throughout the world. The usage of Chlorpyrifos is not banned in India and different studies suggest that Chlorpyrifos is the fourth most used pesticide in India for agriculture and termite treatment of the foundations of new buildings.

In present investigation, the spatio-temporal distribution of Chlorpyrifos (Figure 2.37 a) in surface water, across zones revealed the sequence as **LZ (0.162 µg/L) > UMZ2 (0.148 µg/L) > UMZ1 (0.127 µg/L) > LMZ (0.047 µg/L) > UZ (0.010 µg/L)** in post-monsoon and **UMZ1 (0.124 µg/L) > UMZ2 (0.103 µg/L) > LZ (0.037 µg/L) > LMZ (0.008 µg/L) > UZ (BDL)** in post-winter. *Chlorpyrifos levels were higher in post-monsoon than in post-winter.*

In surface sediments, the spatio-temporal distribution of Chlorpyrifos (Figure 2.37 b) across zones showed the trend as **UZ (2.644 µg/kg) > UMZ2 (1.426 µg/kg) > LMZ (1.181 µg/kg) > LZ (1.105 µg/kg) > UMZ1 (0.847 µg/kg)** in post-monsoon. In the post winter season the trend was **LZ (2.153 µg/kg) > LMZ (1.727 µg/kg) > UMZ1 (1.366 µg/kg) > UMZ2 (1.092 µg/kg) > UZ (0.133 µg/kg)**. *A mixed trend was observed for seasonal distribution of Chlorpyrifos in sediment. The levels were higher in post-monsoon for zones UZ and UMZ2 whereas the levels were higher in post-winter for zones LZ and LMZ.*

The site-wise seasonal variation of Chlorpyrifos in surface water and sediments of Ganga River is presented in Figure 2.38a and 2.38b respectively. In post-monsoon season, the Chlorpyrifos concentration ranged from **0.006-0.375 µg/L** and **BDL-5.412 µg/kg** in water and sediment respectively. In post-winter season, the Chlorpyrifos concentration ranged from **BDL-0.328 µg/L** and **BDL-7.823 µg/kg** in water and sediment respectively.

SURFACE WATER

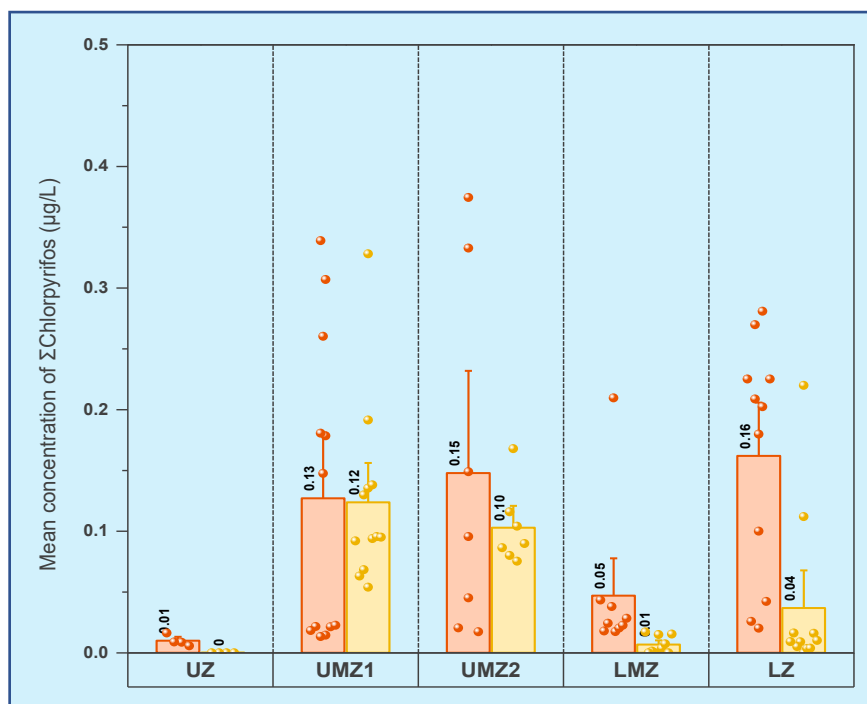


Figure 2.37a: Seasonal variation and site-specific distribution of Chlorpyrifos in surface water

High contamination prevails in LZ and UMZs whereas lowest contamination was observed at UZ

SEDIMENT

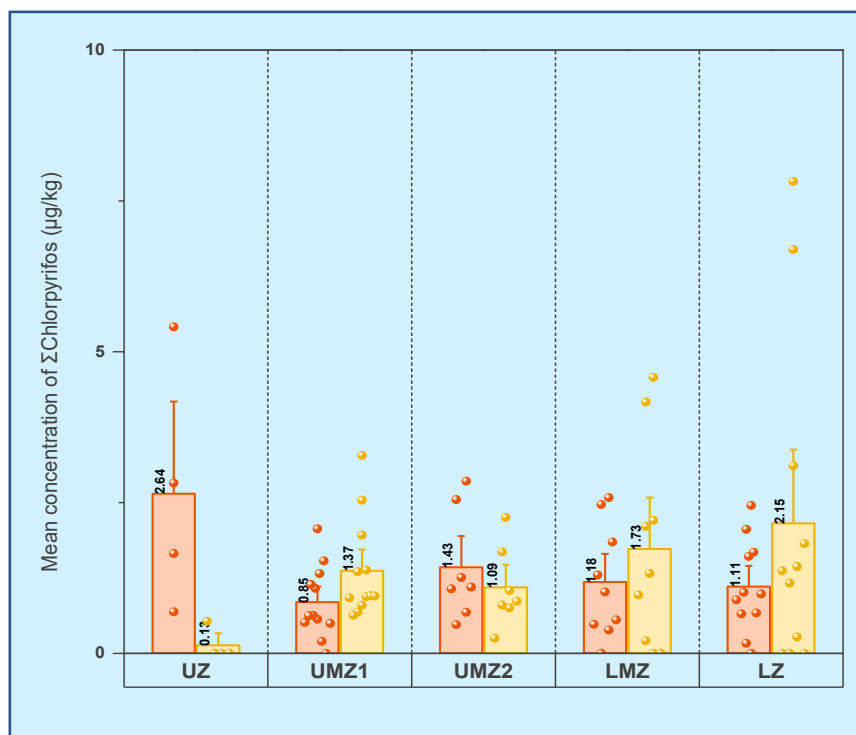


Figure 2.37b: Seasonal variation and site-specific distribution of Chlorpyrifos in surface sediments

Homogenous distribution of Chlorpyrifos was generally observed across zones and both seasons indicating prevalent ongoing usage of this pesticide.

SURFACE WATER

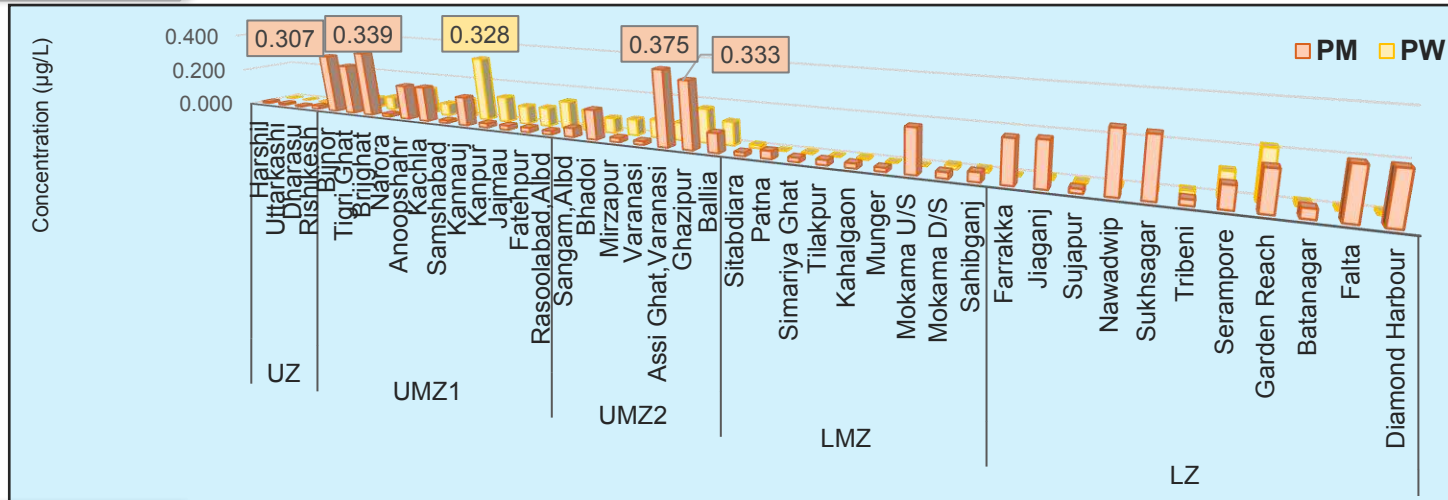


Figure 2.38a: Seasonal variation and site-specific distribution of Chlorpyrifos in surface water

Highest Chlorpyrifos contamination was recorded at sites such as Assi Ghat, Brijghat, Ghazipur, and Bijnor in PM and Kannauj in PW

Lowest contamination was observed for sites belonging to UZ

SEDIMENT

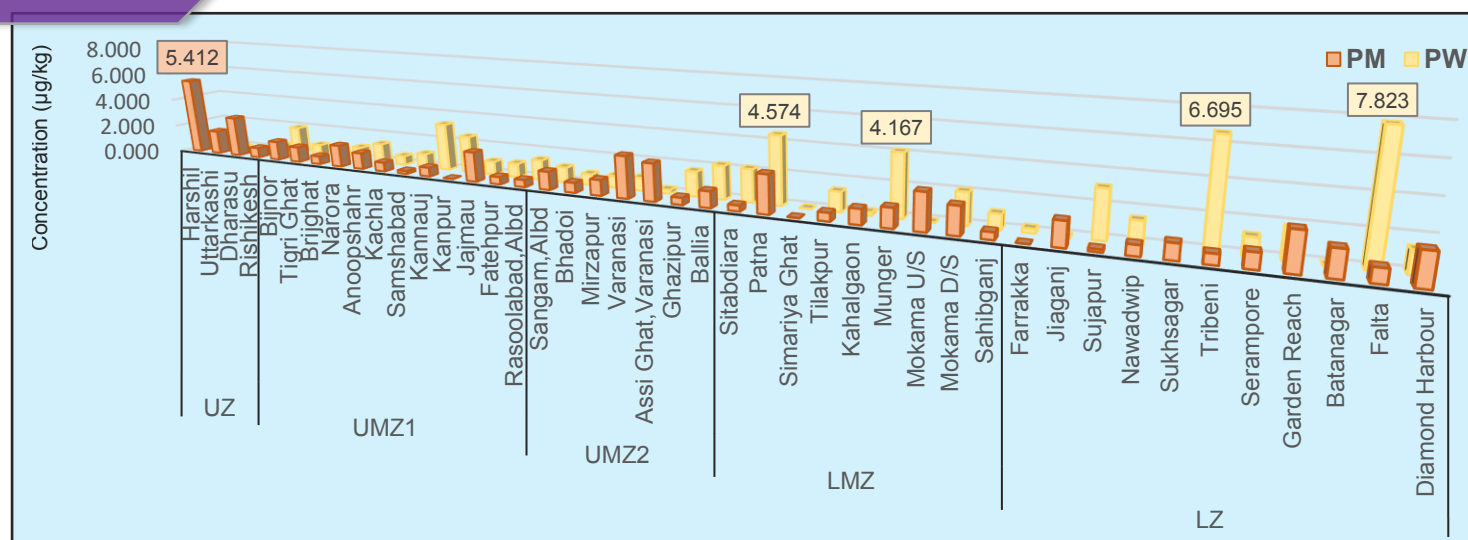


Figure 2.38b: Seasonal variation and site-specific distribution of Chlorpyrifos in surface sediments

Highest Chlorpyrifos contamination was recorded at sites such as Falta, Tribeni, Patna (PW) and Harshil (PM)

Lowest contamination was observed for LZ sites

10. Methyl Parathion

Methyl parathion (MP), a toxic organophosphate insecticide approved for outdoor use only, is classified by the World Health Organization (WHO) as a Category I A (extremely toxic) and by the United States Environmental Protection Agency (U.S. EPA) as a Toxicity Category I (most toxic) insecticide. Methyl parathion is banned from manufacture, use, export and import from 8th August, 2018 in India.

In the present investigation, the spatio-temporal distribution of Methyl parathion (Figure 2.39a) in surface water, across zones revealed the sequence as **UMZ2 (0.019µg/L) > UMZ1 (0.008µg/L) > LZ (0.006µg/L) > LMZ (0.004µg/L) > UZ (0.003µg/L)** in post-monsoon and **UMZ1 (0.048µg/L) > UMZ2 (0.025µg/L) > LZ (0.020 µg/L) > LMZ (0.004µg/L) > UZ (BDL)** in post-winter. *Methyl parathion levels were generally higher in post-winter than in post-monsoon.*

In sediments samples, the spatio-temporal distribution of Methyl parathion (Figure 2.39b) across zones showed the trend as **UMZ1 (6.905µg/kg) > LMZ (5.589µg/kg) > UMZ2 (5.507µg/kg) > UZ (5.435µg/kg) > LZ (4.100µg/kg)** in post-monsoon and **LZ (2.189µg/kg) > LMZ (1.092µg/kg) > UMZ1 (0.882µg/kg) > UMZ 2 (0.837µg/kg) > LMZ (1.092µg/kg)** in post-winter.

The site-wise seasonal variation of Methyl parathion in surface water and sediments of Ganga River is presented in Figure 2.40a and 2.40b respectively. In post-monsoon season, the Methyl parathion concentration ranged from **BDL-0.082 µg/L (Mean: 0.008 µg/L; Median: 0.006 µg/L)** and **0.374-13.048 µg/kg (Mean: 5.531 µg/kg; Median: 5.792 µg/kg)** in water and sediment respectively. In post-winter season, the Methyl parathion concentration ranged from **BDL-0.213 µg/L (Mean: 0.025 µg/L; Median: 0.013 µg/L)** and **BDL-4.710 µg/kg (Mean: 1.365 µg/kg; Median: 0.871 µg/kg)** in water and sediment respectively. *Farrakka, Anoopshahr, Jajmau, Fatehpur recorded highest methyl parathion concentration in the post*

winter season and Bhadoi recorded highest concentrations in post monsoon in water compartment.

For sediment matrix, Narora, Kanpur, Patna, Harshil and Samshabad had high contamination in PM whereas Sukhsagar and Balia recorded high contamination in PW.

SURFACE WATER

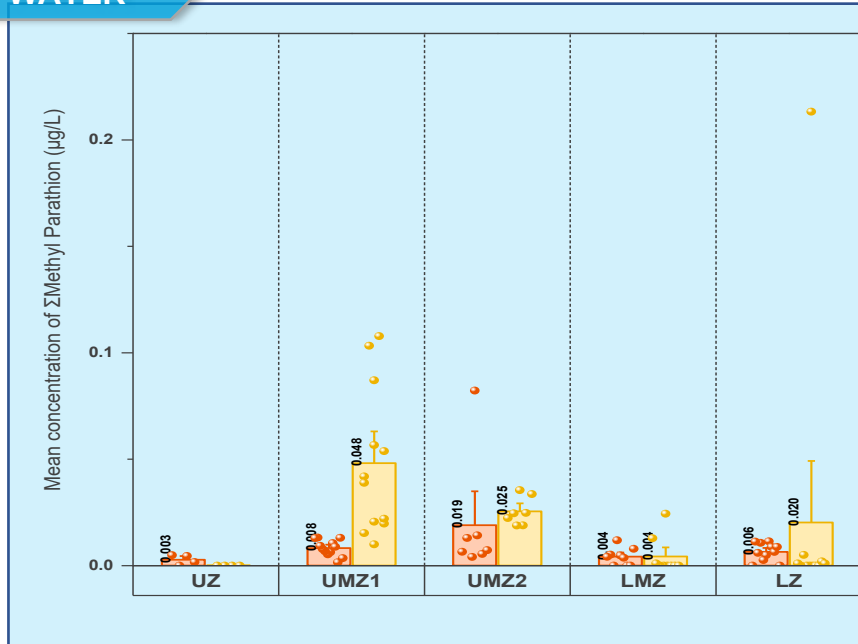


Figure 2.39a: Zone-wise seasonal distribution of Methyl Parathion in surface water

Levels were generally higher in post-winter than in post-monsoon

High contamination prevails in UMZ1 whereas lowest contamination was observed at UZ

SEDIMENT

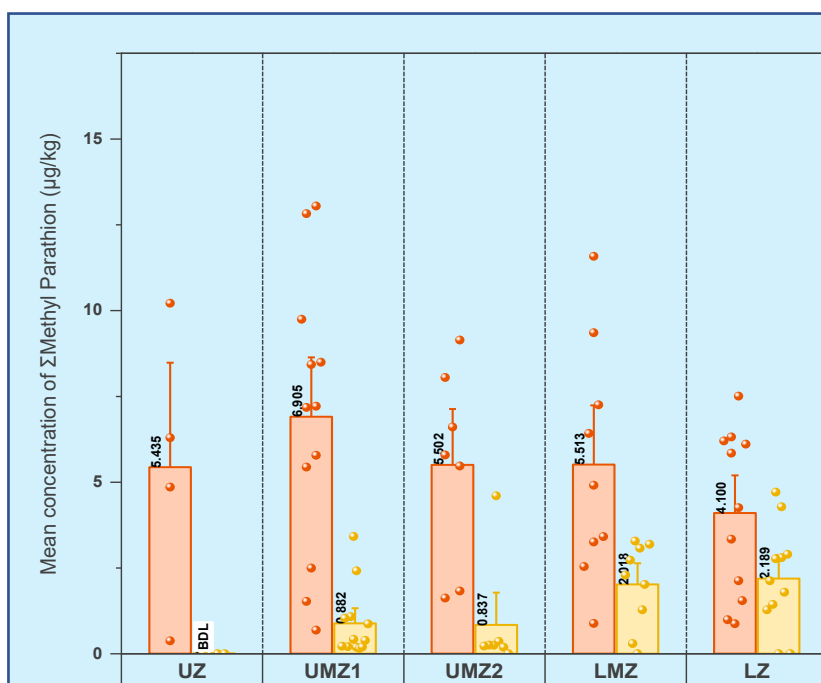


Figure 2.39b: Seasonal variation and site-specific distribution of Methyl Parathion in surface sediments

Levels were higher in post-monsoon than in post-winter

High contamination prevails in UMZs and LMZ whereas lowest contamination was observed at UZ

SURFACE WATER

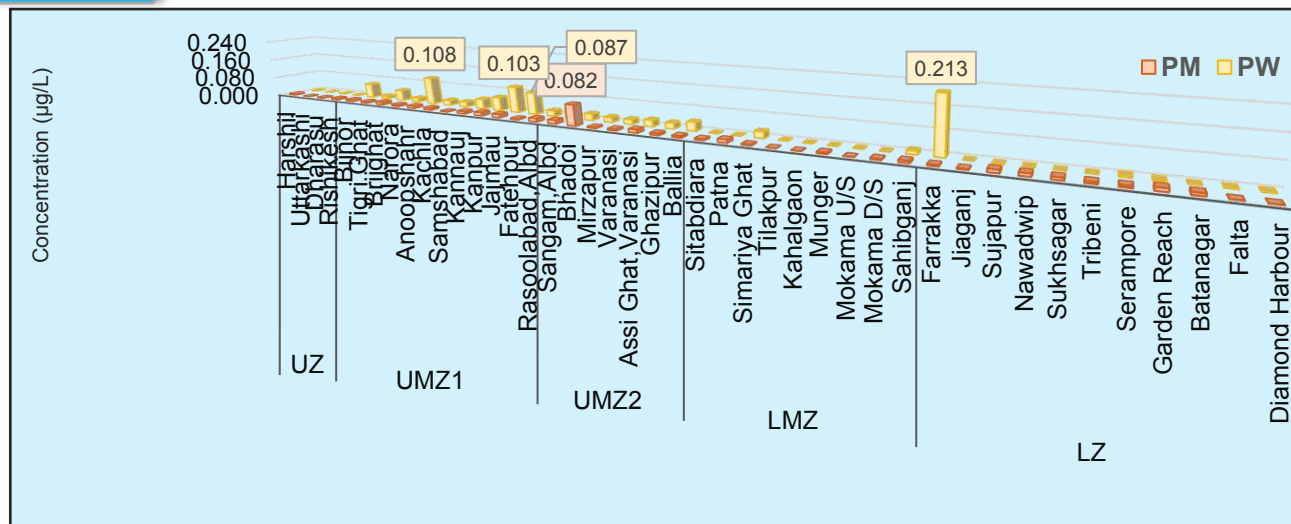


Figure 2.40a: Seasonal variation and site-specific distribution of Methyl Parathion in surface water

Highest contamination was recorded at sites such as Farrakka, Anoopshahr, Jajmau, Fatehpur (PW), Bhadoi (PM)

Except Farrakka, relatively low contamination prevails in sites belonging to LZ

SEDIMENTS

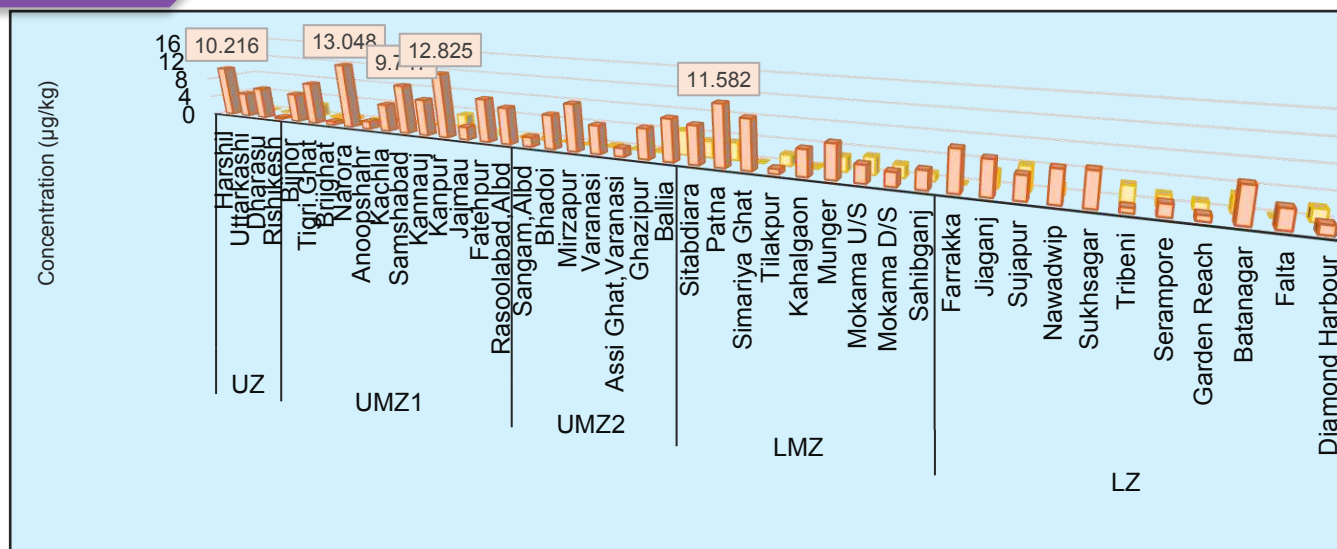


Figure 2.40b: Seasonal variation and site-specific distribution of Methyl Parathion in surface sediments

A unique observation was high distribution of Methyl Parathion across all the sites in post-monsoon season

Some of the highly contaminated sites are Narora, Kanpur, Patna, Harshil, and Samshabad

Overview of findings and Priorities for filling information gaps – Pesticides

Overview of findings

- a) The spatial distribution of most pesticides was consistent with the agricultural activities of the area or their urban applications. The temporal distribution showed differences between zones related to the different sources, hydrological differences in the system, and different land-use patterns.
- b) The study showed that Heptachlor and its metabolite, γ -HCH (Lindane), p,p'-DDE, *trans*- chlordane, Chlorpyrifos, and Malathion were the most frequently detected OCPs and OPPs across all the zones.
- c) The group-wise seasonal and spatial distribution of OPP revealed the predominance of Chlorpyrifos and Malathion in water compartment whereas in sediment it was dominance of Methyl parathion and Malathion, that could be attributed to their current usage in agricultural activities and public health programmes.

Spatial distribution of OCPs in water revealed highest concentrations in intensive agricultural and estuarine lower zone (LZ). Whereas spatial distribution in sediment reveal highest concentration in pristine UZ.

Priorities for filling information gaps

- (i) Improve tracking of pesticide use in agricultural and non-agricultural areas, including amounts, locations, and timing.
- (ii) Reliable information on use is key to efficient and cost-effective water-quality monitoring and assessment, including development of predictive models.
- (iii) Assessments of new pesticides and others not yet studied. Regular updates to water-quality assessments are needed to keep findings relevant to present-day use patterns.
- (iv) We also recommend a continuous monitoring campaign to follow up on the occurrence of pesticide residues in the Ganga.
- (v) Sustain and expand long-term monitoring for trends. Pesticide use is constantly changing over time, including phaseouts of some products and introductions of new ones, making long-term monitoring critical for up-to-date water-quality assessment and evaluation of trends.

- e) The emergence of the lower zone LZ, representing state of West Bengal, as the most polluted zone is an equally grave matter. We expect that massive cultivation of crops and vegetables, high cropping intensity, flow abstraction due to dams/barrages, tidal flushes, and flood currents of the estuarine region (LZ) are the possible reasons for highest OCP pollution in LZ
- f) High levels of OCPs in sediment from in the pristine upper zone (Uttarakhand) is a serious concern and validate sediment acting as sink for these pesticides which are brought by long-range atmospheric transport and fresh inputs.
- g) The significant finding is the data pointing towards continuous illegal use of HCH (including lindane) and chlordane in all the zones and Endosulfan in the lower zone and parts of the middle zone.
- h) The results point towards slow environmental decay as well as the consequences of continued use of DDT in Health programs in India.
- i) For most of the pesticides (water), LMZ (Bihar & Jharkhand) is identified as the lowest contaminated zone, and highlights the importance related to the river flow. The high-flow (contribution of tributaries) produced a pesticide dilution??? effect, generating lower levels in water and accumulation in sediments.

- (vi) Monitoring of the drains along the river need to be taken up for the presence of pesticide concentrations and loads.
- (vii) Awareness campaigns and training programs for farmers must be taken up on a priority basis to eliminate the use of toxic pesticides and adopt integrated pest management, mixed intercropping systems, and organic agroforestry systems.
- (viii) Stricter implementations of the NIP on POPs and timely updates for the next phase is also recommended.
- (ix) To ensure a healthy ecosystem for the biodiversity of the Ganga, we propose a holistic ecological risk assessment that includes population-level risk assessment at each critical habitat to evaluate the long-term effects of multiple stressors on aquatic populations.

5.1 Heavy Metals

Contamination status of *Heavy Metals* in Ganga River and five zones

A summary of descriptive analysis of the nine target heavy metals detected in the Ganga River is presented in Figure 2.41. The total heavy metal (Σ HM) concentration in water in the post-monsoon season ranged from **BDL to 9135.9 ug/l (Mean: 2740.38 ug/l and Median: 2694.1 ug/l)**. In the post-winter season Σ HM concentration ranged from **BDL to 25890.1 ug/l (Mean: 2390.97 ug/l and Median 592.89 ug/l)**. The Σ HM concentrations were higher in post-monsoon than the post-winter season.

Metals can accumulate in sediments which acts as a sink, or be released from sediments, acting as a source back to overlying water via natural or anthropogenic disturbance. The concentrations of **heavy metals in soil samples were in the range of 7953.2 mg/kg to 39770.5 mg/kg (Mean: 21332.0 and Median 21658.4)** in post-monsoon season and **6488.9 mg/kg to 38885.6 mg/kg (Mean: 18340.2 and Median: 16586.1)** in the post-winter season. The heavy metals often occur as cations and have high affinity towards the soil matrix therefore as compared to water samples, the detection frequencies metals were higher in soil samples.

The detection frequencies (Figure 2.42a) of heavy metals, in water, were in the range of BDL-95% in both the seasons. For sediment samples, the detection frequencies were in the BDL-100% for both the seasons. Fe and Zn were recorded with highest concentration as well as frequency in both the seasons as well as matrix (water and soil). These are naturally occurring abundant elements therefore their higher detection frequencies and levels could be due to dominance of chemical weathering and higher erosion in the catchment area. The lower detection rate and relatively low concentrations of highly toxic metals such Cadmium and Lead in sediment and water samples, could be attributed to their relatively low solubility (water) and lower usage. The seasonal variation in distribution of heavy metals in water and sediments samples of the Ganga River are presented in Figures 2.41a and 2.41b.

Zone-wise and seasonal pollution gradient of heavy metals in surface water and sediments are presented in Figure.2.43a and 2.43b

Figure 2.41a: Seasonal variation in distribution of heavy metals in surface water

For post-monsoon season, heavy metals concentration followed the order as $Fe > Zn > Cu > Cr > Ni$ whereas other metals namely Pb, Cd, As, and Hg were below the detection limits (BDL). In post-winter season, heavy metals concentration followed the order as $Fe > Zn > Cr > Pb > Ni > Cu > As$ whereas other metals namely Cd, and Hg were BDL.

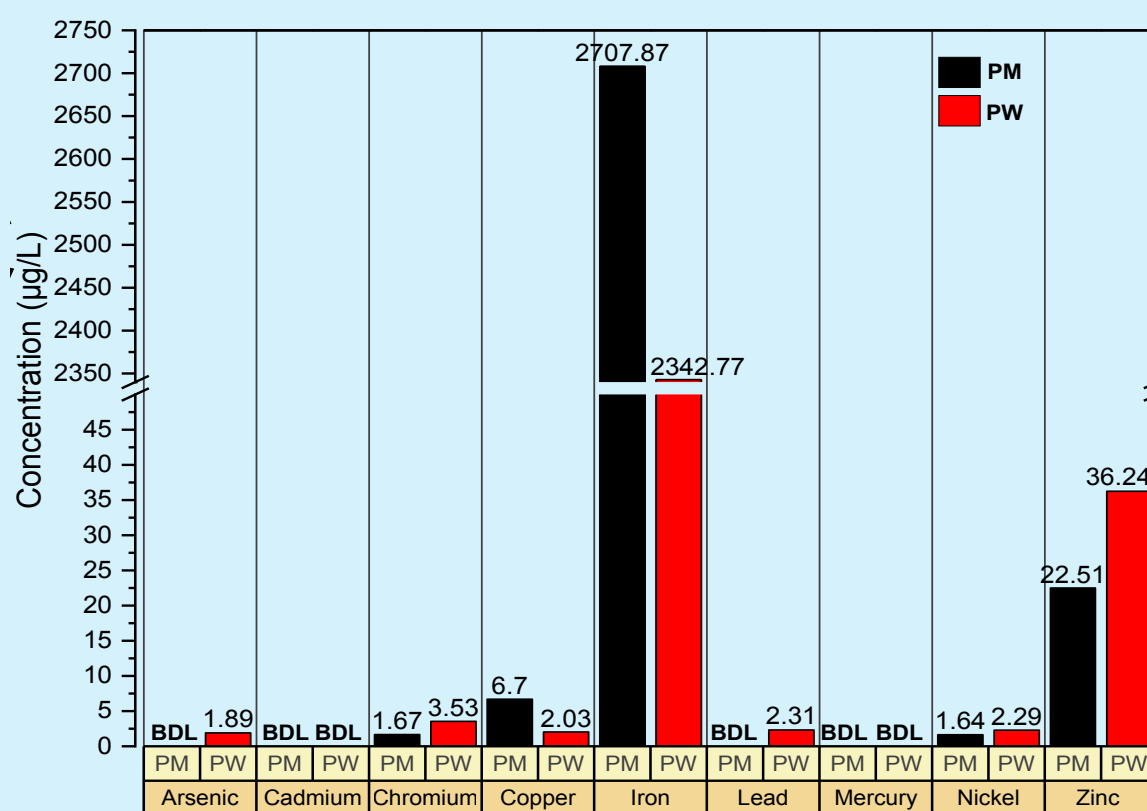


Figure 2.41b: Seasonal variation in distribution of heavy metals in surface sediments

For post-monsoon season, heavy metals concentration followed the order as $Fe > Cr > Zn > Ni > Pb > Cu > As > Cd$ whereas in post-winter season, heavy metals concentration followed the order as $Fe > Cr > Zn > Ni > Cu > Pb > As > Cd$. For both the seasons the Hg concentrations were BDL.

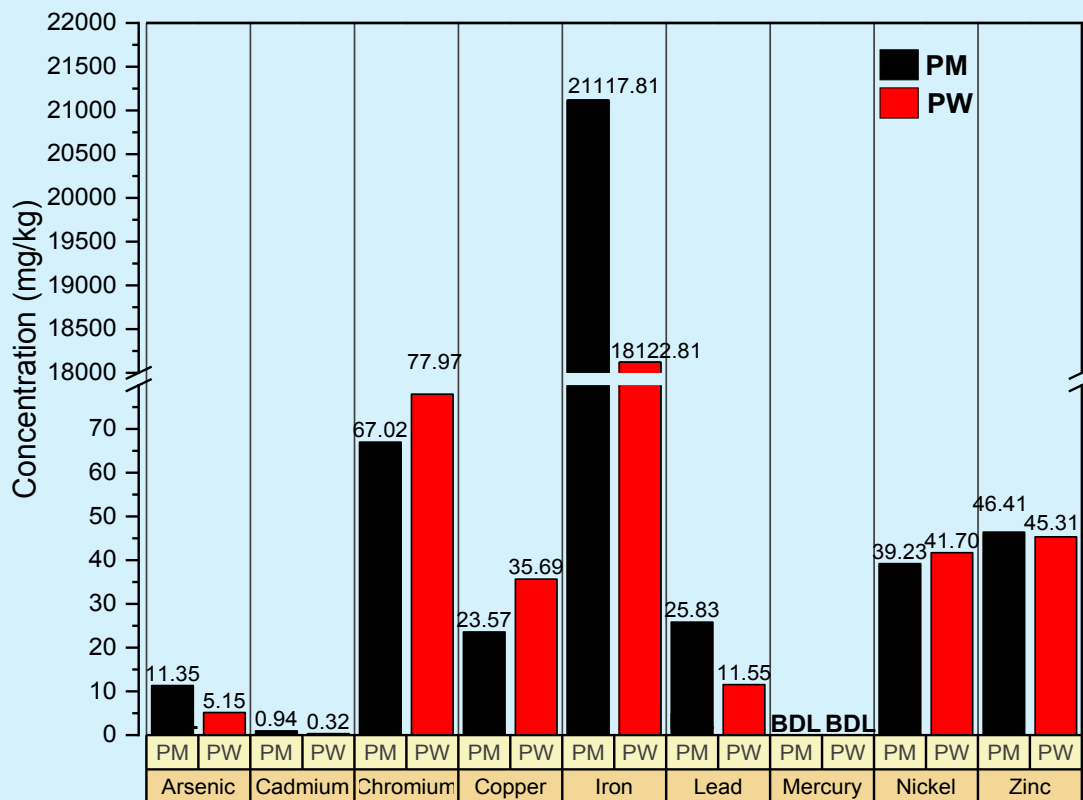


Figure 2.42a: Most frequently detected heavy metals in surface water

The most frequently detected heavy metals, for both the seasons, are Fe, Zn, Cu, Cr, and, Ni. In the dry season (post-winter) presence of other heavy metals such as Arsenic, and lead (Pb) are also highlighted due to low dilution. The least detection rate (BDL), in both seasons, were observed for Cd, Hg, and Pb.

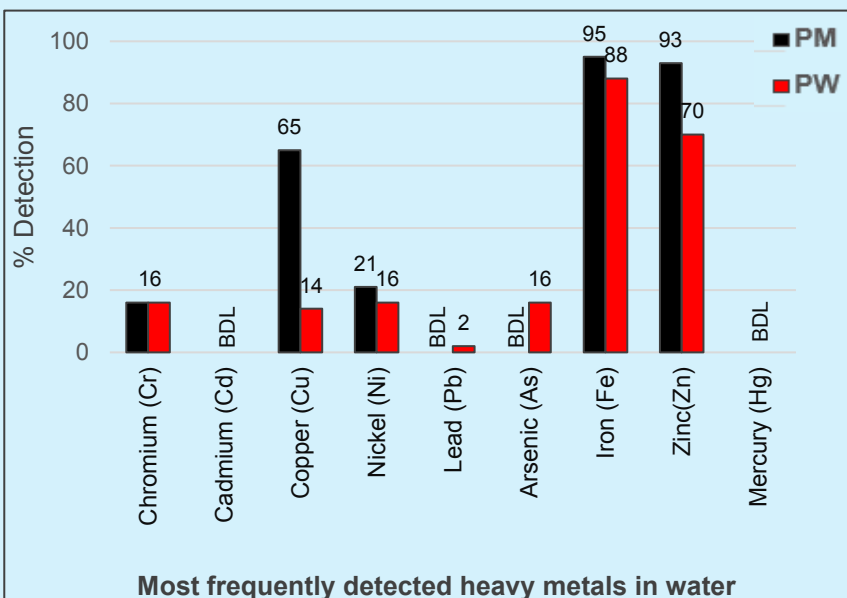
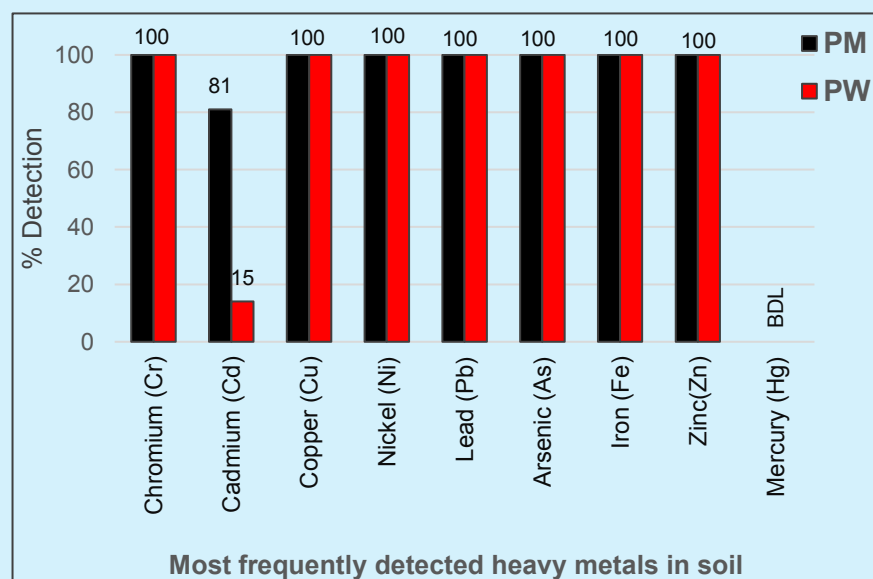


Figure 2.42b: Most frequently detected heavy metals in surface sediments

Detection frequencies for Fe, Zn, Cu, Cr, As, and, Ni are 100% for both seasons. The least detection rate (BDL), in both seasons, were observed for Cd (81% in post-monsoon and 14% in post-winter) and, whereas Hg was BDL (Below Detection Limits) for both the seasons.



SURFACE WATER

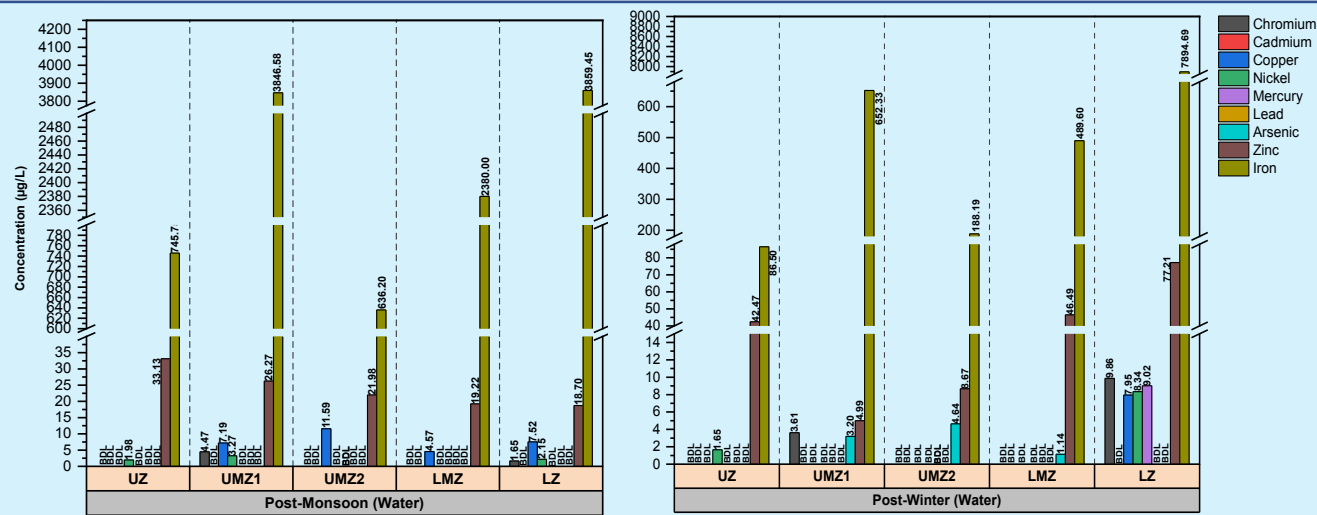


Figure 2.43a: Zone-wise and seasonal pollution gradient of heavy metals in surface water

LZ (representing state of West Bengal) is identified as the most contaminated zone followed by UMZ in both the season. The reason could be the presence of industries in these zones.

SEDIMENTS

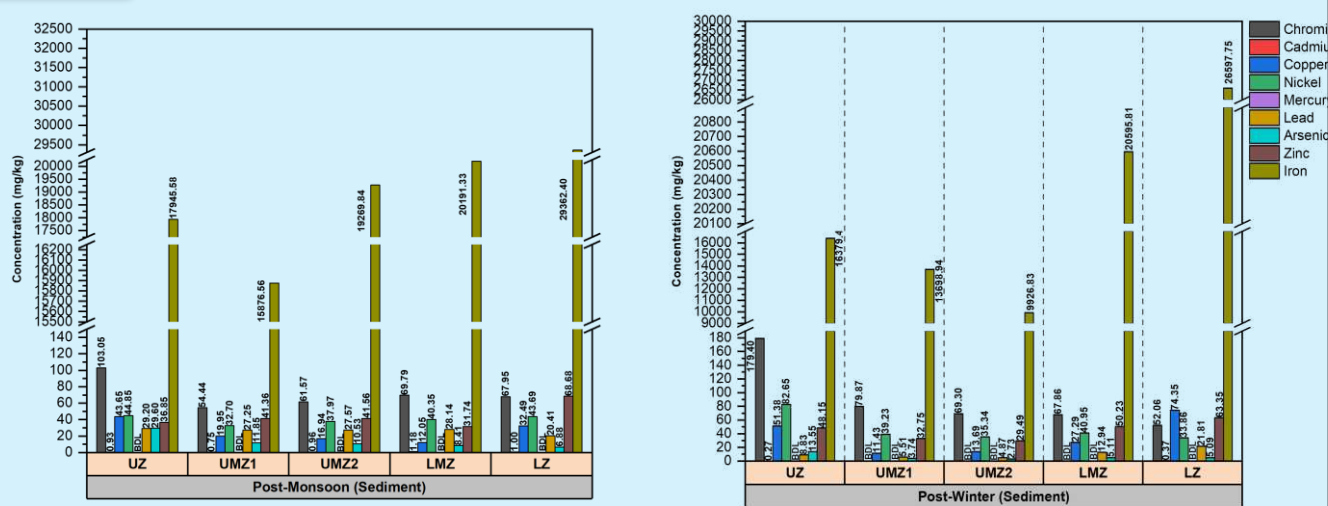


Figure 2.43b: Zone-wise and seasonal pollution gradient of heavy metals in surface sediment

LZ (representing state of West Bengal) is identified as the most contaminated zone followed by UMZ.

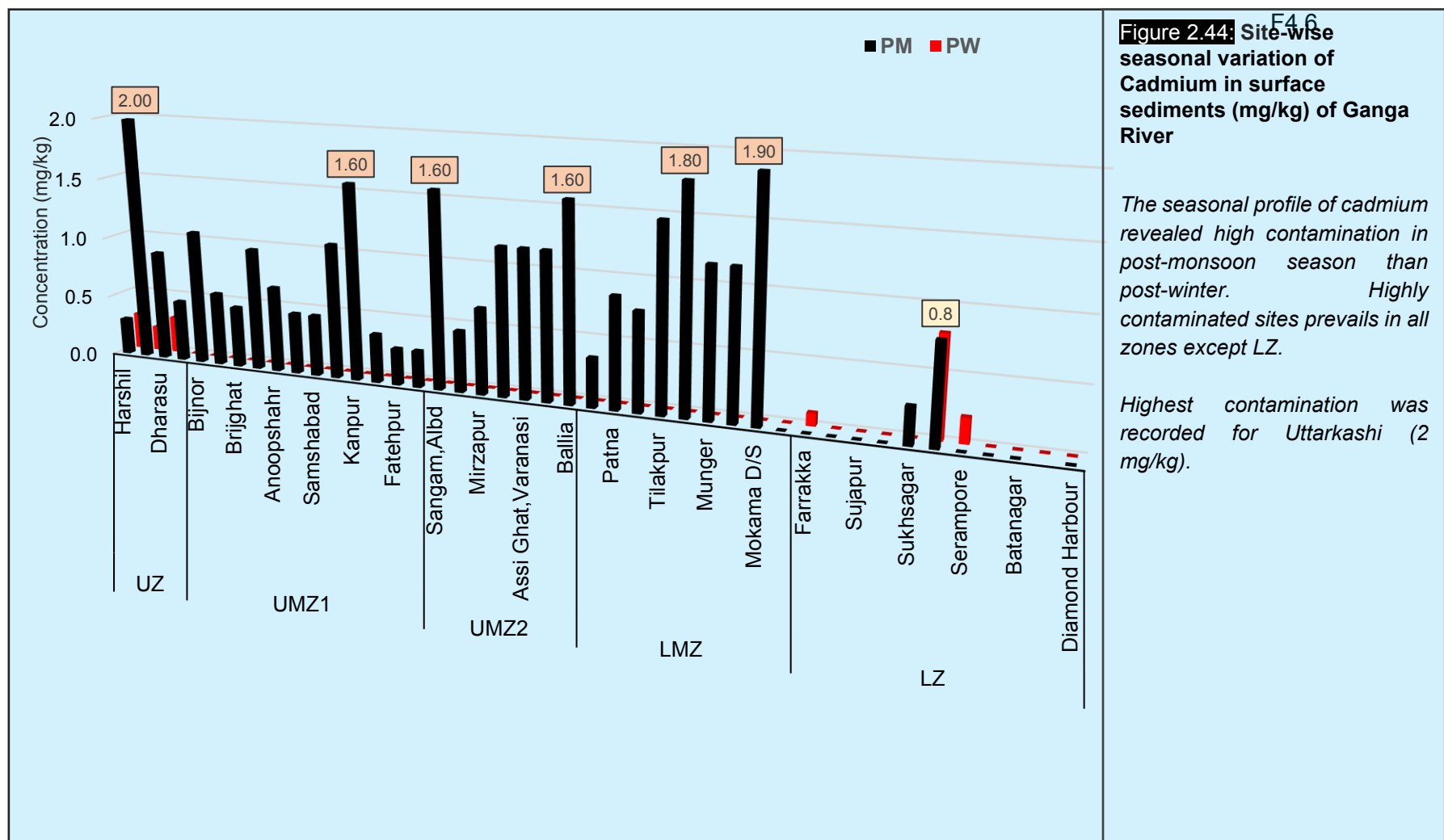
In addition, the high levels of heavy metals recorded in relatively pristine UZ could be attributed to geochemical cycling and dispersion of rocks and soils in upper Bhagirathi and Alaknanda catchment

5.1.1 Individual abundance of Heavy metals in each zone

1. *Cadmium*

The cadmium levels in water samples, for both the seasons, were below detection limits (BDL) of analytical method.

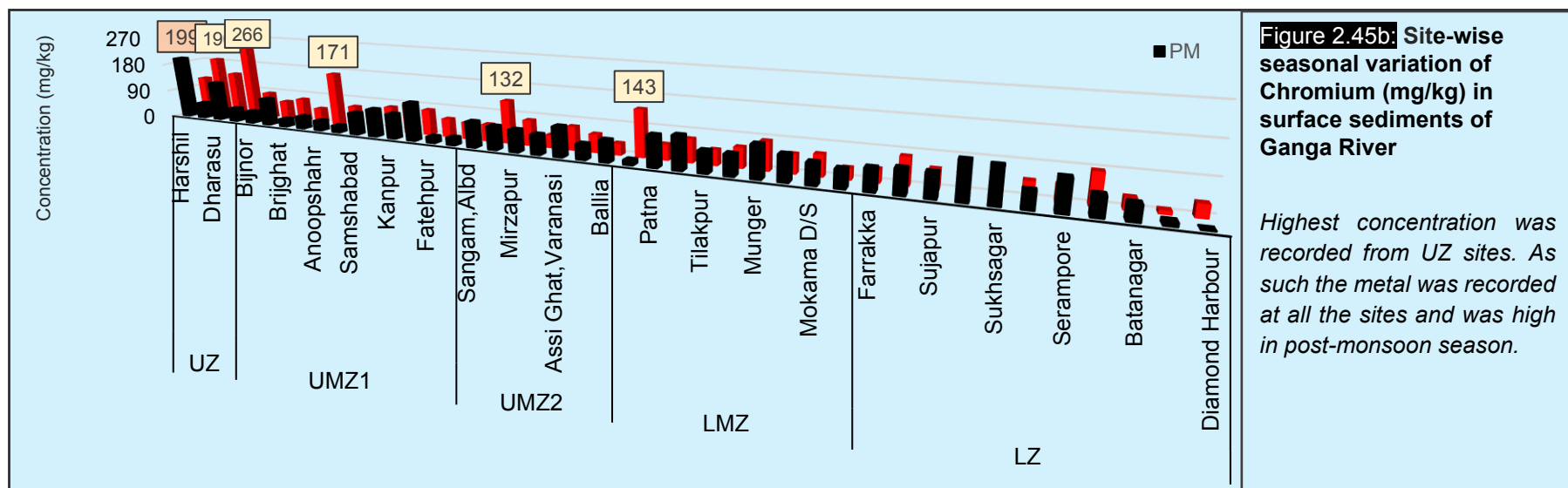
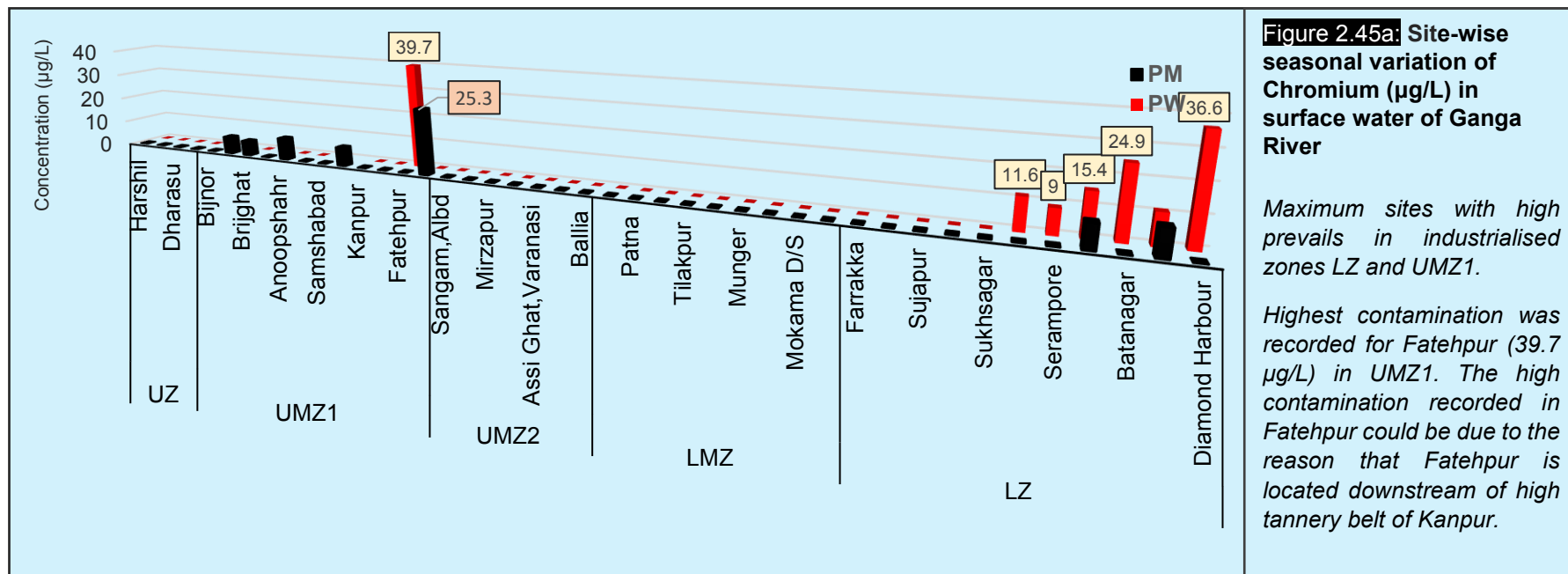
In sediment samples, the concentration of Cadmium in the post-monsoon season was 0.3 - 2 mg/kg with highest concentration observed at Uttarkashi followed by Hashimpur, *Mokama upstream, Kanpur and Tela (Figure 2.44 a). For post-winter the concentration ranges from 0.1 -0.8 mg/kg having high concentration recorded in Garden reach, Harshil, Dharasu, Uttarkashi and Batanagar (Figure 2.44a). The distribution of cadmium in sediment across zones (Figure 2.44a) during post monsoon season showed the order as LMZ (1.2mg/kg) > LZ = ~UMZ2 (1 mg/kg) > UZ (0.9 mg/kg) >UMZ1 (0.8 mg/kg). In post winter season it was LZ (0.4 mg/kg)>UZ (0.3 mg/kg). In other zones, Cadmium was BDL in post-winter.



2. Chromium

In water samples, chromium concentration ranged from BDL-25.3 µg/L in post-monsoon recording highest concentration at Rasoolabad, Allahabad and Falta (Figure 2.45a). Whereas, for post winter the concentration ranges from BDL-39.7 µg/L with high concentrations recorded at Fatehpur, Diamond Harbour and Batanagar (Figure 2.45a). In the present study, the distribution of chromium, in water samples, across zones (Figure 2.45a) showed the order as UMZ1(4.47 µg/L)>LZ(1.65µg/L)>UMZ2(BDL)=UZ(BDL)=LMZ(BDL) in post-monsoon and LZ(9.86µg/L)>UMZ1(3.61)> UMZ2(BDL) = UZ(BDL) = LMZ(BDL) in post-winter.

In sediment samples, the concentrations ranged from 13.3 mg/kg to 198.9 mg/kg in post-monsoon season (highest concentrations at Harshil, Dharasu and Fatehpur) and 32.9 mg/kg to 266 mg/kg in post-winter season (highest concentration at Rishikesh, Uttarkashi and Anoopshahr downstream) (Figure 2.45b). The distribution of chromium across zones (Figure 2.45b) showed the order as UZ(103.1mg/kg)>LMZ(69.79 mg/kg)>LZ(67.9 mg/kg)>UMZ2(61.6mg/kg)>UMZ1(51.3 mg/kg) in post-monsoon and UZ(179.4 mg/kg)>UMZ1(79.9 mg/kg)>UMZ2(69.3 mg/kg)>LMZ(67.9 mg/kg)>LZ(52.1 mg/kg).



3. Copper

The concentration of copper (Cu) in water samples ranged from BDL-66.2 µg/L in post-monsoon, whereas for post winter the concentration ranges from BDL-24.2 µg/L. The distribution of Cu across zones (Figure 2.46 a) showed the order as UMZ2 (11.59µg/L)>LZ (7.52µg/L)>UMZ1(7.19 µg/L)>LMZ(4.2 µg/L)>UZ (BDL) in post-monsoon whereas in post-winter Cu was detected only in LZ(7.95 µg/L) only. Highest concentration was detected at Tela, Tigrighat and Rasoolabad (Allahabad) in post-monsoon season while in post-winter, highest concentration was recorded at Diamond Harbour, Batanagar and Garden reach from LZ (Figure 2.46 a).

In sediment samples, the distribution of copper across zones (Figure 2.46 b) showed the order as UZ (43.7 mg/kg)>LZ (32.5 mg/kg) > UMZ1 (18.7 mg/kg) >UMZ2(16.9 mg/kg)>LMZ (11.7 mg/kg) in post-monsoon and LZ(74.3 mg/kg)>UZ (51.4 mg/kg) > LMZ(27.3 mg/kg) >UMZ2(13.7 mg/kg)> UMZ1 (11.4 mg/kg) in post-winter. The sites with highest concentrations in sediment samples belonged to Rishikesh (126 mg/kg) in post-monsoon and Sukhsagar (229.9 mg/kg) in post-winter season (Figure 2.46 b).

Figure 2.46a: Site-wise seasonal variation of Copper in surface water of Ganga River

Highest contamination and detection frequency were observed in UMZ1 and LZ (Tribeni-Diamond Harbour).
Highest contamination was recorded for Bhadoi (66.2 µg/L) in UMZ2.

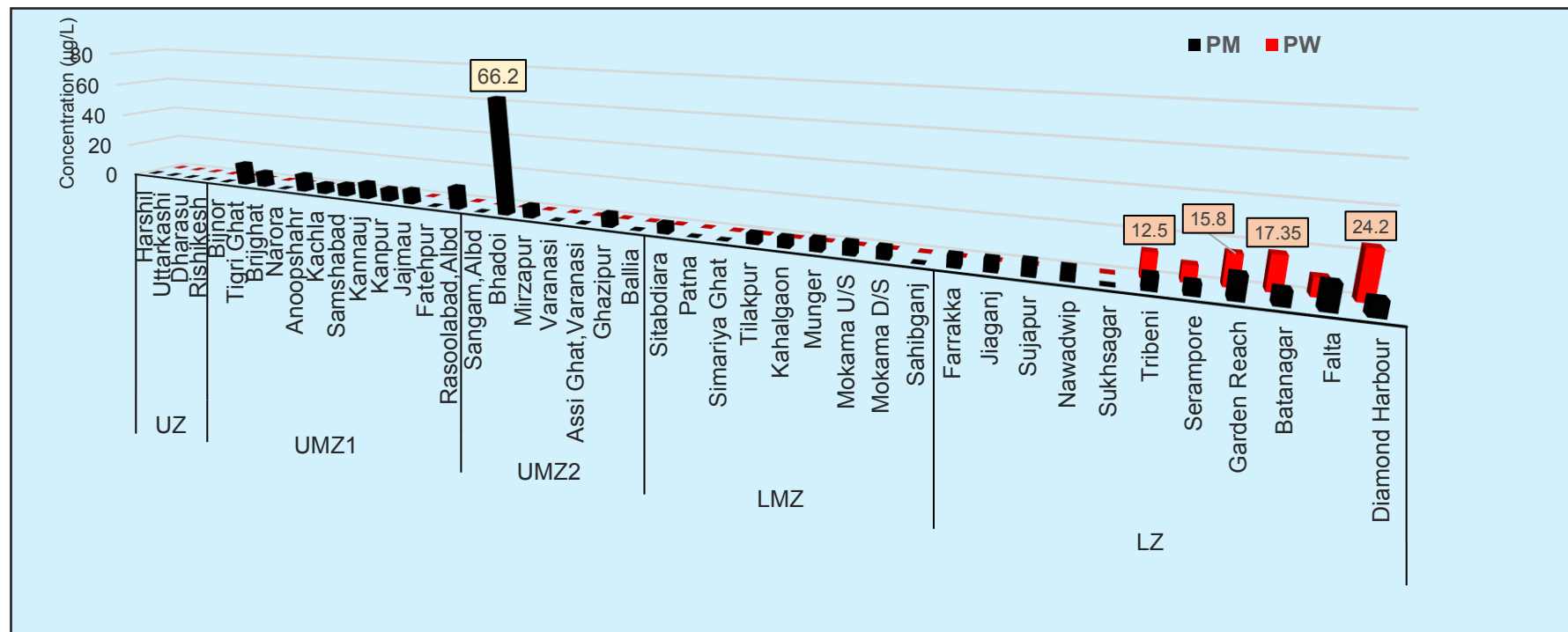
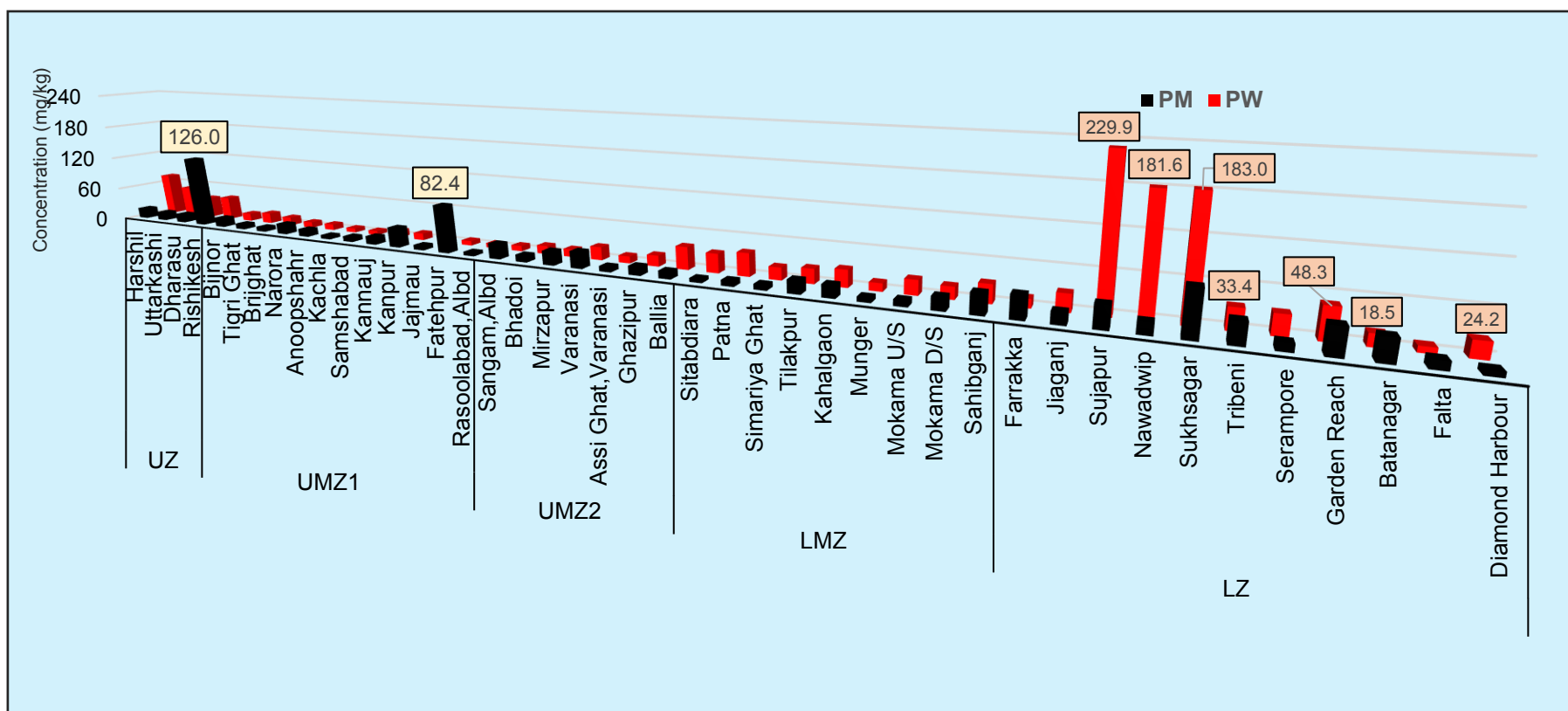


Figure 2.46b: Site-wise seasonal variation of Copper (mg/kg) in surface sediments of Ganga River

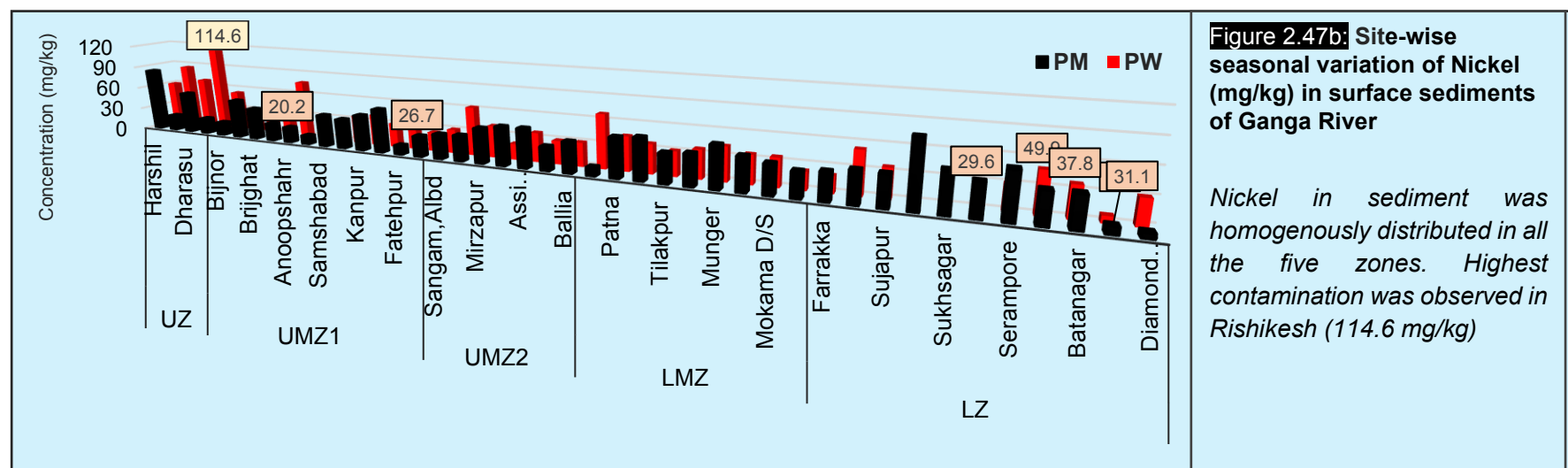
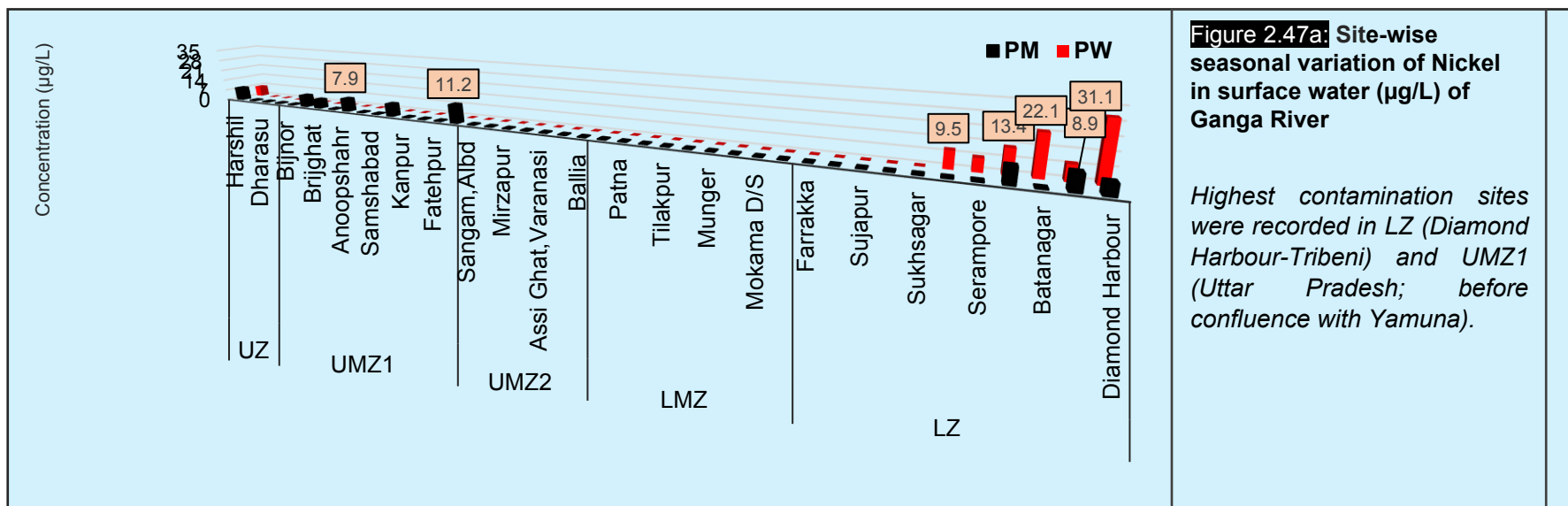
*Highest contamination and detection frequency were observed in LZ (particularly Sujapur-Diamond Harbour).
Highest contamination was recorded for Sukhsagar (229.9 mg/kg)*



4. Nickel

The Nickel (Ni) concentration, in water samples, for post-monsoon season was BDL-11.2 µg/L whereas for post winter the concentration ranges from BDL-31.1 µg/L. The distribution of nickel across zones, in post-monsoon, showed the distribution pattern as UMZ1 (3.27µg/L)>LZ (2.15µg/L)>UZ (1.98µg/L) whereas in UMZ2 and LMZ nickel concentrations were below the method detection limits (Figure 2.47a). In post-winter, the distribution pattern of nickel was recorded as follows: LZ (8.34µg/L)>UZ (1.65µg/L) whereas in UMZ1, UMZ2 and LMZ nickel concentrations were below the method detection limits. Highest concentration was recorded at sites namely Rasoolabad (Allahabad), Falta and Garden reach in post-monsoon and Diamond Harbour, Batanagar and Garden Reach in post-winter

In sediment samples, the distribution of nickel across zones showed the spatial pattern as UZ(44.9 mg/kg)>LZ (43.7 mg/kg) > LMZ(41.5 mg/kg) >UMZ2(38.0 mg/kg)>UMZ1 (31 mg/kg) in post-monsoon and UZ(82.7 mg/kg)>LMZ (40.1 mg/kg) > UMZ1(39.9 mg/kg) >UMZ2(35.3 mg/kg)>LZ (33.9 mg/kg) in post-winter (Figure 2.47 b). The top sites contaminated with Nickel were Harshil, Tribeni, Fatehpur and Batanagar in post-monsoon and mostly UZ sites - Rishikesh, Uttarkashi, Dharasu and Anoopshahr in post-winter.



5. Lead

The lead levels in water samples, for both the seasons, were below the method detection limits (BDL) except one site I LZ i.e. Diamond Harbour which recorded 99.2 µg/L of Lead in post-winter season.

6. Arsenic

Arsenic (As) concentration, in water samples, in in the post-monsoon season was below the method detection limit whereas for post winter the concentration ranges from BDL-15.09 µg/L (Figure 2.48a). Highest concentration was recorded at Fatehpur (15.09 µg/L), followed by Kachla, Varanasi, Ghazipur and Rasoolabad (Allahabad) all of which belonged to UMZ in Uttar Pradesh (Figure 2.48a) .The zone-wise distribution of arsenic in post-winter season is recorded as UMZ2 (4.64 µg/L) > UMZ1 (3.20 µg/L)> LMZ (1.14µg/L). In UZ and LZ, arsenic concentrations were below method detection limits.

In sediment samples, the arsenic concentration in the post-monsoon season was 2.4 mg/kg - 70.6 mg/kg whereas for post winter the concentration ranges from 1.7 mg/kg -27.7 mg/kg (Figure 2.48b). The distribution of arsenic in post-monsoon season across zones showed the order as UZ (29.6 mg/kg) >UMZ1 (11.8 mg/kg)> UMZ2 (10.5 mg/kg) >LMZ (8.4 mg/kg) > LZ (6.9 mg/kg) and in the post-winter season it followed the order as UZ (13.6 mg/kg) > LZ (5.1 mg/kg) >LMZ (5 mg/kg) >UMZ1 (3.7 mg/kg)> UMZ2 (2.7 mg/kg) (Figure 2.48b). The sites with highest contamination were from UZ in both the seasons which signifies the natural and geogenic origin of the metal in Himalayas.

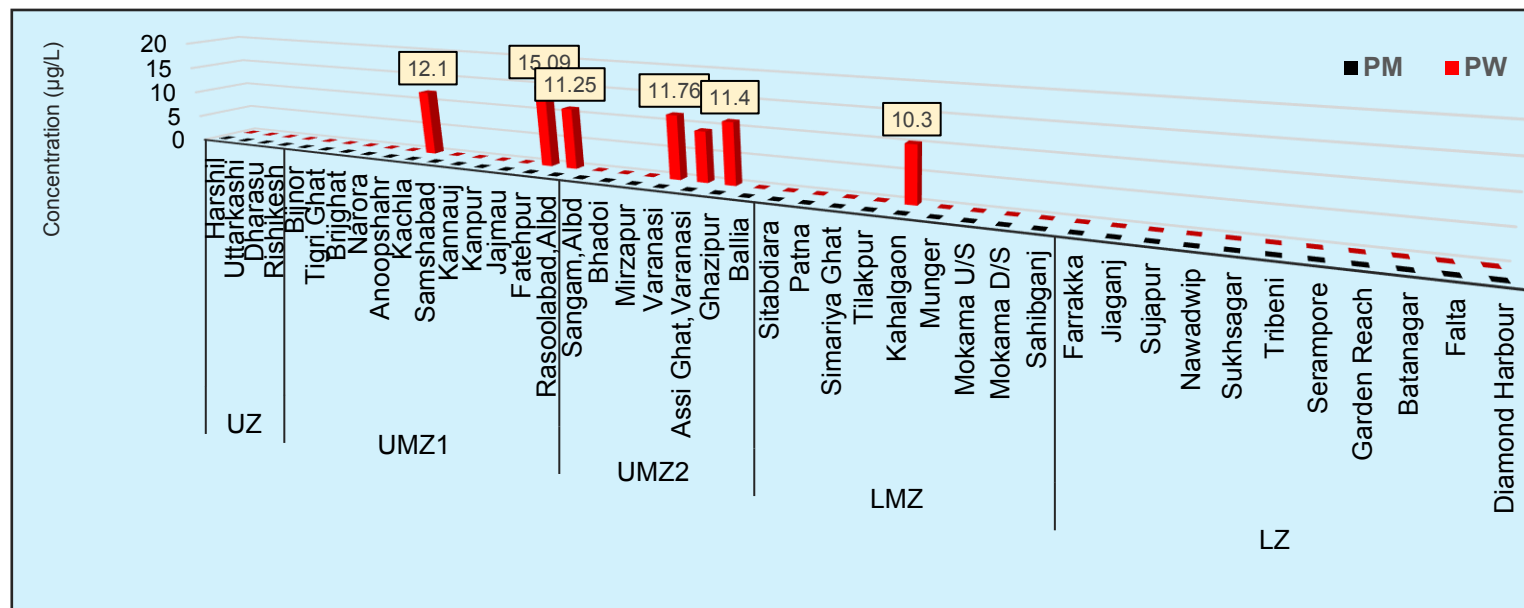


Figure 2.48a: Site-wise seasonal variation of Arsenic (µg/L) in surface water of Ganga River

High contamination recorded in the UMZ and at one site in LMZ (Kahalgaon).

Highest contamination was recorded at Fatehpur (15.1 µg/L)

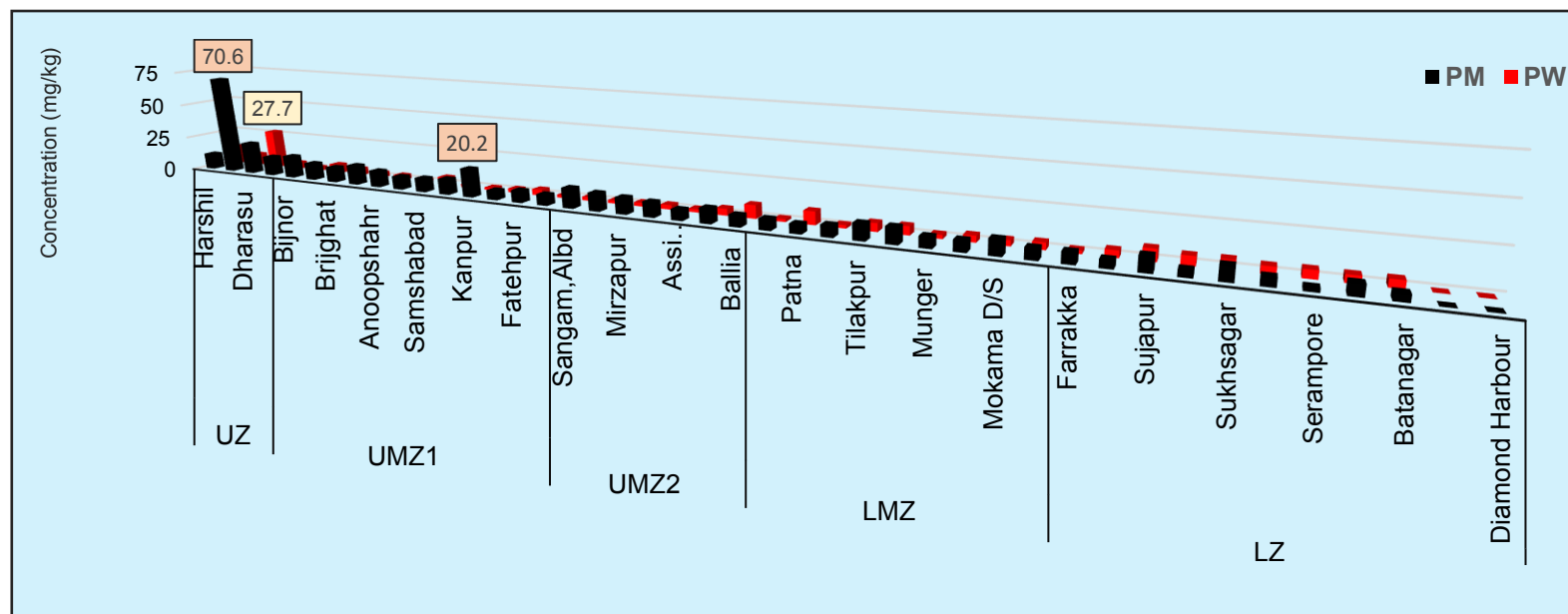


Figure 2.48b: Site-wise seasonal variation of Arsenic (mg/kg) in surface sediments of Ganga River

Highest contamination sites prevails in UZ and UMZ. Highest contamination was recorded at Uttarkashi (70.6 mg/kg)

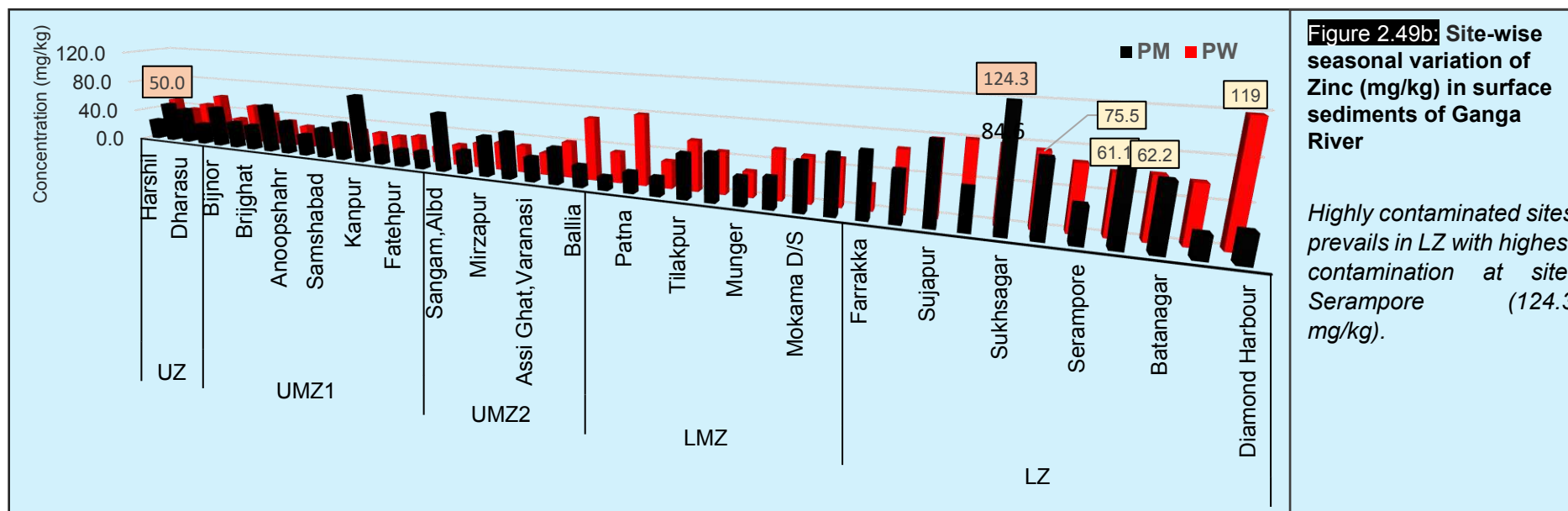
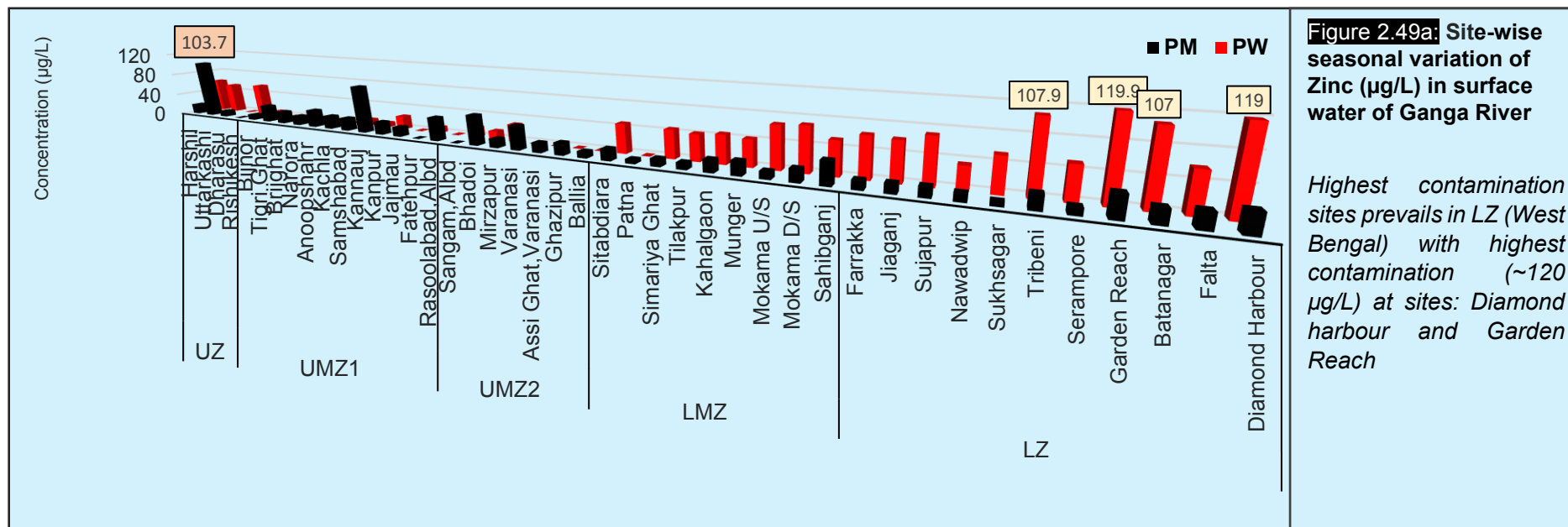
7. Mercury

The mercury levels in water and sediments samples, for both the seasons, were below the method detection limits (BDL).

8. Zinc

Zinc is an abundant and highly essential element (micronutrient) required for flora and fauna. The zinc concentration, in surface water of Ganga River, for post-monsoon season was BDL-103.7 µg/L whereas for post winter the concentration ranges from BDL-119.9 µg/L (Figure 2.49a). The distribution of zinc across zones, in post-monsoon, showed the pattern as UZ (33.125 µg/L) > UMZ1 (26.27 µg/L) > UMZ2 (21.98 µg/L) > LMZ (19.22 µg/L) > LZ (18.70 µg/L) whereas in post-winter, the distribution was as follows: LZ (77.21 µg/L) > LMZ (46.49 µg/L) > UZ (42.47 µg/L) > UMZ2 (8.67 µg/L) > UMZ1 (4.99 µg/L). Uttarakhand, Kannauj and Tela recorded highest concentrations for Zinc in post-monsoon and Sites from LZ (Garden Reach, Diamond Harbour, Tribeni, Batanagar) recorded highest concentration in post-winter season.

In sediment samples, the zinc concentration in the post-monsoon season was 15.5 -124.3 mg/kg whereas for post winter the concentration ranges from 20.1 mg/kg -80.5 mg/kg (Figure 2.49 b). The spatial distribution of zinc across zones (Figure 2.49b) was as LZ (68.68 mg/kg) > UMZ2 (41.56 mg/kg) > UMZ1 (41.36 mg/kg) > UZ (36.85 mg/kg) > LMZ (31.74 mg/kg) in post-monsoon season. In the post-winter season it was LZ (63.4 mg/kg) > LMZ (50.2 mg/kg) > UZ (48.2 mg/kg) > UMZ1 (32.7 mg/kg) > UMZ2 (29.5 mg/kg). Serampore, Sukhsagar, Kanpur and Falta recorded highest Zinc concentration in post-monsoon season, while Tribeni, Simariya Ghat, Sukhsagar and Serampore recorded highest concentration during post-winter season.



9. Iron

Iron is also one of the highly abundant and essential elements for humans, as well as fauna and flora. In the present study, the iron concentration in the post-monsoon season was BDL-9046 µg/L whereas for post winter the concentration ranges from BDL - 25580 µg/L (Figure 2.50a). The distribution of iron across zones (Figure 2.50a), in post-monsoon, showed the distribution pattern as LZ (3859.49µg/L)> UMZ1 (3846.58 µg/L)> LMZ (2380 µg/L)> UZ (745.75 µg/L)> UMZ2 (636.20 µg/L). In post-winter, the distribution was recorded as follows LZ (7894.69µg/L)> UMZ1 (652.33 µg/L)> LMZ (489.60 µg/L)> UMZ2 (188.19 µg/L)> UZ (86.50 µg/L). Highest contamination between both the seasons was recorded at Diamond Harbour (25580 µg/L).

In sediment samples, the iron concentration in the post-monsoon season was 7589.5 mg/kg - 39514.7 mg/kg whereas for post winter the concentration ranges from 6378 mg/kg - 38527 mg/kg (Figure 2.50b). The distribution of iron across zones showed was as LZ (29362.4 mg/kg) >LMZ (20191.3 mg/kg)>UMZ2 (19269.8 mg/kg) >UZ (17945.6 mg/kg)> UMZ1 (15378.3 mg/kg) in post-monsoon and LZ (26597.7 mg/kg) >LMZ (20595.8mg/kg) >UZ (16379.4 mg/kg)>UMZ1 (13698.9 mg/kg) UMZ2 (9926.8 mg/kg) in post-winter. Sukhsagar recorded highest contamination (39514.7 mg/kg) between both the seasons (Figure 2.50b).

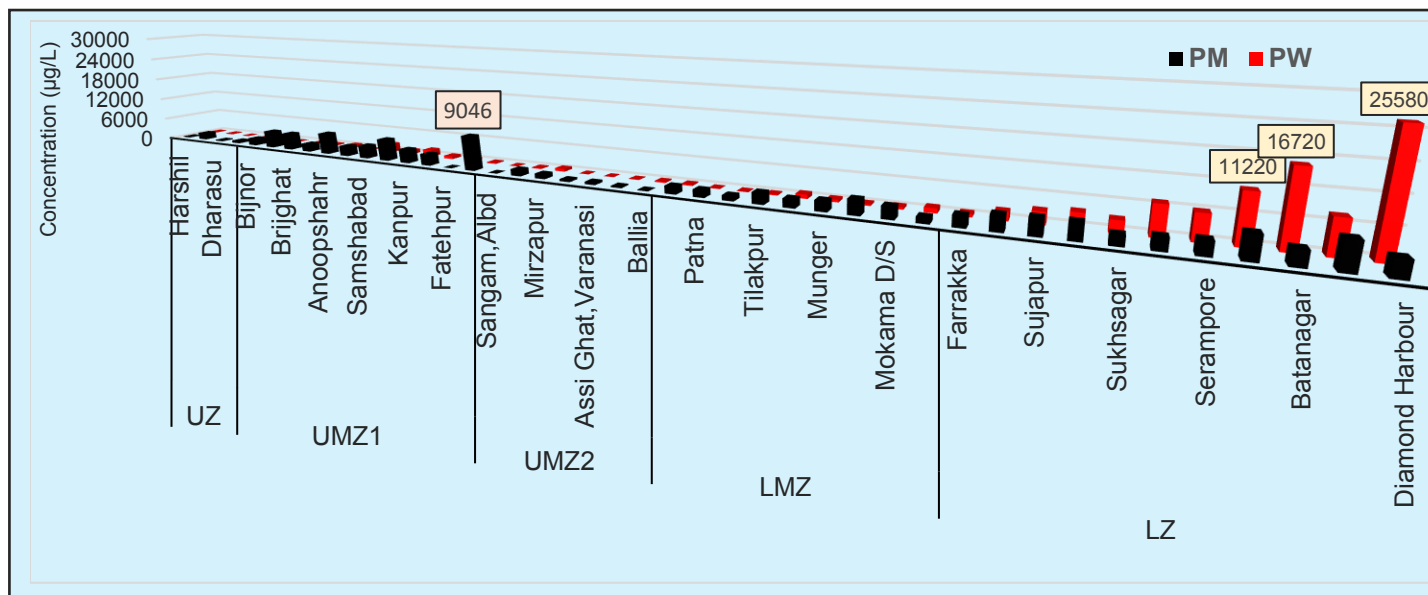


Figure 2.50a: Site-wise seasonal variation of Iron (µg/L) in surface water of Ganga River

Highest contamination and detection frequency were recorded for LZ followed by the UMZ1 (Uttar Pradesh; before confluence with Yamuna). The highest iron contamination was recorded for Diamond Harbour (25580 µg/L) and Batanagar (16720 µg/L) in LZ.

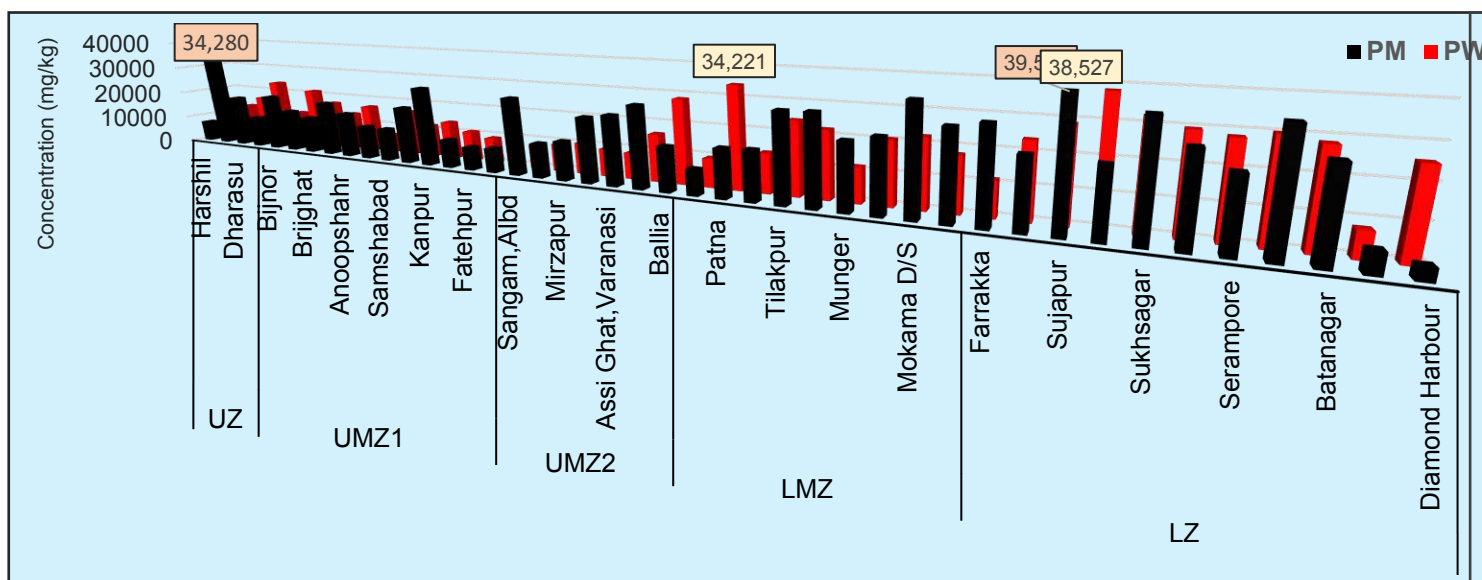


Figure 2.50b: Site-wise seasonal variation of Iron (mg/kg) in surface sediments of Ganga River

Homogenous distribution at all the sites in both the seasons observed. Highest contaminated sites prevails in LMZ and LZ.

5.1.2. Indices of heavy metal pollution

Pollution indices seem to be promising and beneficial in assessing the metal enrichment and/or contamination in the water-sediment quality, identify metal concentrations of environmental concerns and describe the contamination adverse effects (Ridgway and Shimmield 2002). For present investigation, heavy metal contamination in surface water and sediments was evaluated by using geo-accumulation index (I_{geo}) and pollution load index (PLI).

5.1.2.1. Geoaccumulation index (I_{geo})

The geoaccumulation index (I_{geo}) introduced by G. Muller (Muller, 1969) was used as a reference of estimating the extent of metal pollution. Geoaccumulation indexes for the metals were determined using Muller's expression:

$$I_{geo} = \text{Log}_2 (C_n)/1.5(B_n)$$

Where C_n is the concentration of metals (n) examined in soil samples and B_n is the geochemical background concentration of the same metal. Factor 1.5 is the background matrix correction factor due to lithospheric effects. The geoaccumulation index consists of seven grades or classes as presented in Table 2.1.

Table 2.1: Grading of I_{geo} values

I _{geo}	Levels	Pollution degree
<0	0	Unpolluted
0–1	1	Unpolluted to moderately polluted
1–2	2	Moderately polluted
2–3	3	Moderately to heavily polluted
3–4	4	Heavily polluted
4–5	5	Heavily to extremely polluted
>5	6	Extremely polluted

The I_{geo} values (Table 2.2), for post-monsoon in all zones for Cr, Cu, Ni, Fe, and Zn is estimated to be less than zero, suggesting that the area is not polluted by these metals. In

contrast, the Igeo values for Cd, reveals moderate pollution at all zones, indicating its significant accumulation in the sediments of the Ganga River. For Pb, the Igeo values in all zones except LZ indicate unpolluted to moderate pollution (Igeo 0-1). For As, the Igeo indicated moderate pollution in UZ and unpolluted to moderate pollution in UMZ1.

Table 2.2: Igeo for metals in different zones for post-monsoon

GEOACCUMULATION INDEX (Igeo)								
	Chromium	Cadmium	Copper	Nickel	Lead	Arsenic	Iron	Zinc
UZ	-0.048	1.624	-0.137	- 0.713	0.283	1.321	-1.585	-2.370
UMZ1	-0.613	1.429	-0.811	- 1.010	0.215	0.554	-1.704	-2.253
UMZ2	-0.791	1.674	-1.502	- 0.953	0.200	-0.171	-1.483	-2.197
LMZ	-0.610	1.970	-1.994	- 0.865	0.229	-0.494	-1.415	-2.586
LZ	-0.648	1.737	-0.563	- 0.750	-0.234	-0.784	-0.875	-1.472

In post-winter, the Igeo values for the target metals (Table 2.3), in all zones for Pb, Zn, and Fe is estimated to be less than zero, suggesting that these metals do not contribute to metal pollution in these zones. Out of all the zones UZ showed relatively high pollution (unpolluted to moderate pollution) due to Cr, Cu, Ni, and As. In addition, UMZ1 also showed unpolluted to moderate pollution for Chromium. Similarly, LZ showed unpolluted to moderate pollution from Cadmium and Copper.

Table 2.3: Igeo for metals in different zones for post-winter

GEOACCUMULATION INDEX (Igeo)								
	Chromium	Cadmium	Copper	Nickel	Lead	Arsenic	Iron	Zinc
UZ	0.752	-0.170	0.098	0.169	-1.443	0.193	-1.717	-1.984
UMZ1	0.059	-0.170	-1.005	-0.477	-1.875	-0.801	-1.889	-2.343
UMZ2	-0.620	ND	-1.810	-1.056	-2.301	-2.119	-2.440	-2.692
LMZ	-0.650	ND	-0.815	-0.844	-0.891	-1.213	-1.387	-1.923
LZ	-1.033	0.290	0.631	-1.118	-0.138	-1.219	-1.018	-1.588

5.1.2.2. Pollution load index (PLI)

PLI provides a simple, relative means for assessing the extent of heavy metal pollution in a specific location/zone. The PLI values >1 (red color) indicates heavy metal pollution whereas <1 (green color) indicates no pollution.

It is calculated from contamination factor (CF) as follows:

$$CF = C_{\text{metal}}/C_{\text{baseline}}$$

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n)^{1/n}$$

n = no. of metals

The results (Table 2.4) showed that the sediments are contaminated with heavy metals in UZ in both the seasons and LZ in post-monsoon season only. The heavy metal contamination in UZ could be attributed to natural geogenic deposition whereas in LZ the heavy metal contamination is mainly of anthropogenic origin. In contrast, the PLI values for all the other zones namely UMZ1, UMZ2, and LMZ reveals no pollution from metals reported in this study.

Table 2.4: PLI values for metals in different zones for post-monsoon and post-winter

	POLLUTION LOAD INDEX (PLI)	
	Post-Monsoon	Post-Winter
UZ	1.27	1.01
UMZ1	0.91	0.57
UMZ2	0.96	0.51
LMZ	0.92	0.78
LZ	1.09	0.83

Overview of findings and Priorities for filling information gaps – Heavy Metals

Overview of findings

- The concentrations of most of the heavy metals, in water and sediment samples were higher in the **post-winter than in post-monsoon season**, which could be attributed to the low river flow and subsequently low dilution of heavy metals in dry season.
- Heavy metals concentrations in **water samples ranged from BDL-25580 µg/L**. Cadmium and Mercury concentrations were BDL in all the water samples.
- Heavy metals often occurs as cations and have high affinity towards the soil matrix therefore as compared to water samples, the detection frequencies metals were higher in soil samples. **In sediments, the heavy concentration ranged from 6488.9 to 39770.5 mg/kg**. Mercury concentrations were BDL in all the sediment samples.
- The most frequently detected heavy metals, were Iron>Zinc>Copper>Nickel>Chromium
- Fe and Zn are naturally occurring abundant elements therefore, there higher detection frequencies and levels could due to dominance of chemical weathering and higher erosion in the catchment area.
- Geoaccumulation index reveals low to moderate pollution in UZ followed by LZ.
- The high levels of heavy metals recorded in relatively pristine UZ, in sediment samples, could be due to geochemical cycling and dispersion of rocks and soils in upper Bhagirathi and Alaknanda catchment.

Priorities for filling information gaps

- Further studies are warranted to identify the potential sources of heavy metal contamination in Ganga River
- Monitoring of the drains along the river need to be taken up for the presence of heavy metals loads.
- We propose a holistic ecological risk assessment that includes population-level risk assessment at each critical habitat to evaluate the long-term effects of multiple stressors on aquatic populations.

6.1. PCB Contamination Profile

This section includes the results of selected PCB congeners that were detected in the soil samples from the Ganga over two seasons. The concentration of $\Sigma_{11}\text{PCB}$ was in the range from BDL-71.5 ng/g (Mean 12.09ng/g) in the post monsoon season and BDL – 84.76 ng/g (Mean 17.09 ng/g) in the post winter season.

Figure 2.51 shows the zone wise distribution of PCBs in post monsoon season. The mean concentration in this season ranged from BDL-26.47 ng/g and the zone wise distribution followed the pattern as **LMZ>UZ>LZ>UMZ2>UMZ1**. LMZ of Bihar and Jharkhand emerged as the most contaminated zone (32.15 ng/g) whereas UMZ1 recorded least contamination (1.85ng/g). The reason for higher concentration in LMZ could be attributed to open municipal dumping sites as a potential emission source of PCBs. PCBs have been used principally in electrical equipment (i.e. transformers that contain large quantities of PCBs fluids). In India, PCBs have been banned in transformers and capacitors since 1997. Old electrical equipment containing PCBs is believed to be the dominant source of PCB off gassing in urban areas (Breivik et al., 2002). The open dumping of e-waste as well as scrap processors handling the e-waste openly in this area may be leading to atmospheric deposits as well as run off of PCBs into the Ganga from this region.

In the post winter season (Figure 2.52) the mean PCB concentration ranged from BDL-28.79 ng/g and the distribution across the zones followed the following order **UMZ2>UMZ1>LMZ>LZ>UZ**. UMZ 2 was found to have highest contamination (Mean conc. 61.07 ng/g) followed by UMZ 1 (Mean conc. 26.21ng/g). UZ was recorded as the least contaminated zone with mean concentration of 0.25 ng/g of total PCBs. Both UMZ1 and UMZ2 in Uttar Pradesh have the highest number of industrial settlements as compared to any other state. Besides, the industrial pockets in the catchments of Ramganga and Kali tributaries and in Kanpur city are significant sources of industrial pollution. The city of Moradabad, located

on the banks of river Ramganga is now the largest e-waste hub in the country (CSE, 2015), as e-waste is brought there for recovery of metals such as copper and traces of silver and gold. Besides, scrap processors dealing in electronic waste scrap from multiple industries are present in both UMZ 1 and UMZ 2. The metal is recovered through unscientific dismantling, crude chemical leaching of printed circuit boards, burning of wires/waste electrical and electronic components, grinding of residue and washing of metal rich residue on the banks of the river. This eventually release/leach the PCBs present in the e-waste into the river stream. Among the congeners the following trend was observed in post monsoon season **PCB126> PCB 153>PCB 52> PCB105>PCB28>PCB 44>PCB 118> PCB 77> PCB 138> PCB 101> PCB 180**. Dominance of heavy congener PCB 126 (44.91 ng/g; 68%) support the view that combustion emission is the source of this congener (Lopez Garcia et al., 1996; Chi et al., 2007). Unscientific and open burning of e-waste near to the Ganga potentially contributes for higher proportion of this PCB in the Ganga. PCB126 (3,3',4,4',5-pentachlorobiphenyl) is considered the most toxic PCB congener, once its biological effects are comparable to those evoked by 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). In this regard, studies have clearly shown that chronic PCB126 exposure causes several toxic effects, including cancer development and impairment of liver, lung and cardiovascular functions (NTP, 2006)

In the post winter season the congeners showed the decreasing trend in the order **PCB 28 > PCB 52> PCB 44> PCB 101> PCB 77> PCB 118> PCB 153> PCB 105> PCB 138> PCB 126> PCB 180**. The dominance of PCB 28 (45%) and PCB 52 (41%), which are lighter congeners having 3 and 4 chlorine atoms implies that This implies that these congeners may be related to the wastewater from nearby paper mills and other industries such as dyeing, paint, insulators, flame retardants, paper mills (bleaching) etc. Also highly chlorinated PCBs could be decomposed to less-chlorinated PCBs by bacteria, fungi and other microorganisms. Furthermore, it is easier for less-chlorinated congeners to be transported over long distances (Wu et al. 2011; Chakraborty et al., 2016). Dominance of lighter tri and tetra PCBs has been

reported in other studies from India and abroad (Lai et al., 2015; Sharma et al., 2015; Baqar et al., 2017; Chakraborty et al., 2016)

Site-wise distribution of PCBs for post monsoon and post winter season is shown in Figure 2.53. As shown in Figure 2.53 Mokama upstream (U/S) site from UMZ2 in Uttar Pradesh recorded maximum \sum_{11} PCB contamination (82.45 ng/g), followed by Sultanganj (55.83 ng/g) in LZ, West Bengal, Sitabdera (43.77 ng/g), Tilakpur (37.58 ng/g) and Mokama downstream (36.96 ng/g) from UMZ 2 in Uttar Pradesh. Six out of top 10 PCB contaminated sites belonged to UMZ 2, two belonged to LZ and two were from UZ. The PCB 126 was the highest contributor at most of these sites.

In post winter (Figure 2.54) highest concentration for \sum_{11} PCB was recorded at Mirzapur (178.82 ng/g), followed by Sangam (122.94), Tela (97.41 ng/g) from UMZ 2 and Kanpur (64.78 ng/g) and Kannauj (62.83 ng/g) from UMZ 1 in Uttar Pradesh. All the top 10 contaminated sites belonged to Uttar Pradesh (5 each from UMZ 1 and UMZ 2 respectively). PCB 126 was the most detected congener at each of these sites followed by PCB 101.

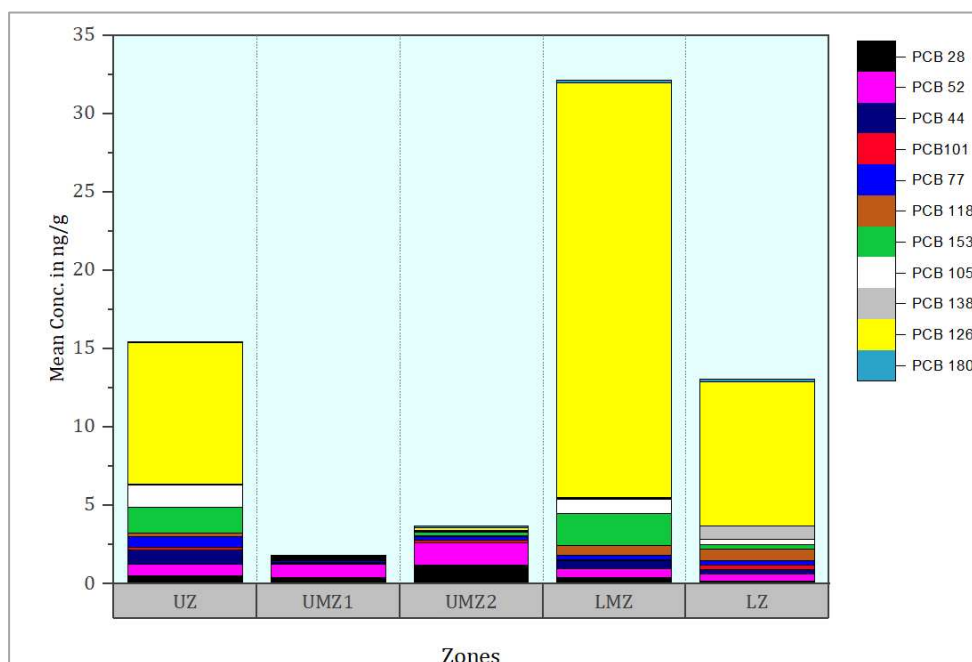


Figure 2.51. Zone wise distribution of PCB congeners in post-monsoon season

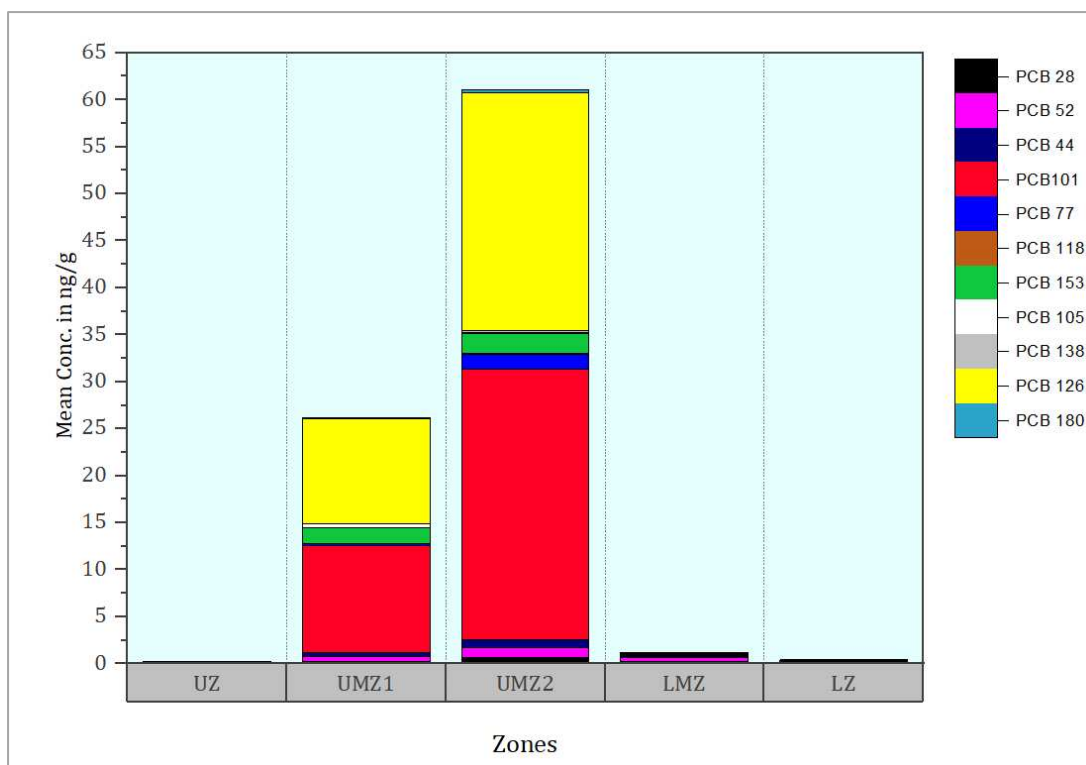


Figure 2.52: Zone wise distribution of PCB congeners in post-winter season

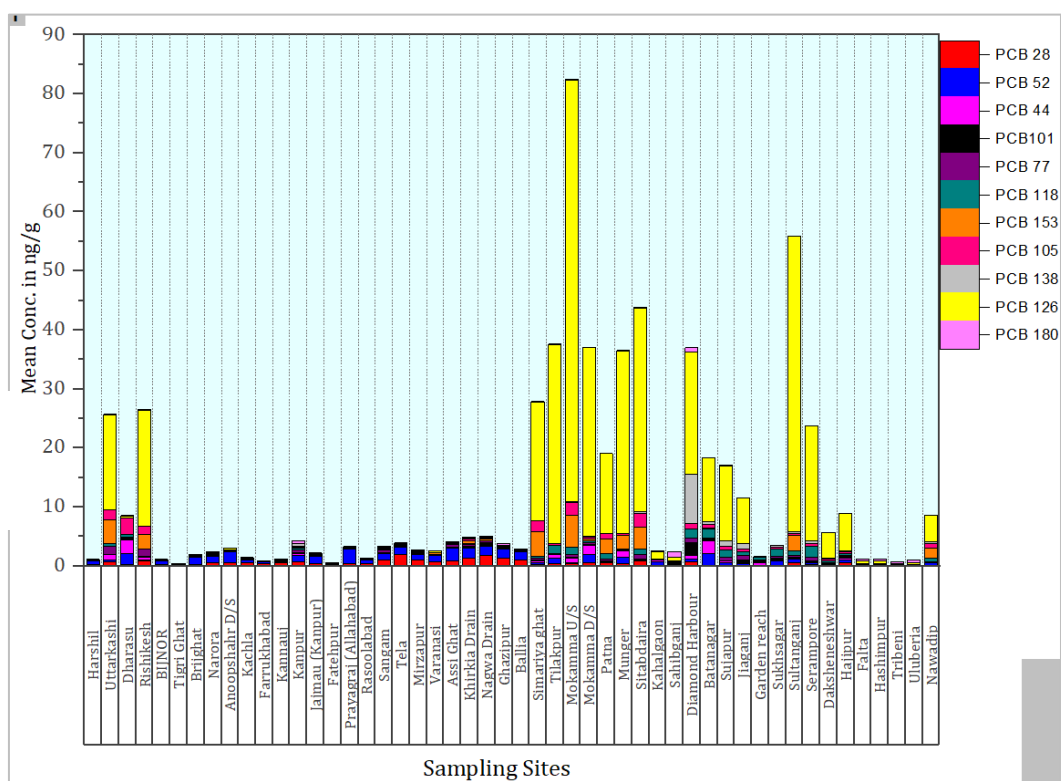


Figure 2.53: Site-wise variation of PCB congeners in post-monsoon season

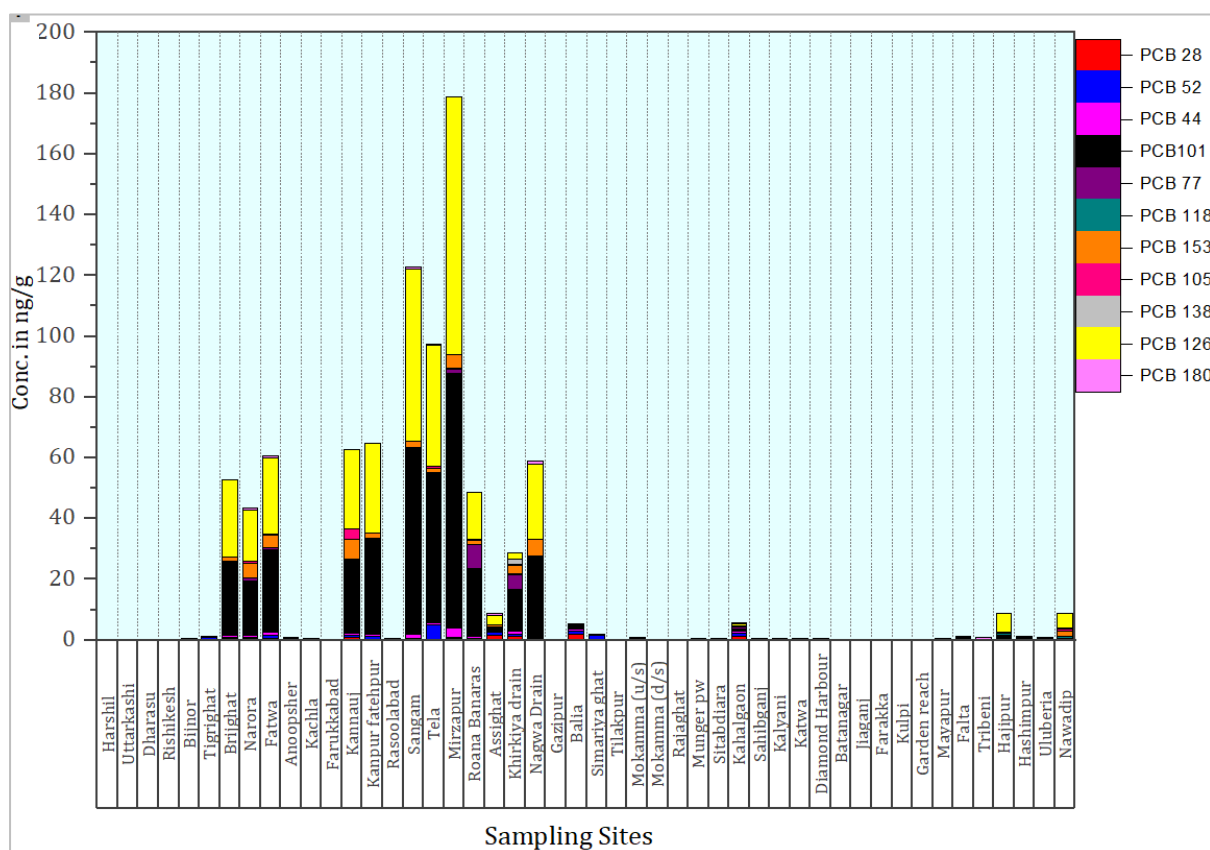


Figure 2.54: Site-wise variation of PCB congeners in post-winter season

7.1. Microplastics Contamination Profile

Microplastics are the newly found class of contaminant (plastic particles <5mm) that is gaining worldwide attention due to their anthropogenic origin, movement from freshwater rivers to oceans and disrupting the freshwater and marine life. This is the first report on quantification of microplastics in the Ganga River conducted as part of the NMCG project. Microplastic quantification was performed in the sediment samples collected from post monsoon season.

Figure 2.55 shows the presence of type of polymers in the sediment. Five types of polymers were detected across the Ganga sediment. The polymer with the highest detection rate was Polypropylene (PP) - 28%, followed by Polyethylene (PE) - 24%, Poly Vinyl Alcohol (PVA)-24%, Polyvinyl chloride (PVC)-19% and Polydimethyl siloxane (PDMS)-5%.

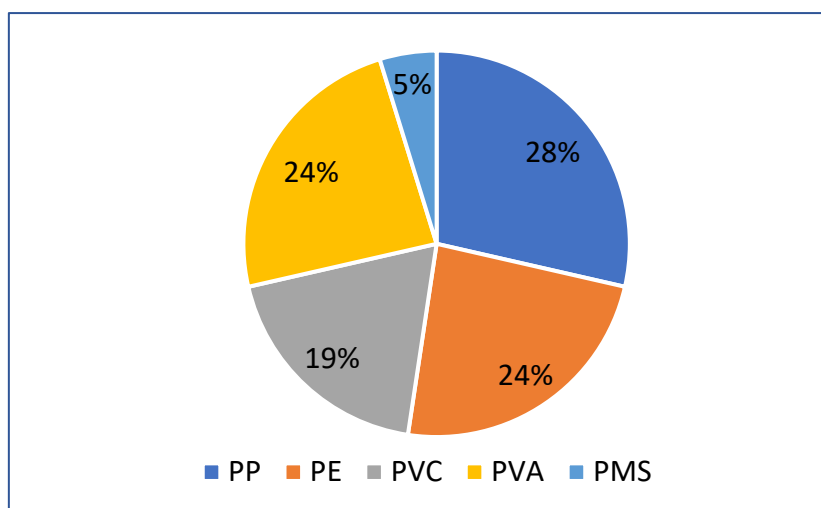


Figure 2.55: Types of Microplastics in Sediment samples across Ganga River

Zone wise assessment of microplastics (Figure 2.56) revealed that abundance of microplastics (MP/Kg) followed the pattern as UMZ > LZ > LMZ > UZ. The UMZ of Uttar Pradesh had highest abundance of microplastics due to larger section of the river flowing through this region and relatively higher input of waste into the river. Total MP load in UMZ was 30.95 MP/Kg of sediment with PVC, PVA and PE as the most abundant microplastics. Besides the highest load, this zone also showed presence of all the types of microplastics (Figure 2.56).

LZ of West Bengal showed an abundance of 20.83 MP/Kg with PP and PE as the two types of microplastics detected in this zone (Figure 2.56). PP was found four times higher than PE.

LMZ (Bihar & Jharkhand) had an abundance of 16.67 MP/Kg with PP and PE found in equal abundance (Figure 2.56).

UZ (Uttarakhand) had the lowest microplastics abundance of 8.33 MP/Kg and only Polyvinyl Aldehyde (PVA) was recorded in this zone (Figure 2.56).

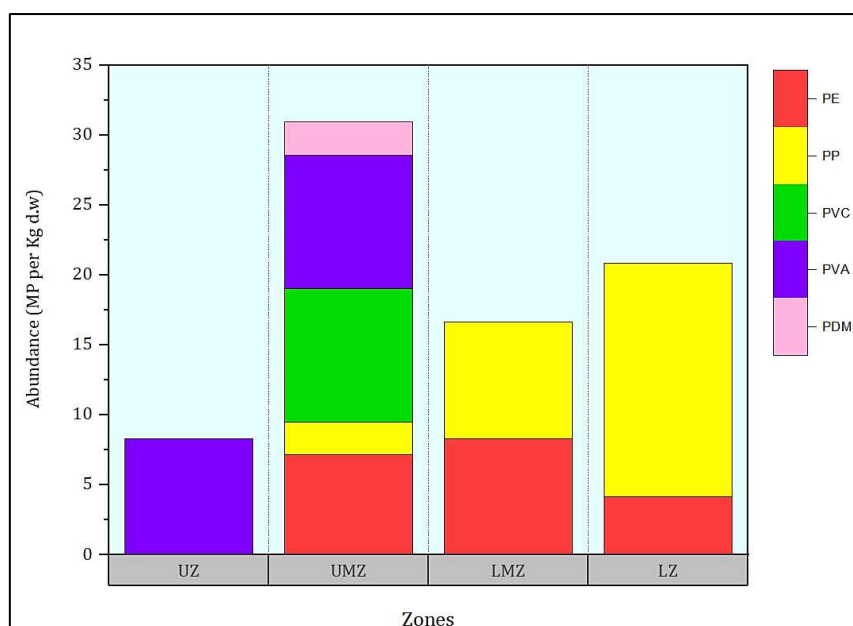


Figure 2.56: Zone wise abundance of Microplastics in Sediment samples

Figure 2.57 shows the percent abundance of microplastics in different zones. Maximum samples (92.9%) from UMZ had microplastics in it followed by LZ (62.5%). 40% of the samples from LMZ recorded microplastics while only 25% of the samples from UZ (25%) showed the presence of microplastics.

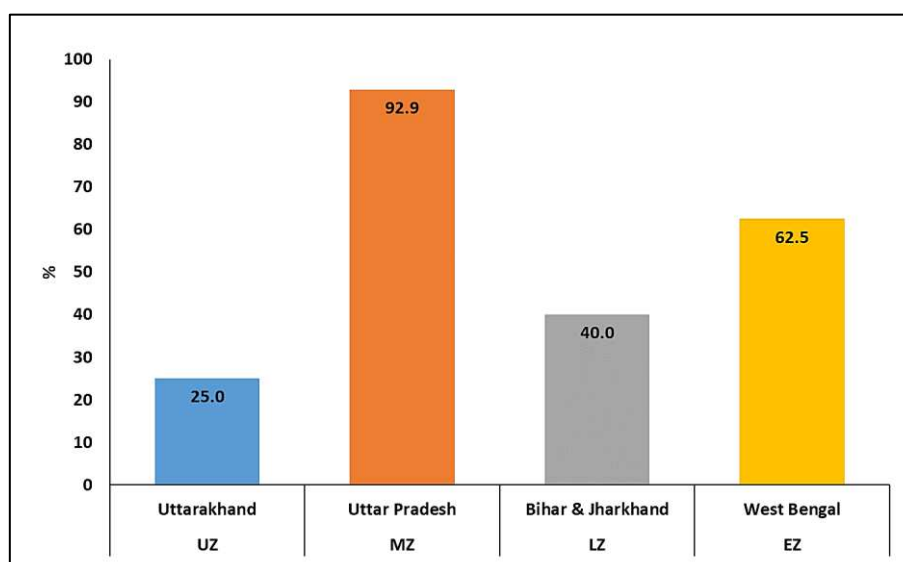


Figure 2.57: Percent abundance of microplastics in sediment samples

The distribution of individual polymer in different zones is shown in Figure 2.58. Polyethylene (PE) which is mostly used in carry bags and packaging industry, was found highest in UP (UMZ) followed by West Bengal (LZ) and Bihar & Jharkhand (LZ) which had equal distribution of PE (Figure 2.58a). We did not find any PE microplastics in UZ of Uttarakhand.

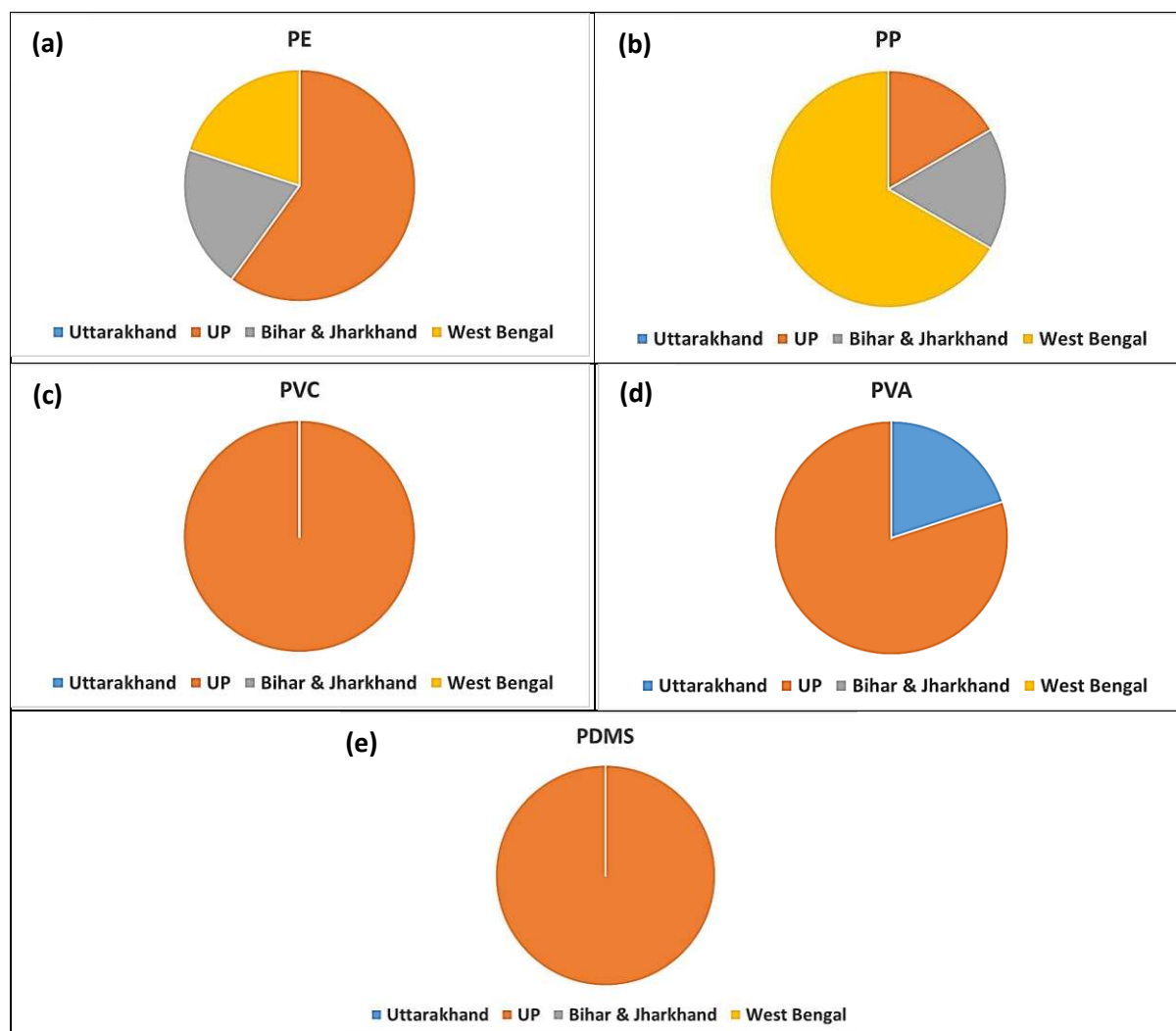


Figure 2.58: State-wise distribution of different types of microplastics

Distribution of PP (Figure 2.58b) based microplastics showed its highest presence in West Bengal (LZ) followed by UMZ and LMZ. No PP microplastics was found in Uttarakhand. Polypropylene (PP) is extensively used in packaging, textiles, healthcare, pipes, automotive and electrical applications

Another type of microplastics detected in the study comes from the polymer PVC or Polyvinyl Chloride. Among the different types of plastics manufactured worldwide, PVC was the second

most produced in 2015 (Plastics Europe, 2017). Their density is higher than seawater and generally sink to the bottom of the ocean or water in general. Due to this property, these particles often end up affecting benthic organisms. PVC can be rigid or flexible, clear or opaque. When PVC is compounded with a plasticizer, it is flexible. Examples of flexible PVC products are upholstery and clothing; wall covering, blood and IV bags, and tubing; wrap film, shower curtains, wire insulation and coatings on metal sheet. Rigid PVC contains rigid-specific additives such as impact modifiers. Rigid PVC applications include pipe, siding, windows, fence and many custom profiles for furniture, automotive, and industrial applications. Distribution pattern of PVC microplastics in sediment samples from Ganga River revealed its presence only in Uttar Pradesh (UMZ). No other zone or state showed its presence. As shown in Figure 2.58c, PVC was recorded only in UMZ (Uttar Pradesh) suggesting the unmanaged disposal of products made from PVC in this state.

Figure 2.58d shows the distribution pattern of Polyvinyl Alcohol (PVA) in different Ganga states. It was recorded in UZ as well as UMZ. The water-soluble macromolecules, such as polyvinyl alcohol (PVA) or polyvinyl acetate (PVAc), are of great commercial interest. They are used, for example, as emulsifiers, stabilisers, protective colloids, complexing agents, cleaning intensifiers, discolouration inhibitors, filming agents or adhesives (Löffler and Morschhäuser 2001; Hartmann et al. 1995). In present study, 80% of the total PVA was recorded in the state of Uttar Pradesh (UMZ) and rest 20% in Uttarakhand (UZ).

Lastly, PDMS (Polydimethyl Siloxane) was recorded only in UMZ. It is used as a food additive (E900), as an anti-foaming agent, anti caking agent, in shampoos, in beverages or in lubricating oils and microfluidic chips. Though it was detected in UMZ, however its abundance was quite low (2.38 MP/Kg) as compared to other microplastics recorded in this zone.

2. Contamination Status in Biota

Pollution of Indian rivers by pesticides and fertilizers, mainly from agricultural surface runoffs, and by heavy metals, largely resulting from industrial effluents, is a matter of increasing concern. Once released into the environment, these contaminants (metals and pesticides) are distributed and transported among different aquatic compartments and enters into aquatic organisms, one of the routes being via membranes. The adverse effect due to exposure of these contaminants on aquatic ecosystems could be either obvious and fatal due to immediate lethal doses, or insidious due to slow and steady accumulation of these contaminants, in the organs and tissues of otherwise healthy organisms. The slow, steady and long-term exposure and bioaccumulation of these contaminants could bring about gradual and dramatic change in the ecosystem, over an extended period of time. The aquatic species are at higher risk because exposures to these contaminants could be life-long and through multiple routes, thus bioaccumulation is frequent, that can ultimately affect their survival. Therefore, it becomes highly imperative to quantify their load and body burden in biotic matrices in order to develop effective mitigation and conservation measures.

Aquatic organisms, in particularly fish, are well-documented and identified as bio-accumulators of heavy metals and pesticides and are used extensively for bioaccumulation and conservation studies. Fishes are appropriate organisms to use in bio-monitoring and bioaccumulation studies because:

- They have a relatively long life span and are good indicators to document chronic and gradual effects as well as habitat changes
- Range of fish communities represents a variety of trophic levels, ideal for assessing contamination in the food chain

- Comparatively easy to collect and identify
- Aquatic life criteria (water quality guideline values) are well characterized

In this chapter, we have documented the bioaccumulation and contamination status of pesticides and heavy metals in different fish species. The fish species from different zones were collected based on their foraging behaviour and habitat preferences (Table 3.1) to study the accumulation pattern of pesticides and heavy metals.

Table 3.1: Feeding habit and habitat stratum of some of the fish species selected for the study			
SCIENTIFIC NAME	FAMILY	FEEDING HABITAT	HABIT STRATUM
<i>Schizothorax richardsoni</i>	Cyprinidae	Herbivorous, periphytonic feeder, feeding by scrapping the food from the rocks and stones	Bottom feeder
<i>Labeo bata</i>	Cyprinidae	Herbivorous (feeds on bottom dwelling organisms)	Bottom feeder
<i>Cirrhinus reba</i>	Cyprinidae	Herbivorous	Bottom feeder
<i>Tenuulosa ilisha</i>	Clupeidae	Plankton feeder	Bottom feeder
<i>Catla-catla</i>	Cyprinidae	Phytoplankton/ Zoo plankton feeder	Surface column-feeder
<i>Cirrhinus Mrigala</i>	Cyprinidae	Detritivorous (decaying vegetation)	Bottom feeder
<i>Tor putitora</i>	Cyprinidae	Carni-omnivore [Feeding habit changes (insectivore, carnivore, herbi-omnivore etc.) depending on the availability of food]	Marginal bottom feeder
<i>Cyprinus Carpio</i>	Cyprinidae	Detritivorous/Omnivorous	Bottom feeder
<i>Eutropiichthys vacha</i>	Schilbeidae	Omnivorous shifting to Omni-carnivorous feeding at adult stage	During monsoon swim in mid and surface waters, and confined to deeper pools for rest of the year
<i>Oreochromis niloticus</i>	Cichlidae	Omnivorous grazer	Surface column feeder
<i>Anguilla bengalensis</i>	Anguillidae	Carnivorous	Bottom feeder
<i>Sperata seenghala</i>	Bagridae	Carnivorous	Adults are column feeder, juveniles are bottom and marginal dwellers; fry inhabit the shallow

			marginal area of river and marginal pits.
<i>Rita rita</i>	Bagridae	Carnivorous	Bottom dweller; prefers muddy or clear water
<i>Wallego attu</i>	Siluridae	Carnivorous	Bottom feeder
<i>Bagarius bagarius</i>	Sisoridae	Carnivorous	Bentho-pelagic

8.1. Bioaccumulation of Pesticides

8.1.1. Zone-wise tissue loads of the pesticides (Total OCPs & OPPs)

The mean pesticides (OCPs and OPPs) concentrations in fish tissue (all species of fish combined) from all the zones is presented in Figure 3.1a. The maximum values of the pesticides (in tissues, species and zones) indicate that there are several outliers in each zone and that there is a large range of pesticide values. The results are expressed as µg/kg (dry weight). The total pesticides concentrations ranged from 3.418 to 372.620 µg/kg (**Mean: 68.21** µg/kg, **Median: 38.814** µg/kg), with the highest residues recorded in fish (Species: *Rita rita*) collected from Tela (Bhadoi, Uttar Pradesh) in UMZ1 whereas the lowest residues recorded in fish (*S.acinaces*) collected from Revalganj (Bihar) in LMZ. The zone-wise mean concentration observed in muscle tissues of different fish species for total pesticides (mean concentration at each zone) was **UMZ2 (195.830 µg/kg)>LZ (81.753 µg/kg)>UMZ1 (69.341 µg/kg)> UZ (48.736 µg/kg)>LMZ (40.076 µg/kg)**.

The zone-wise (Figure 3.1a) contamination status of pesticides in fish closely follows the contamination pattern observed in water compartment thus indicating the fresh inputs and bioavailability of these contaminants, for uptake by fish species.

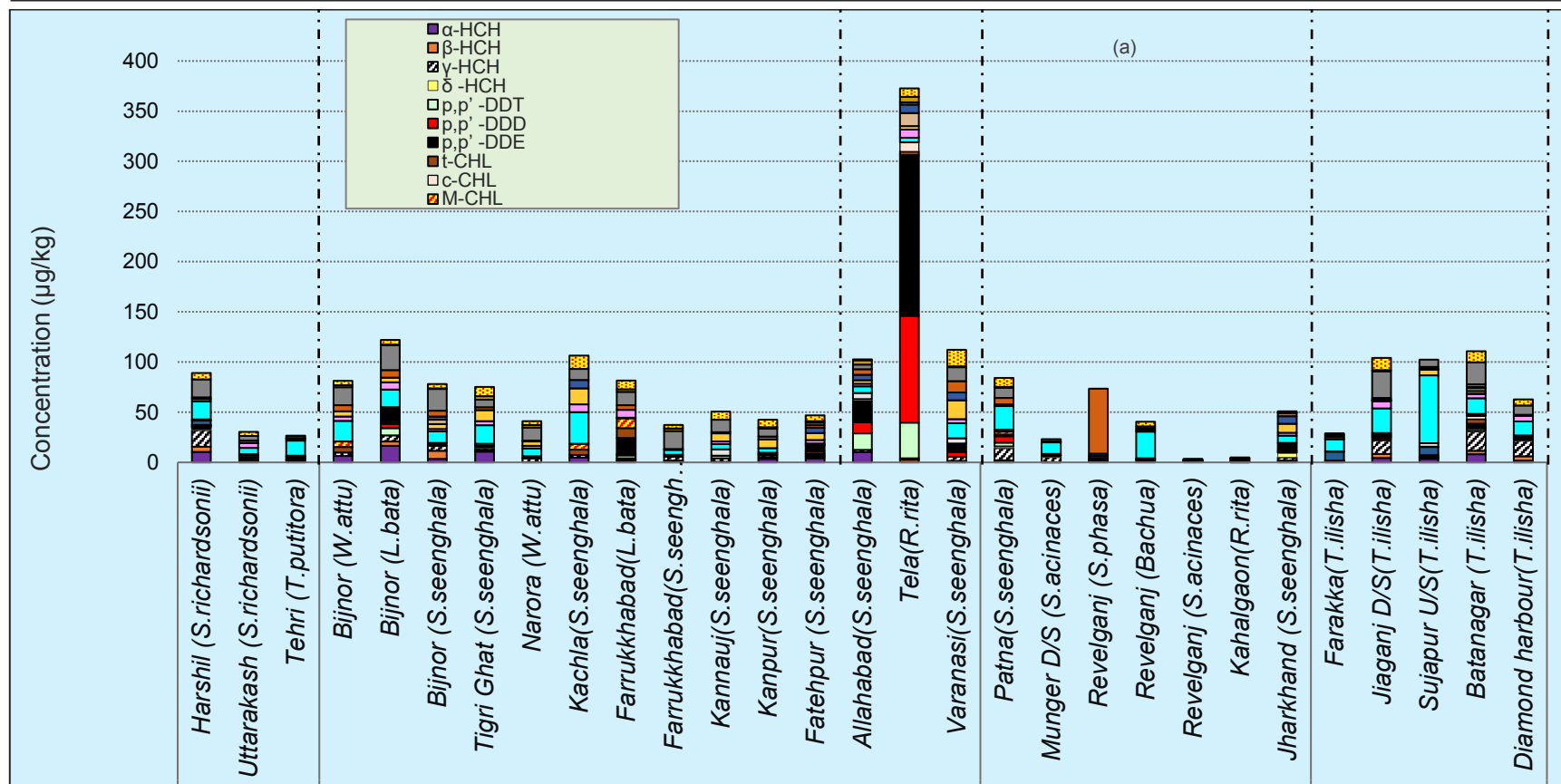
Among the total pesticides (Figure 3.1 b), the OCPs concentrations ranged from 2.956 to 356.621 µg/kg (**Mean: 59.496** µg/kg, **Median: 50.498** µg/kg), with the highest residues recorded in fish (Species: *Rita rita*) collected from Tela (Bhadoi, Uttar Pradesh) in UMZ1 whereas the lowest residues recorded in fish (*S.acinaces*) collected from Revalganj (Bihar) in LMZ. The OPPs concentrations ranged from BDL to 39.676 µg/kg (**Mean: 15.875** µg/kg, **Median: 16.334** µg/kg), with the highest residues recorded in fish (Species: *Tenuialosa ilisha*)

collected from downstream of Jiaganj (West Bengal) in LZ whereas the lowest residues recorded in fish (***S.acinaces***) collected from Revalganj (Bihar) in LMZ.

Figure 3.1: Tissue loads of the pesticides (OCPs & OPPs) per species of fish from different (a) zones (b) sites

Highest contamination and bioaccumulation is observed in fishes from UMZ, and LZ

(b)



The mean concentrations & Detection Frequency (DF) of individual OCPs residues, presented in **Figure 3.2 a & b**, revealed the predominance of Heptachlor (H-CHL), Methyl Parathion, p,p'-DDE, Chlorpyrifos, p,p' DDD, Endrin Ketone, γ -HCH, Aldrin, and α -HCH with mean concentrations as 13.573, 9.360, 8.667, 5.431, 5.180, 4.755, 4.477, 4.044, and 3.414, in $\mu\text{g/kg}$, respectively. The detection frequency of above pesticides ranged from 97-59%.

Figure 3.3 a & b indicates the highest (Figure 3.3a) and lowest (Figure 3.3b) pesticide loads in the specific species of fish. The results revealed different accumulation pattern in different fish species based on their habitat preferences and foraging behaviour. **High accumulation is mostly observed in carnivorous and bottom dwelling fish species belonging to UMZ and LZ. We hypothesize that the fish species that inhabit the lower region of the water column (e.g. *R.rita*, *L.bata*, etc.), are likely to have higher contaminant concentrations than fishes that inhabit the upper or surface water column. The greater contact with polluted sediments and greater uptake of contaminants from zoobenthic predators would lead to higher contaminants residues in their tissues.**

The species (Figure 3.3 a) with the highest body pesticide loads are

R.rita (Tela in UMZ1; Mean: 16.201 $\mu\text{g/kg}$; Sum: 372.620 $\mu\text{g/kg}$), ***L.bata*** (Bijnor in UMZ1; Mean: 5.301 $\mu\text{g/kg}$; Sum: 121.925 $\mu\text{g/kg}$), ***S.seenghala*** (Varanasi in UMZ2; Mean: 4.875 $\mu\text{g/kg}$; Sum: 112.124 $\mu\text{g/kg}$), ***T.illisha*** (Batanagar in LZ; Mean: 4.815 $\mu\text{g/kg}$; Sum: 110.746 $\mu\text{g/kg}$), ***S.seenghala*** (Kachla in UMZ1; Mean: 4.624 $\mu\text{g/kg}$; Sum: 106.360 $\mu\text{g/kg}$), ***T.illisha*** (Jiaganj U/S in LZ; Mean: 4.521 $\mu\text{g/kg}$; Sum: 103.973 $\mu\text{g/kg}$), ***S.seenghala*** (Allahabad, in UMZ2; Mean: 4.467 $\mu\text{g/kg}$; Sum: 102.733 $\mu\text{g/kg}$) and ***T.illisha*** (Sujapur U/S in LZ; Mean: 4.450 $\mu\text{g/kg}$; Sum: 102.347 $\mu\text{g/kg}$).

The species with the lowest body pesticide loads are (Figure 3.3 b).

S. phasa (Revalganj in LZ; Mean 0.1486 $\mu\text{g/kg}$; Sum: 3.418), ***R. rita*** (Kahalgaon in LMZ; Mean: 0.281; Sum: 4.823 $\mu\text{g/kg}$; Sum). ***S.acinaces*** (Munger in LMZ; Mean 1.00; Sum: 23.071), ***T. putitora*** (Tehri in UZ; Mean: 1.158 $\mu\text{g/kg}$; Sum: 26.645 $\mu\text{g/kg}$), ***T.illisha*** (Farakka

in LZ; Mean: 1.254 $\mu\text{g/kg}$; Sum 28.839 $\mu\text{g/kg}$), ***S.richardsoni*** (Uttarkashi in UZ; Mean: 1.324 $\mu\text{g/kg}$; Sum : 30.459 $\mu\text{g/kg}$), ***S.Seenghala*** (Farrukhabad in UMZ1; Mean: 1.624 $\mu\text{g/kg}$; Sum: 37.347 $\mu\text{g/kg}$).

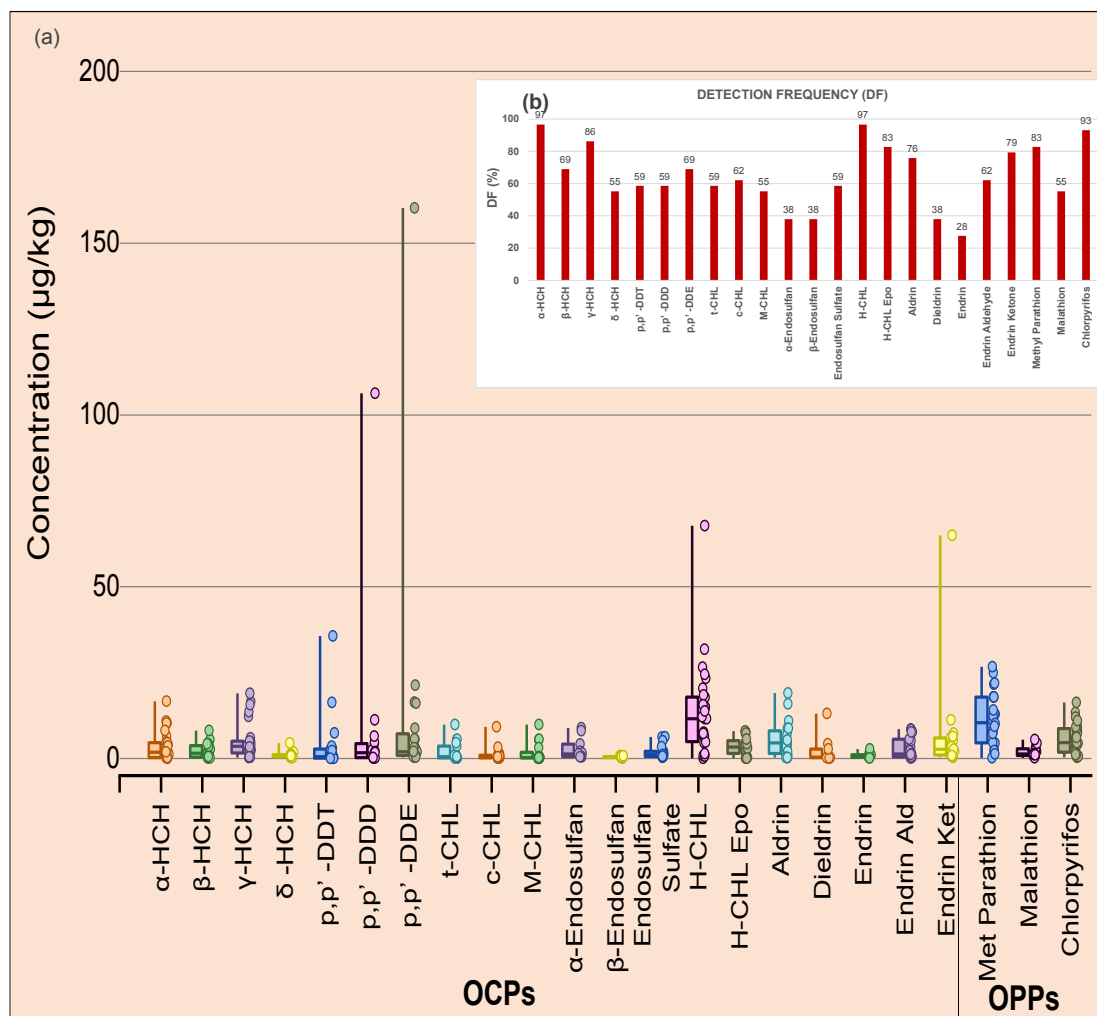


Figure 3.2: (a) Range of pesticides concentrations in fish tissues (b) Detection frequency (DF) of pesticides residues

Highest concentration was observed for Heptachlor (H-CHL), Methyl Parathion, p,p'-DDE, Chlorpyrifos, Endrin Ketone, γ -HCH, Aldrin, and α -HCH.

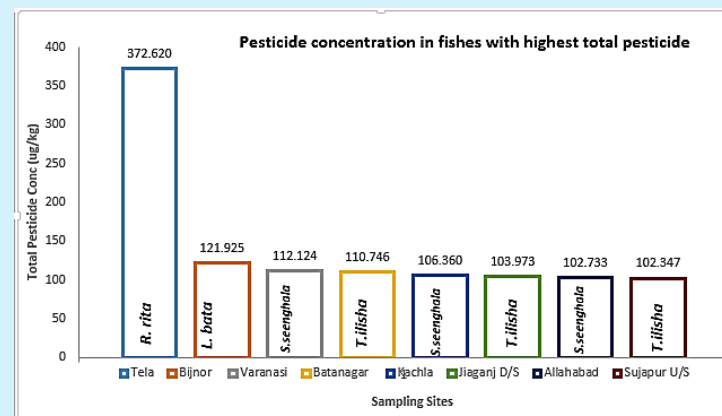
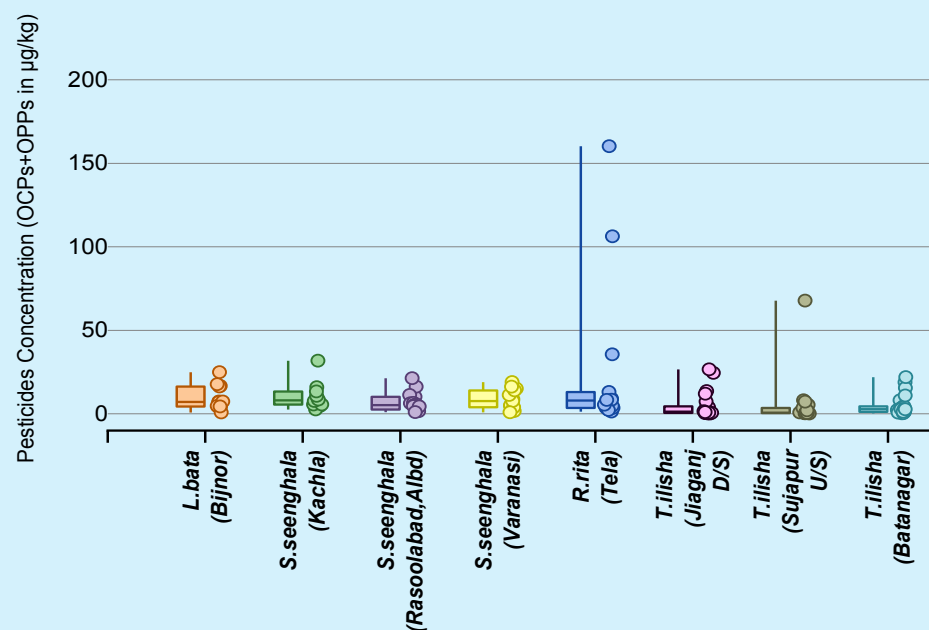
As expected, the pesticide residues with highest detection (DF in range 97-59%) were the ones which are excessively used either in present or heavily in the past.

Graph (a) represents box plots with data scatter in the right (as circles).

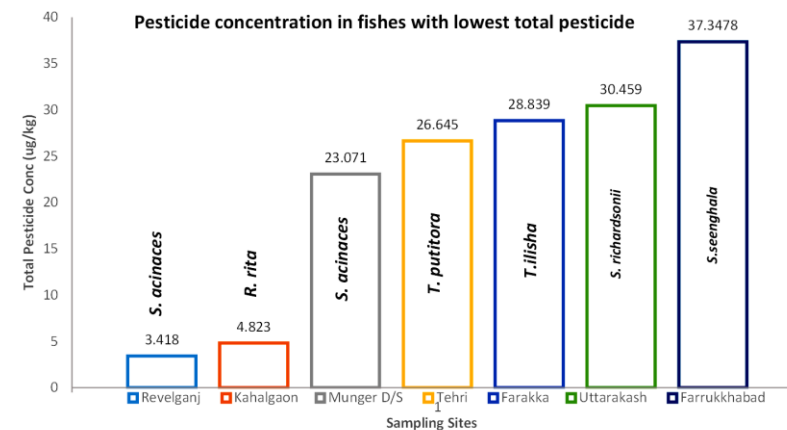
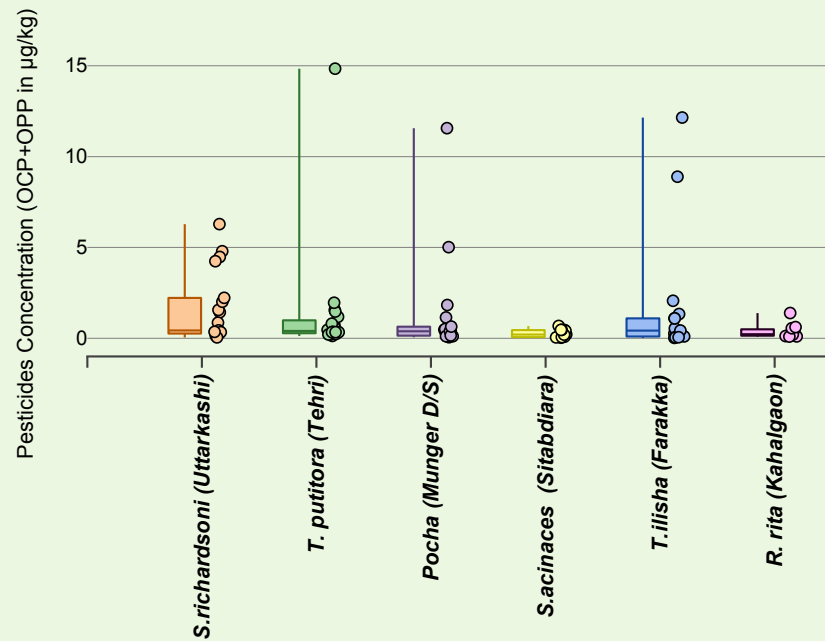
Figure 3. 3: Fish species accumulating (a) highest and, (b) lowest pesticides loads

Results revealed different accumulation pattern in different fish species based on their habitat preferences. Highest pesticides accumulation recorded in *S.Seenghala* (UMZ), *R.rita* (UMZ), and *T.ilisha* (LZ; particularly downstream Farrakka) whereas lowest accumulation were recorded in fishes from LMZ

(a) Fish Species with highest pesticide load



(b) Fish Species with lowest pesticide load



OCPs

Hexachlorocyclohexanes (HCH)

The Σ HCHs (Figure 3.4) concentrations in the fishes ranged from 0.740 to 33.520 $\mu\text{g/kg}$ (**Mean: 9.883 $\mu\text{g/kg}$, Median: 7.301 $\mu\text{g/kg}$**), with the highest residues recorded in fish (Species: ***S.richardsonii***) collected from Harshil (Uttarakhand) in UMZ1 whereas the lowest residues recorded in fish (Species: ***R.rita***) collected from Kahalgaon (Bihar) in LMZ. The highest accumulation of Σ HCHs in fish (***S.richardsonii***) collected from relatively pristine zone indicates the long-range transport as well as fresh usage of these banned pesticides, that are accumulating in these fishes at alarming levels. High concentration of HCH in water and sediment along with bottom-dwelling behaviour of ***S.richardsonii*** is responsible for accumulation of high level of these pesticides in this species. The zone-wise mean concentration observed in muscle tissues of different fish species for Σ HCHs was LZ (16.496 $\mu\text{g/kg}$)>UZ (12.807 $\mu\text{g/kg}$)>UMZ1 (9.853 $\mu\text{g/kg}$)>UMZ2 (7.360 $\mu\text{g/kg}$)>LMZ (5.288 $\mu\text{g/kg}$). The results of our study showed the dominance of γ -HCH and α -HCH in all collected fish samples (Figure 3.4).

Dichlorodiphenyltrichloroethanes (DDTs)

The Σ DDTs (Figure 3.5) concentrations ranged from BDL to 302.125 $\mu\text{g/kg}$ (**Mean: 17.806 $\mu\text{g/kg}$, Median: 2.086 $\mu\text{g/kg}$**), with the highest residues recorded in fish (Species: ***Rita rita***) collected from Tela (Bhadoi, Uttar Pradesh) in UMZ1 whereas the lowest residues recorded in fish (***W Attu and S Seenghala***) collected from Bijor and Kachla in UMZ1 respectively. The most interesting observation on DDT accumulation was observed in the species ***Rita rita*** from Tela (Uttar Pradesh) in UMZ1 showing surprisingly highest level of Σ DDT (302.12 $\mu\text{g/kg}$). This species has a very long life span and such high levels of Σ DDT in this species indicates historic accumulation of this pesticide over years in it and the high tolerance level of the species towards this pesticide. The zone-wise mean concentration observed in muscle tissues of different fish species for Σ DDTs was UMZ2 (121.454 $\mu\text{g/kg}$)>UMZ1 (6.165 $\mu\text{g/kg}$)>LMZ (2.911 $\mu\text{g/kg}$)>LZ (2.640 $\mu\text{g/kg}$)>UZ (1.823 $\mu\text{g/kg}$). The results of our study showed the dominance

of metabolites namely DDE followed by DDD as compared to their parent compound DDT (Figure 3.5).

Figure 3.4: Tissue loads of the Σ HCHs per species of fish from different zones

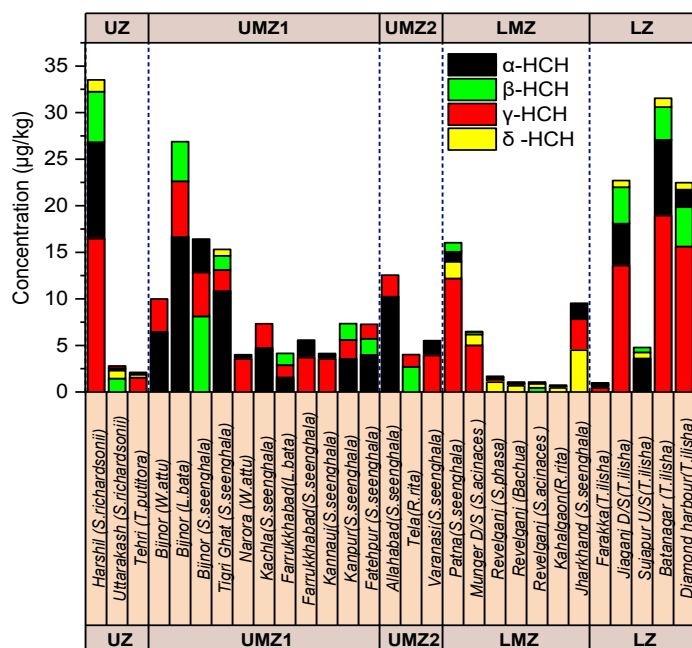


Figure 3.5: Tissue loads of the Σ DDTs per species of fish from different zones

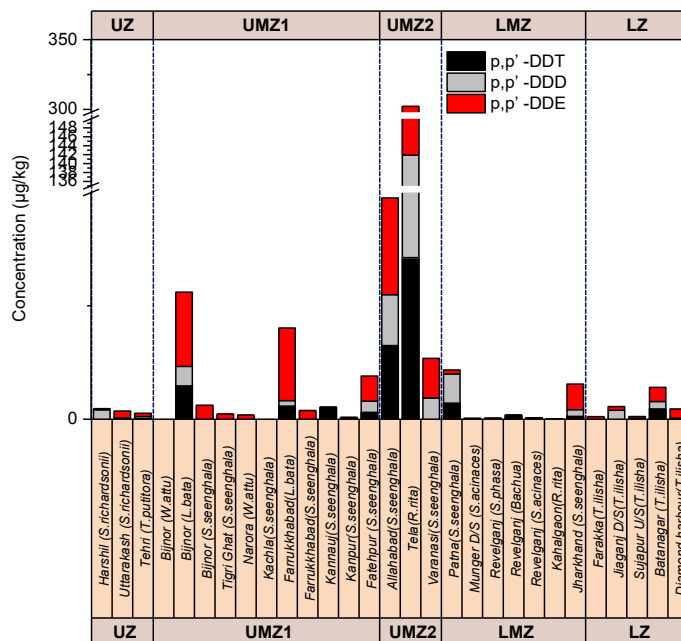


Figure 3.6: Tissue loads of the Σ HCHLs per species of fish from different zones

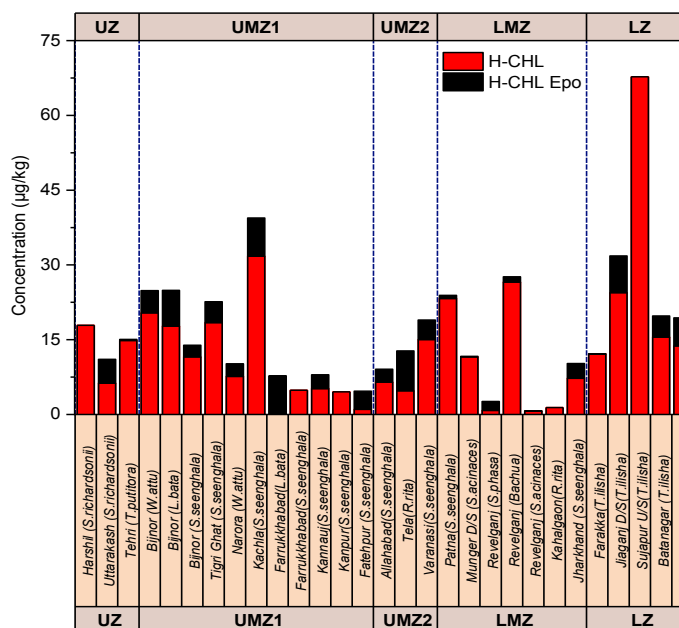
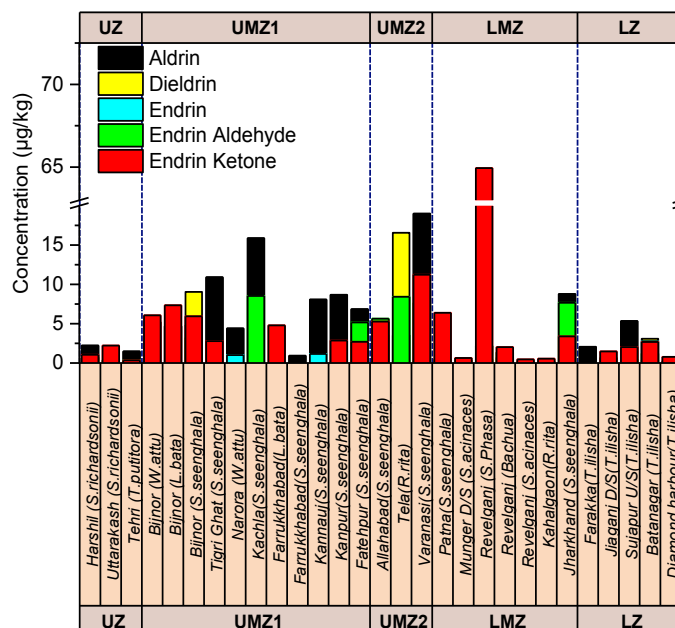


Figure 3.7: Tissue loads of the Σ Drins per species of fish from different zones



Heptachlors (HCHLs)

The Σ HCHLs (Figure 3.6) concentrations ranged from 0.735 to 67.751 $\mu\text{g/kg}$ (**Mean: 16.136** $\mu\text{g/kg}$, **Median: 13.743** $\mu\text{g/kg}$) with the highest residues recorded in fish (Species: *T. ilisha*) collected from Sujapur (West Bengal) in LZ whereas the lowest residues recorded in fish (Species: *S. acinaces*) collected from Revalganj (Bihar) in LMZ. The zone-wise mean concentration observed in muscle tissues of different fish species for Σ HCHLs was LZ (30.178 $\mu\text{g/kg}$)>UMZ1 (15.055 $\mu\text{g/kg}$)>UZ (14.677 $\mu\text{g/kg}$)>UMZ2 (13.592 $\mu\text{g/kg}$)>LMZ (11.165 $\mu\text{g/kg}$). The results of our study showed the predominance of parent compound Heptachlor (Figure 3.6), indicating its possible fresh usage in the region.

Drins

The Σ Drins (Figure 3.7) concentrations ranged from 0.659 to 67.600 $\mu\text{g/kg}$ (**Mean: 11.657** $\mu\text{g/kg}$, **Median: 8.712** $\mu\text{g/kg}$). The only species showing highest level (67.6 $\mu\text{g/kg}$) of Σ Drins (including Aldrin, Dieldrin, Endrin and its metabolites) was *S. phasa* found in Revalganj, Bihar highlighting that the banned class of Drins is still used in this region for controlling pests. Interestingly, the species (*S. acinaces*) with lowest level of Σ Drins was also found in Revalganj. The zone-wise mean concentration observed in muscle tissues of different fish species for Σ Drins was UMZ2 (25.777 $\mu\text{g/kg}$)>LMZ (14.525 $\mu\text{g/kg}$)>UMZ1 (11.472 $\mu\text{g/kg}$)>LZ (4.854 $\mu\text{g/kg}$)>UZ (3.022 $\mu\text{g/kg}$). The results of our study showed the dominance of Endrin ketone, a break-down product of Endrin, followed by Aldrin>Endrin Aldehyde> Dieldrin> Endrin (Figure 3.7) with mean concentration as 4.64, 3.95, 1.82, 0.75, and 0.22 in $\mu\text{g/kg}$, respectively.

Chlordanes (CHLs)

The Σ CHLs (Figure 3.8) concentrations ranged from BDL to 12.732 $\mu\text{g/kg}$ (**Mean: 1.865** $\mu\text{g/kg}$, **Median: 0.870** $\mu\text{g/kg}$), with the highest residues recorded in fish (Species: *Rita rita*) collected from Tela (Bhadoi, Uttar Pradesh) in UMZ, whereas, as shown in Figure 3.8, the CHLs

residues were below detection limits (BDL) in some fishes collected from UMZ1 and UMZ2. The zone-wise mean concentration observed in muscle tissues of different fish species for Σ CHLs was UMZ2 (4.765 $\mu\text{g/kg}$)>LZ (2.247 $\mu\text{g/kg}$)>UMZ1 (2.020 $\mu\text{g/kg}$)>UZ (0.976 $\mu\text{g/kg}$)>LMZ (0.500 $\mu\text{g/kg}$). Similar to water samples, the residues in fish tissues showed the dominance of isomer t-CHLs in all the fish samples (**Figure 3.8**), indicating the fresh usage of this pesticide in Ganga catchment.

Endosulfans (ESs)

The Σ ESs (Figure 3.9) concentrations ranged from BDL to 11.955 $\mu\text{g/kg}$ (**Mean: 2.364 $\mu\text{g/kg}$, Median: 1.250 $\mu\text{g/kg}$**), with the highest residues recorded in fish (Species: *T.illisha*) collected from Sujapur U/S (West Bengal) in LZ whereas, as shown in Figure 3.9, the ESs residues were below detection limits (BDL) in some fishes collected from UMZ1 and UMZ2. The zone-wise mean concentration observed in muscle tissues of different fish species for Σ ESs was LZ (5.345 $\mu\text{g/kg}$)>UMZ2 (3.794 $\mu\text{g/kg}$)>UZ (3.483 $\mu\text{g/kg}$)>UMZ1 (1.065 $\mu\text{g/kg}$)>LMZ (1.035 $\mu\text{g/kg}$). The results showed the dominance of Endosulfan Sulfate (ESSs), a breakdown product Endosulfan, in all the fish samples (**Figure 3.9**) followed by α -ES and β -ES with a mean concentration of 1.153, 1.056 and 0.162 $\mu\text{g/kg}$ respectively.

Methoxychlor (M-CHL)

The M-CHL (Figure 3.10) concentrations ranged from BDL to 9.868 $\mu\text{g/kg}$ (**Mean: 0.863 $\mu\text{g/kg}$, Median: 0.107 $\mu\text{g/kg}$**), with the highest residues recorded in fish *L.bata* collected from Farukhabad in UMZ1 whereas, the M-CHLs residues were below detection limits (BDL) in several fishes collected from UMZ and LMZ (Figure 3.10). The zone-wise mean concentration observed in muscle tissues of different fish species for M-CHL was UMZ1 (1.900 $\mu\text{g/kg}$)>LMZ (0.549 $\mu\text{g/kg}$)>LZ (0.245 $\mu\text{g/kg}$)>UZ (0.181 $\mu\text{g/kg}$)>UMZ2 (BDL).

Figure 3.8: Tissue loads of the Σ CHLs per species of fish from different zones

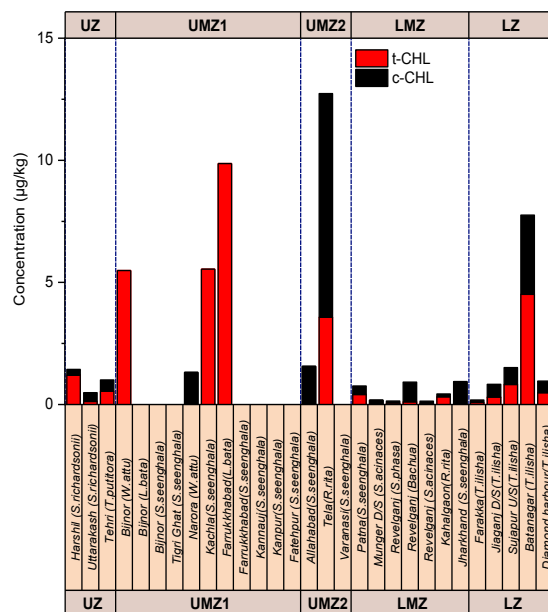


Figure 3.9: Tissue loads of the Σ ESs per species of fish from different zones

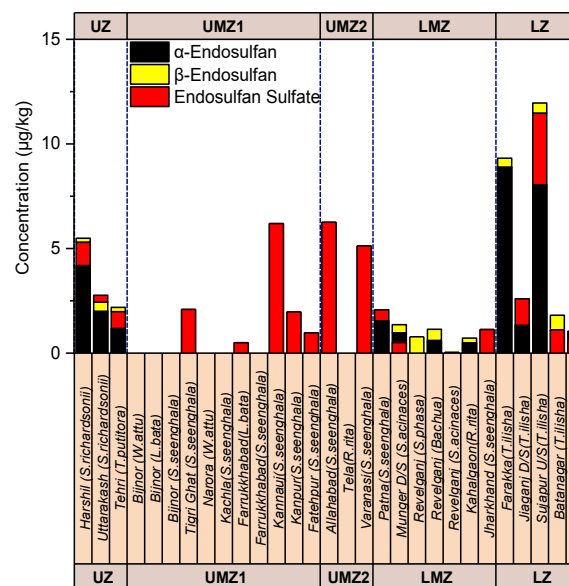
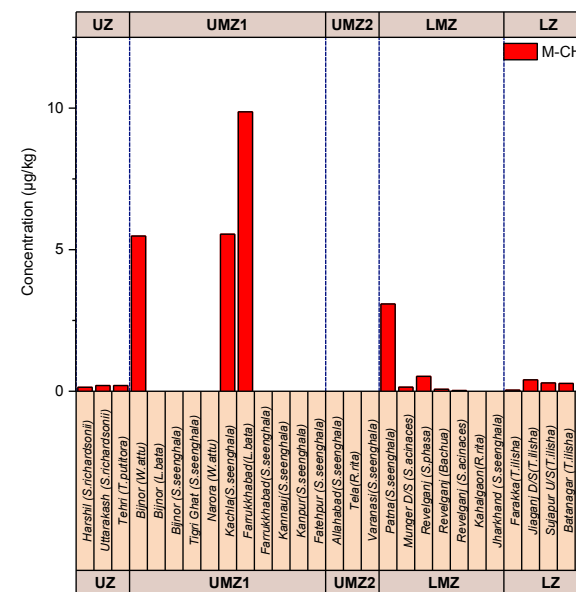


Figure 3.10: Tissue loads of the M-CHLs per species of fish from different zones



OPPs

Methyl Parathion

The Methyl Parathion (Figure 3.11) concentrations ranged from BDL to 26.658 µg/kg (**Mean: 9.107 µg/kg, Median: 8.018 µg/kg**) with the highest residues recorded in fish (Species: *T. illisha*) collected from Jiaganj (W,Bengal) in LZ whereas, the Methyl parathion residues were below detection limits (BDL) in *fishes* collected from Munger, Revalganj, Kahalgaon in Bihar. The zone-wise mean concentration observed in muscle tissues of different fish species for Methyl Parathion was UMZ1(13.587 µg/kg)>LZ (13.290 µg/kg)>UZ (8.096 µg/kg)> UMZ2 (6.977µg/kg)>LMZ (1.472 µg/kg).

Malathion

The Malathion (Figure 3.11) concentrations ranged from BDL to 5.486 µg/kg (**Mean: 1.082 µg/kg, Median: 0.371 µg/kg**) with the highest residues recorded in fish (Species: *R. rita*) collected from Tela (Uttar Pradesh) in UMZ2 whereas, the Malathion residues were below detection limits (BDL) in *species from all the zones except a few from UMZ1 and UMZ2*. The zone-wise mean concentration observed in muscle tissues of different fish species for Malathion was UMZ2 (3.593µg/kg)>UMZ1 (1.599 µg/kg)>LZ (0.424 µg/kg)> LMZ (0.137 µg/kg)>UZ (BDL).

Chlorpyrifos

The Chlorpyrifos (Figure 3.11) concentrations ranged from BDL to 16.251 µg/kg (**Mean: 5.369 µg/kg, Median: 4.465 µg/kg**) with the highest residues recorded in fish (Species: *S.seenghala*) collected from Varanasi (Uttar Pradesh) in UMZ2. Its residues were below detection limits (BDL) in *S.phasa* collected from Revalganj (Bihar) in LMZ and *T. illisha* from Sujapur u/s in LZ. The zone-wise mean concentration observed in muscle tissues of different fish species for Chlorpyrifos was UMZ2 (8.514 µg/kg)>UMZ1 (6.628 µg/kg)>LZ (6.030 µg/kg)>UZ (3.671 µg/kg)>LMZ (2.554 µg/kg).

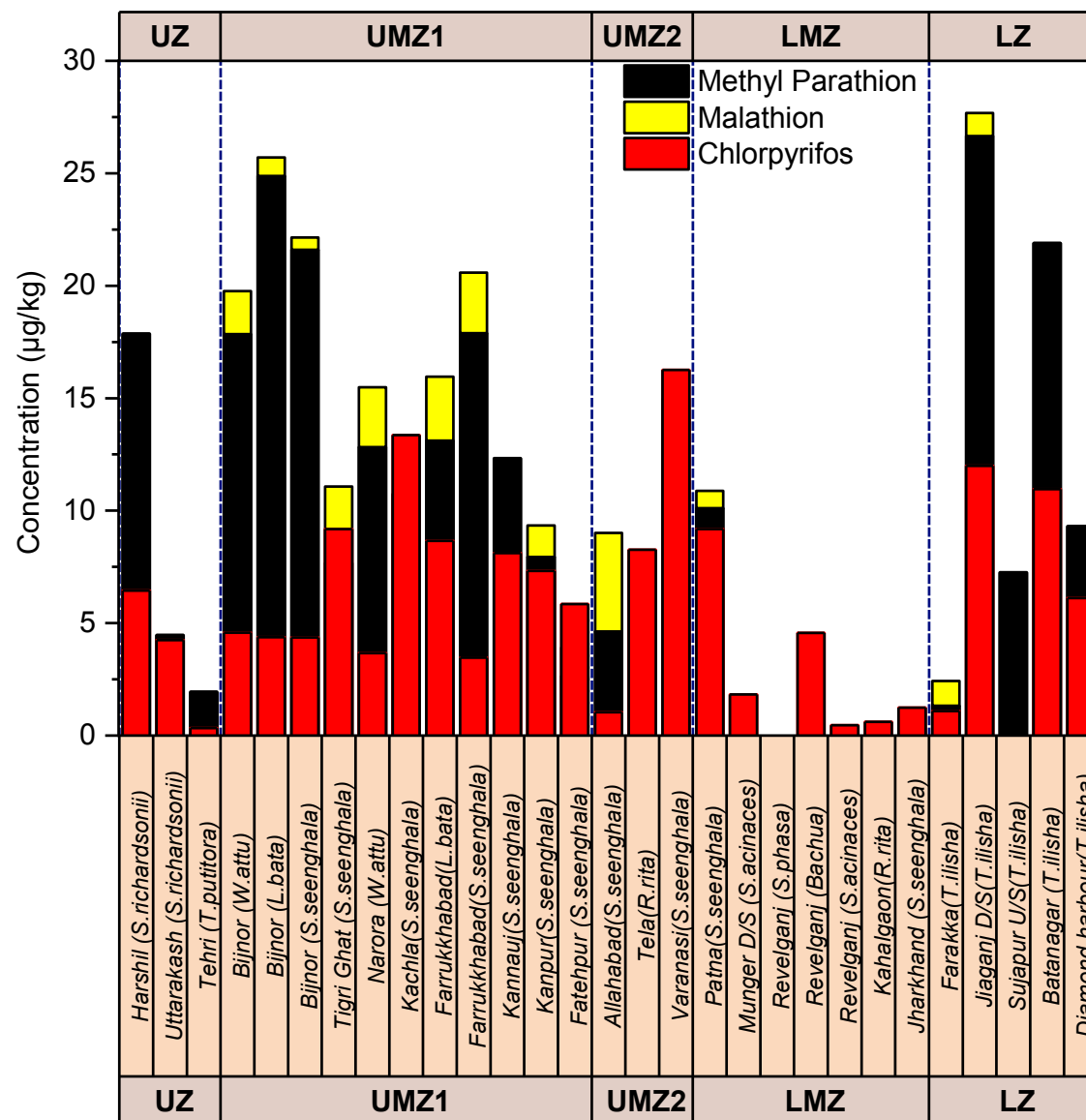


Figure 3.11: Tissue loads of the Σ OPPs per species of fish from different zones

*Highest residues recorded in fish species collected from LZ (*Tenulosa ilisha*), UMZ (*S. seenghala*, *L. bata*, and *W. attu*) as well as *S. richardsonii* collected from UZ.*

Relatively higher accumulation of Chlorpyrifos, in fish tissues, indicates its high usage in all the zones

8.2. Bioaccumulation of Heavy Metal

8.2.1. Total Heavy Metals - Zone-wise tissue loads of heavy metals between species of fish

The mean heavy metals bioaccumulation in fish muscle tissues (all species of fish combined) determined per species, site, and zone, is presented in **Figure 3.12 a & b**. We have observed outliers in the maximum values of the heavy metals obtained for different zones and metals indicating that there is a large variation in the range of metal values. These high values can be related to species tolerance, spatial dynamics, and individual heavy metal concentrations. The results are expressed as mg/kg on a dry weight basis in fish tissues.

The total heavy metal concentrations ranged from 4.021 to 201.92 mg/kg (**Mean: 24.222 mg/kg, Median: 14.035 mg/kg**), with the highest metal concentrations recorded in fish (Species: ***S.acinaces***) collected from Munger D/S (Bihar) in LMZ whereas the lowest residues recorded in fish (Species: ***S.seenghala***) collected from Bijnor (Uttar Pradesh) in UMZ1.

The zone-wise mean concentration, of heavy metals, observed in muscle tissues of different fish species was **LMZ (Mean: 42.71 mg/kg) >UZ (Mean: 35.874 mg/kg)>UMZ2 (Mean: 23.763 mg/kg) > UMZ1 (Mean: 15.065 mg/kg) > LZ (Mean: 12.830 mg/kg)**.

The species with the highest heavy metal loads in their body are

S.acinaces (Munger in LMZ; Mean: 22.441 mg/kg; Sum: 201.924 mg/kg), ***S.richardsonii*** (Dharasu in UZ; Mean: 11.224 mg/kg ; Sum:100.942 mg/kg), ***L.bata*** (Farrukhabad in UMZ1; Mean: 4.333 mg/kg; Sum:39.001 mg/kg), , ***L.bata*** (Rishikesh

in UZ; Mean: 3.839 mg/kg; Sum: 34.552 mg/kg), and, **S.seenghala** (Farrukhabad in UMZ1; Mean: 3.680 mg/kg; Sum:33.124 mg/kg).

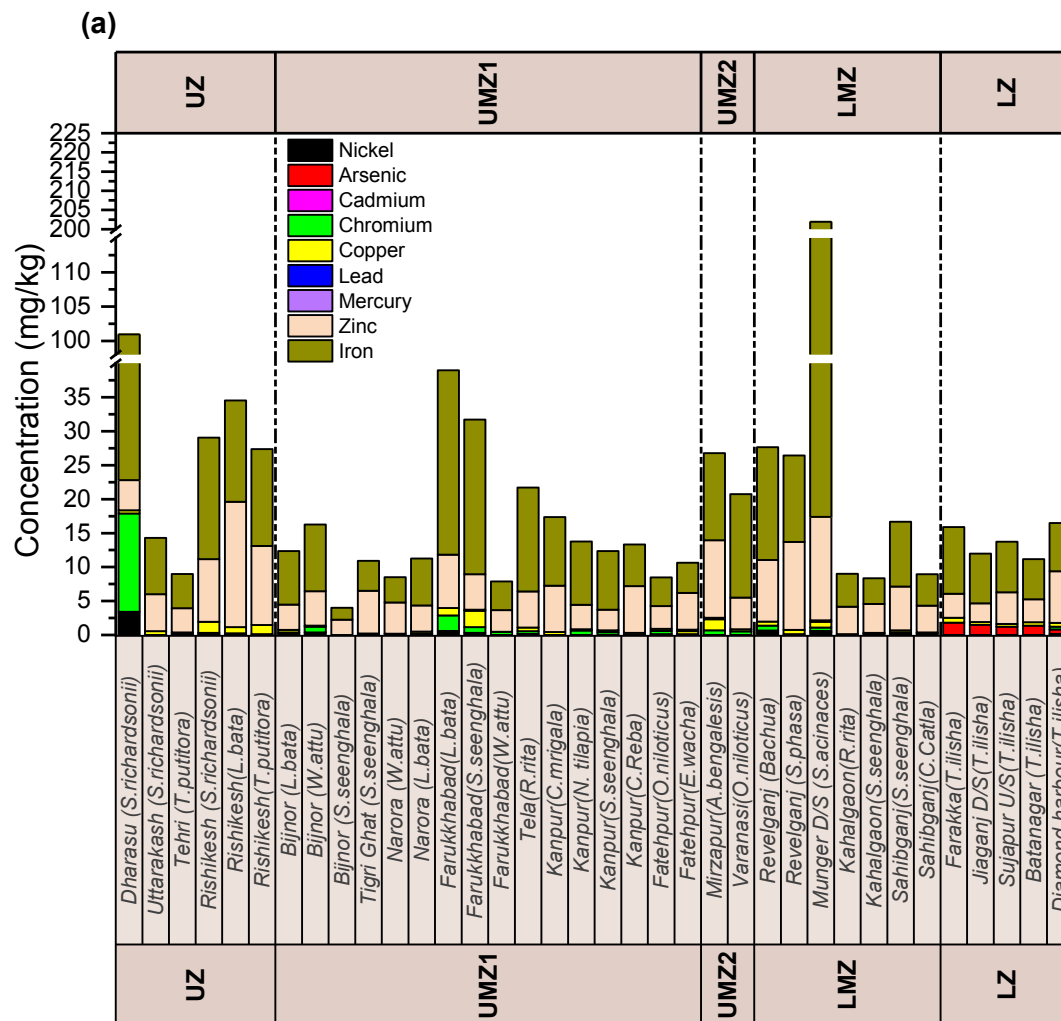
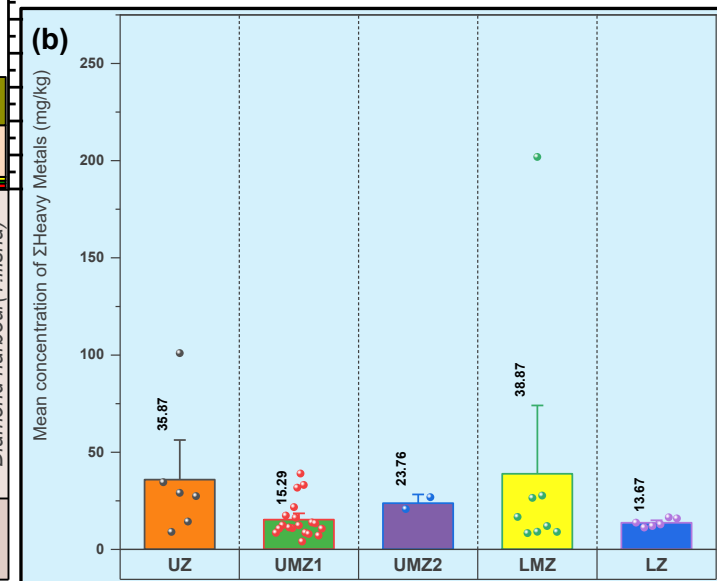


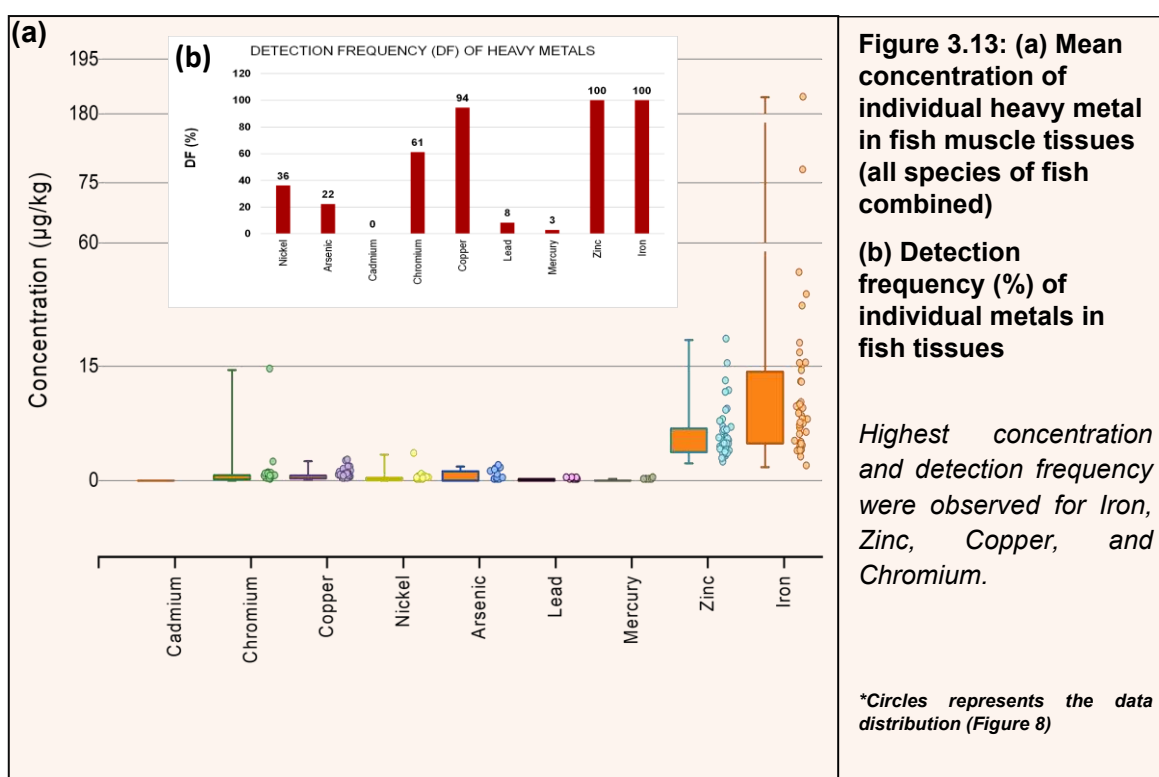
Figure 3. 12: Tissue loads of the (a) heavy metals per site and per species of fish from different zones (b) Mean total heavy metal concentration in fish muscle tissues (all species of fish combined) in each zone

This observed trend of zone-wise comparison of heavy metal accumulation in fish species was mainly due to high accumulation of Iron, and zinc.

****Graph represents bar with data scatter as circles in the right (Figure 3.12b)**



The mean concentrations and Detection Frequency (DF) of individual metals is, presented in **Figure 3.13 a & b**. In fish muscle tissues, iron and zinc concentrations were highest (100%) while the other metals varied in following sequence irrespective of sampling locations: Copper>Chromium>Nickel>Arsenic>Lead>Mercury>Cadmium(BDL). Iron, Zinc, and Copper are essential metals for normal biological function and metabolic activities however excess amount could led to adverse changes and may induce damage.



1. Cadmium

Cadmium concentration in muscles tissues of all the fish species was below detection limits (BDL).

2. Chromium

Chromium (Figure 3.14) concentrations ranged from BDL to 14.490 mg/kg (**Mean: 0.693 mg/kg, Median: 0.140 mg/kg**) with the highest residues recorded in fish (Species: *S.richardsonii*) collected from Dharasu (Uttarakhand) in UZ. The zone-wise mean

concentration observed in muscle tissues of different fish species for Chromium was UZ (2.514 mg/kg)>UMZ2 (0.615 mg/kg)>UMZ1 (0.430 mg/kg)>LMZ (0.190 mg/kg)>LZ (0.086 mg/kg). The high accumulation of chromium in fishes collected in the UZ could be attributed to natural geogenic deposition (in the absence of industrial settlements).

3. Copper

In fishes, copper is an essential component of many glycoproteins and enzymes, however, it is also one of the most toxic metal to aquatic species, at levels above the threshold concentrations. As it is an essential metal, therefore it was detected in all the fish species. Copper (Figure 3.15) concentrations ranged from BDL to 2.540 mg/kg (**Mean: 0.550 mg/kg, Median: 0.413 mg/kg**) and highest concentration was detected in *S. Seenghala* from Farrukhabad from UMZ1 in Uttar Pradesh. The zone-wise mean concentration observed in muscle tissues of different fish species for Copper was UMZ2 (0.955 mg/kg)>UZ (0.854 mg/kg)>LZ (0.541 mg/kg)>LMZ (0.515 mg/kg)>UMZ1 (0.463 mg/kg)>LMZ (0.399 mg/kg).

Figure 3.14: Chromium concentration in fish muscle tissues

Highest chromium levels were observed in *S.richardsonii* (Dharasu), *L.bata* (Farrukhabad), *W.attu* (Bijnor), and, *S.seenghala* (Farrukhabad)

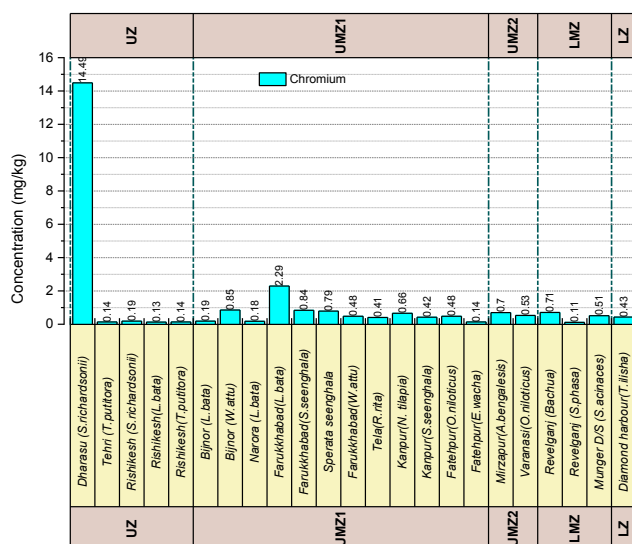
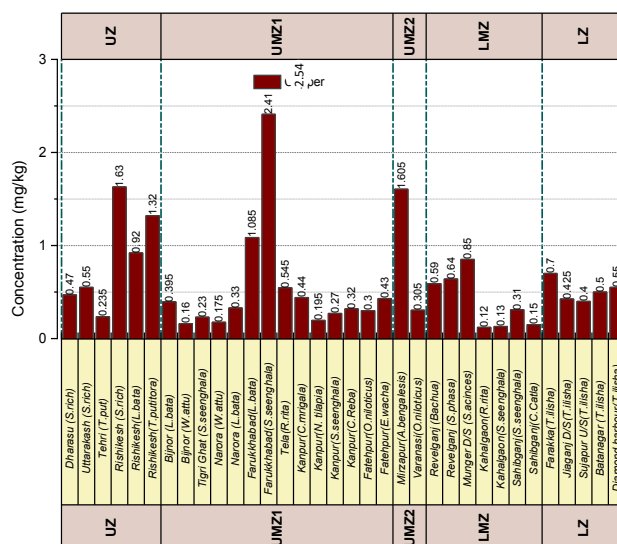


Figure 3.15: Copper concentration in fish muscle tissues

Highest copper levels were observed in *S.seenghala* (Farrukhabad), *S.richardsonii* (Rishikesh), *A.bengalensis* (Mirzapur), *T.putitora* (Rishikesh) and, *L.bata* (Farrukhabad)



4. Nickel

Nickel (Figure 3.16) concentrations ranged from BDL to 3.400 mg/kg (**Mean: 0.203 mg/kg, Median: BDL**). High concentration of Nickel (3.40mg/kg) was recorded in *S. richardsonii* collected from Dharasu in UZ. In the absence of industrial settlements in UZ these high concentrations could be attributed to natural geogenic deposition in sediments and their subsequent bioavailability under different aerobic and anaerobic conditions. The zone-wise mean concentration observed in muscle tissues of different fish species for Nickel was UZ (0.587 mg/kg)> LMZ (0.266 mg/kg)> UMZ1 (0.097 mg/kg)> LZ (0.043 mg/kg)> UMZ2 (BDL).

5. Arsenic

Arsenic (Figure 3.17) concentrations ranged from BDL to 1.820 mg/kg (**Mean: 0.195 mg/kg, Median: BDL**). Interestingly, as compared to other zones, high Arsenic contamination was recorded in fish species (*T. ilisha*) collected from Farakka in LZ, which could be associated with high distribution of arsenic in Ganga-Brahmaputra river basin due to both natural and anthropogenic sources. The zone-wise mean concentration observed in muscle tissues of different fish species for Arsenic was LZ (1.309 mg/kg)> LMZ (0.027 mg/kg) > UZ (0.018)> UMZ1 (0.011 mg/kg)> UMZ2 (BDL).

Figure 3.56: Nickel concentration in fish muscle tissues

Highest Nickel levels were observed *S.richardsonii* (Dharasu), *Bachua* (Revalganj), and, *L.bata* (Farrukhabad)

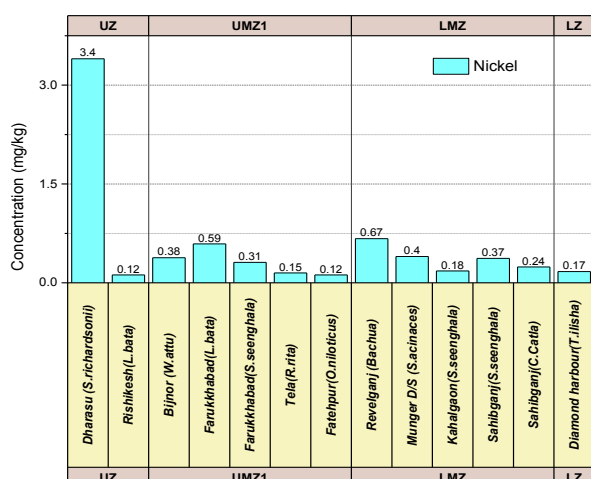
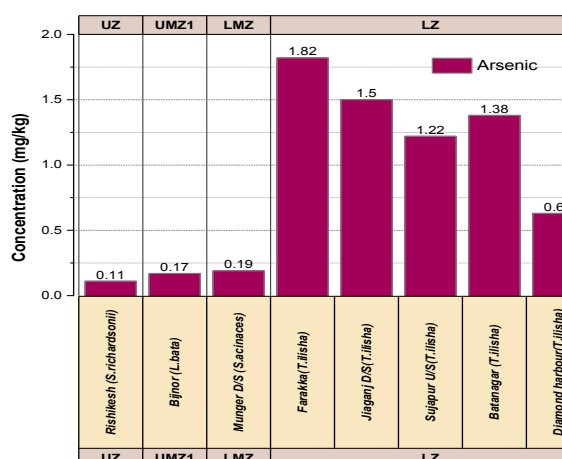


Figure 3.17: Arsenic concentration in fish muscle tissues

Highest Arsenic levels were observed *T.ilisha*, a fish species inhabitant of LZ (West Bengal)

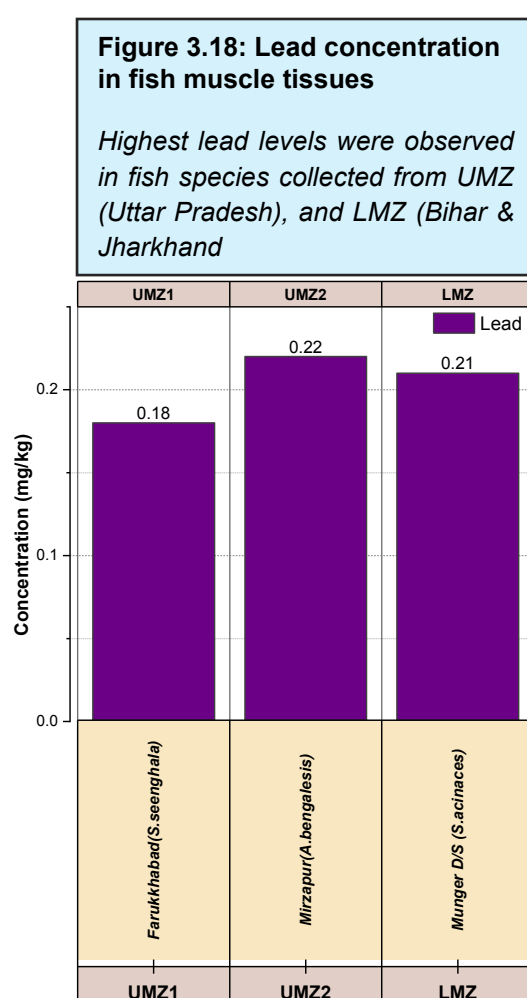


6. Mercury

Mercury concentration was recorded only in one fish species i.e. *Eutropiichthys vacha* (0.205 mg/kg) collected from the Fatehpur in UMZ2.

7. Lead

The Lead concentration were recorded in some fish species (Figure 3.18) such as *Anguilla bengalesis* (0.220 mg/kg), *S. acinaces* (0.21 mg/kg) and *Sperata seenghala* (0.180 mg/kg), collected from the heavily industrialised sites of UMZ.



8. Zinc

Zinc is an essential constituent of many enzymes important for growth in most organisms, including fish. However, its extreme levels could be detrimental to health of aquatic species. Zinc (Figure 3.19), in present study, was detected in all fish species and its concentrations ranged from 2.265 to 18.440 mg/kg (**Mean: 6.197 mg/kg, Median: 4.835 mg/kg**). Highest concentration was detected in *L.bata* (18.440 mg/kg) from Rishikesh in UZ whereas lowest was recorded in *S. Seenghala* (2.265 mg/kg) from Bijnor in UMZ1. The zone-wise mean concentration observed in muscle tissues of different fish species for Zinc was UZ (8.805 mg/kg)>UMZ2 (8.050 mg/kg)>LMZ (7.991 mg/kg)>UMZ1 (4.767 mg/kg)>LZ (4.391 mg/kg).

9. Iron

Like zinc, iron is also an essential metal for normal biological and metabolic functions and consequently was detected in all fish species. Though an essential element, however excess amount could led to adverse effects and damages in the body. Iron (Figure 3.20) concentrations ranged from 1.755 to 184.530 mg/kg (**Mean: 16.367 mg/kg, Median: 8.455 mg/kg**) among the fish species. Fish species with highest Iron concentration was *S. acina* found in Munger. The zone-wise mean concentration observed in muscle tissues of different fish species for Iron was LMZ (33.812 mg/kg)> UZ ((23.088 mg/kg) >UMZ2 (14.033 mg/kg) >UMZ1(9.273 mg/kg) >LZ(7.510 mg/kg).

Figure 3.19: Zinc concentration in fish muscle tissues

Although uniformly distributed, highest levels were observed in fish species collected from UZ, and UMZ.

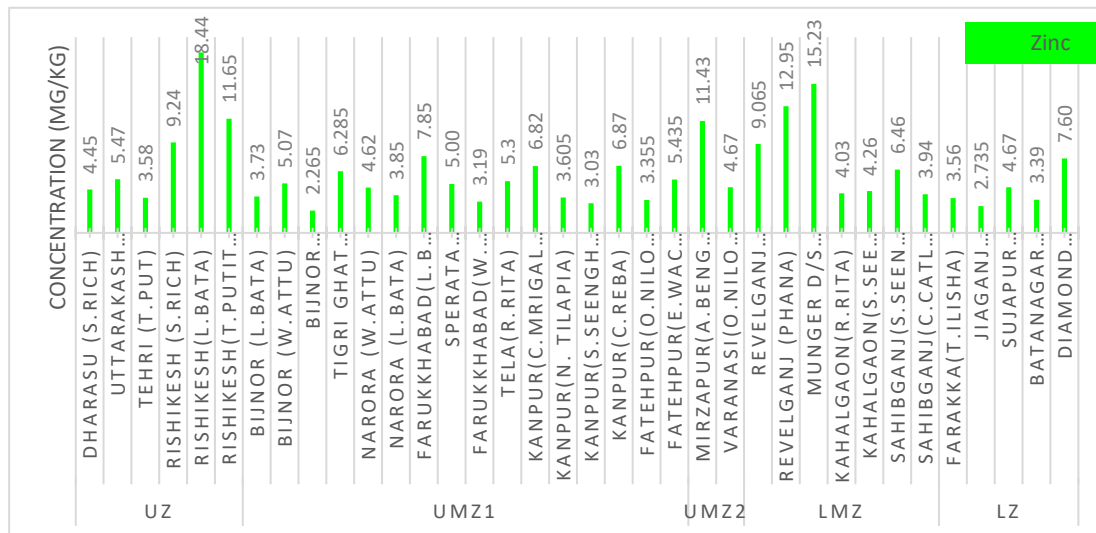
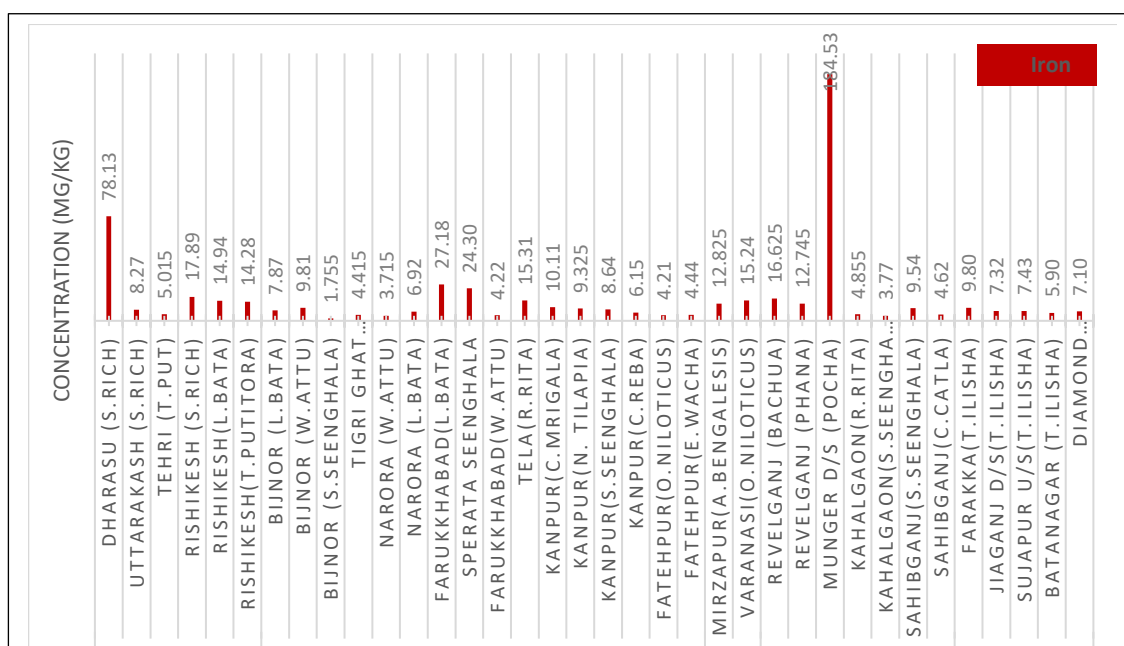


Figure 3.20: Iron concentration in fish muscle tissues

Although uniformly distributed, highest levels were observed in fish species collected from UZ, and UMZ.



Overview of findings and Priorities for filling information gaps – Bioaccumulation

Overview of findings

- The study of heavy metal contamination in fishes of Ganga River revealed different accumulation pattern in different fish species based on their habitat preferences habitat preferences and foraging behaviour.
- The zone-wise contamination status of some pesticides (such as HCHs, CHLs, H-CHLs) in fish species closely follows their dynamics observed in water compartment thus indicating the fresh inputs and bioavailability of these contaminants, for uptake by fish species.
- Since sediments from all zones did contain high levels of pesticides and heavy metals, uptake from sediments potentially plays a role in their subsequent bioavailability, under different aerobic and anaerobic conditions, especially among bottom dwelling and benthic fauna/fish that inhabit the lower zone of the water column such as *R.rita* and *L.bata*.
- Among the fish species, *S.richardsonii* (UZ; for HCHs, H-CHLs, OPPs, Nickel, and Chromium), *S.seenghala* (UMZ; for OCPs, OPPs, Copper, Chromium, and Lead), *T.ilisha* (LZ; for Pesticides and Arsenic), *L.bata* (UMZ; for OCPs, OPPs, Copper, Chromium, Arsenic, and Nickel), *R.rita* (UMZ; for DDTs), *A. bengalesis* (UMZ; for Copper, and Lead) showed highest accumulation suggesting risk for bio-magnification in the food-web (including risk for human consumption).

Priorities for filling information gaps

- Fishes are an important indicator of the level of pollution in an aquatic ecosystem. High levels of pesticides and heavy metals in fishes point towards bioaccumulation of these pollutants in the food chain and the ecological risk posed to different species, which can affect their survival and population in long term.
- There is a need to carry out controlled lab experiments to determine the metals, pesticide, and other emerging contaminants of concern (ECoC) uptake rates, response times and bioaccumulation in fish tissues, in order to monitor the behavioural changes (or any sub-lethal effects), fish population dynamics (fecundity, mortality etc.), breeding migrations, and predator-prey responses etc.
- Bioaccumulation and fish health indices need to be developed for effective biological monitoring and ecological mitigation measures
- Zones/stretchers with high bioaccumulation rates in fish species needs to be recognized nationally and the local people should be educated and informed about possible health risk.

Potential ecological risk assessment

In the present study, relatively higher concentrations of pesticides and heavy metals are reported from different stretches of Ganga River. Such high concentrations of these toxic chemicals have been reported earlier as well. Considering that most of target analytes in present study are endocrine disrupting compounds (particularly OCPs) and have the potential to cause an adverse health effect at very low concentrations, it raises concerns that measurable concentrations of such chemicals are found in Ganga River. Based on the differences in sensitivity of aquatic organisms to pesticides and heavy metals toxicity, chronic or short-term exposure to these toxic compounds can adversely affect their population dynamics. Therefore, it becomes highly imperative to evaluate the potential negative impacts of these contaminants on aquatic ecosystem of Ganga River. In this study, we have done a systematic assessment of ecological risk posed to aquatic species due to exposures to pesticides and heavy metals

5.1. Pesticides:

(i) Surface Water

An ecological risk assessment across a stretch of the Ganga was conducted using the ecological risk quotient (RQ) model. RQ is established based on Eq. (1).

$$RQ = \frac{MEC}{PNEC} \quad (1)$$

Where, MEC is the mean or maximum measured environmental concentration and PNEC is the predicted no-effect concentration. PNEC is derived from the lowest toxicity value (i.e., no-observed effect concentration (NOEC) value) observed for the most sensitive species. When NOEC values were not available, we used LC50 or EC50 values after correction by an assessment factor intended to extrapolate from acute to chronic toxicity and for

removing the uncertainty arising from the extrapolation from intra- and interspecies variability in sensitivity (European Commission, 2000).

In this assessment, the respective NOEC, LC50 or EC 50 values for three trophic levels (primary producers i.e., algae; primary consumers i.e., aquatic invertebrates; secondary consumers i.e., fish) were used to determine the PNEC.

Furthermore, to identify the high-risk zones, the average concentrations at each zone, of both seasons, was used for determination of the ecological risk scenarios, respectively.

The risk to aquatic species, based on risk ratios, was subsequently classified into four risk levels comprising high, medium, low, and negligible ecological risks, corresponding to RQ values ≥ 1 , 0.1–1, 0.01–0.1, and < 0.01 , respectively (Sanchez-Bayo et al., 2002; Palma et al., 2014; Zhang et al., 2016).

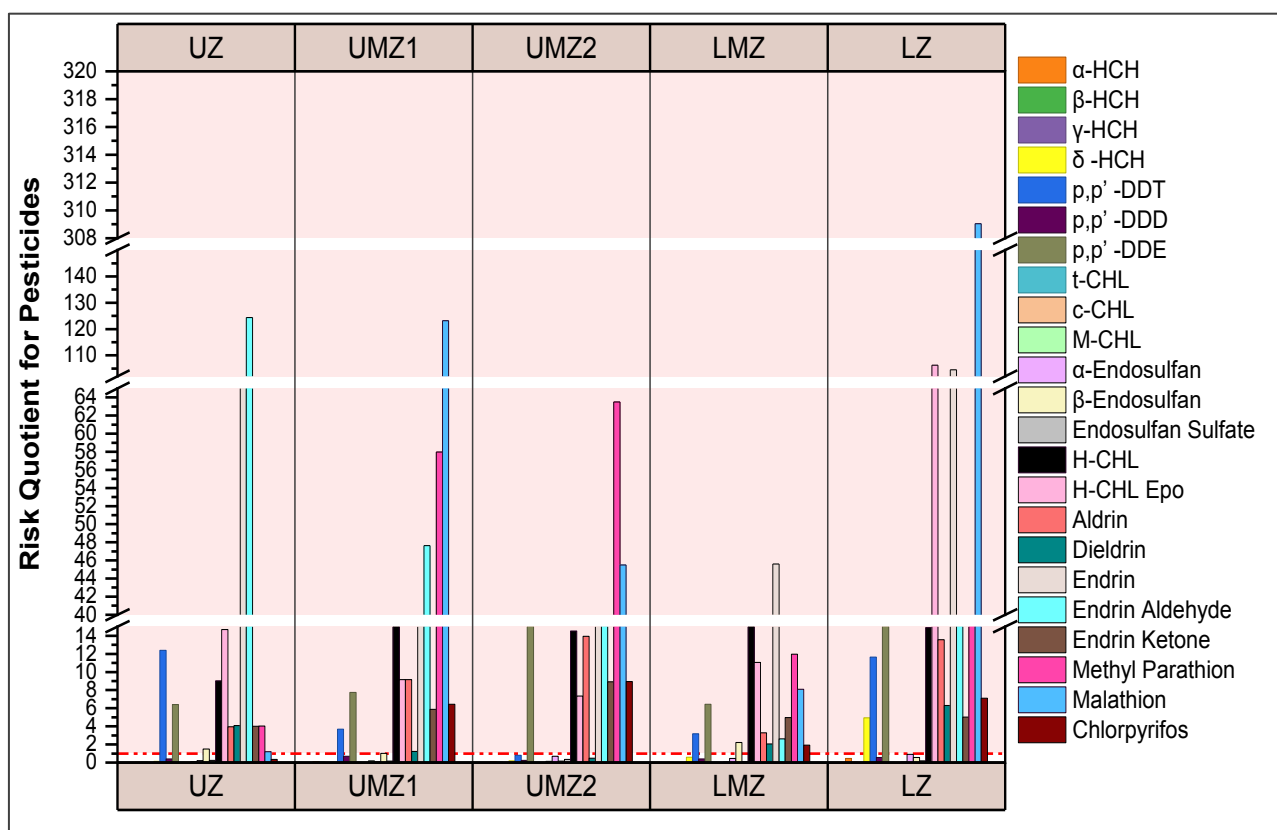
The RQ values (Figure 4.1a) derived from the seasonal data results revealed a high ecological risk (high RQ values (> 1)) in the LZ, due to majority of target pesticides, followed by zones UMZ2, LMZ, and UZ=UMZ1. These zones showed high risk for > 10 pesticides at 64%, 43%, 33% and 25% of the sampled sites respectively. High risk ($RQ > 1$) was observed for p,p'-DDT, p,p'-DDE, Heptachlor, H-Epoxy, DDTs, Methyl parathion, malathion and chlorpyrifos at majority of sites for both seasons. The high risk posed by these contaminants is mainly due to their relatively high toxicity to fish, algae or aquatic invertebrates. The mean RQ of individual OCPs and OPPs in the surface water of the Ganga River, for all the sites is presented in Figure 4.1b.

SURFACE WATER

Figure 4.1a: Zone-wise RQ of individual OCPs in surface water of the Ganga River in (a) Post-Monsoon and, (b) Post-Winter

High risk ($RQ > 1$), due to majority of the pesticides, was observed in LZ, followed by UMZ, LMZ, and UZ.

Drins, Heptachlors, p, p' DDT, p, p' DDE, Methyl Parathion, Malathion, and Chlorpyrifos were observed as pesticides posing higher risks to aquatic biodiversity



SURFACE WATER

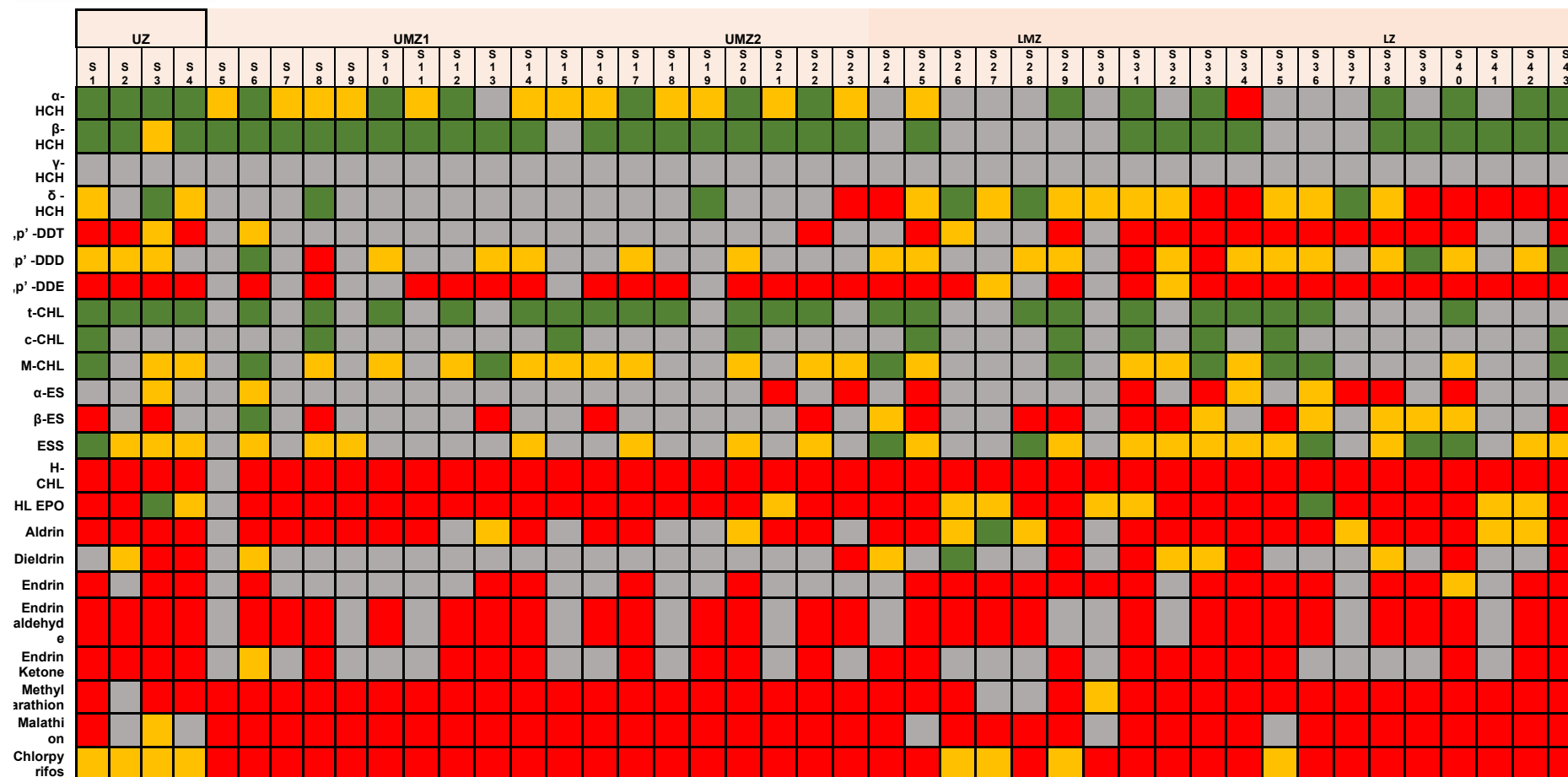


Figure 4.1b: Site-wise Ecological Risk Assessment of individual OCPs in surface water of the Ganga River

Mokama D/S(S31), Farrakka(S33), Jiaganj (S34), Garden Reach(S40), Diamond Harbour (S43), Narora(S8), Sangam, Prayagraj (S17), were identified as sites with high ecological risks to aquatic biodiversity

High Risk Moderate Risk Low Risk Negligible Risk

Ecological risk assessment for the Ganga River revealed that at all the sites there is high ecological risk to the aquatic organisms due to one or more than one pesticide (Figure 4.1a & b). As shown in figure 1, the ecological risk from all 23 pesticides at each site is depicted in red (high risk), orange (moderate risk), green (low risk) and grey as negligible risk. Accordingly, the sites in the upper zone i.e., state of Uttarakhand have high risk from 7-11 pesticides out of 23 pesticides investigated. In Uttar Pradesh, which constitutes middle zone 1 & 2 we found that the sites have high ecological risk from up to 11 pesticides investigated in this study. Narora, Kanpur, Jajmau, from UMZ1 and Sangam, Assi ghat, and Balia in UMZ2 showed high risk from more than 10 pesticides. Bijnor is the only site where only 3 pesticides (all OPPs) showed high ecological risk whereas, rest of the pesticides showed negligible risk. In LMZ of Bihar and Jharkhand, 3-12 pesticides were recorded to pose high ecological risk where Patna, Munger and Mokama downstream showed high risk from more than 10 pesticides. Mokama downstream surprisingly showed risk from 14 pesticides, making it one of the sites with ecological risks from highest number of pesticides. The samples from Patna reported risk from 12 pesticides. In LZ of West Bengal, most of the 11 sites reported high ecological risk from a large number of pesticides. Three sites (Farakka, Jiaganj and Diamond Harbour) reported high risk from 14 pesticides.

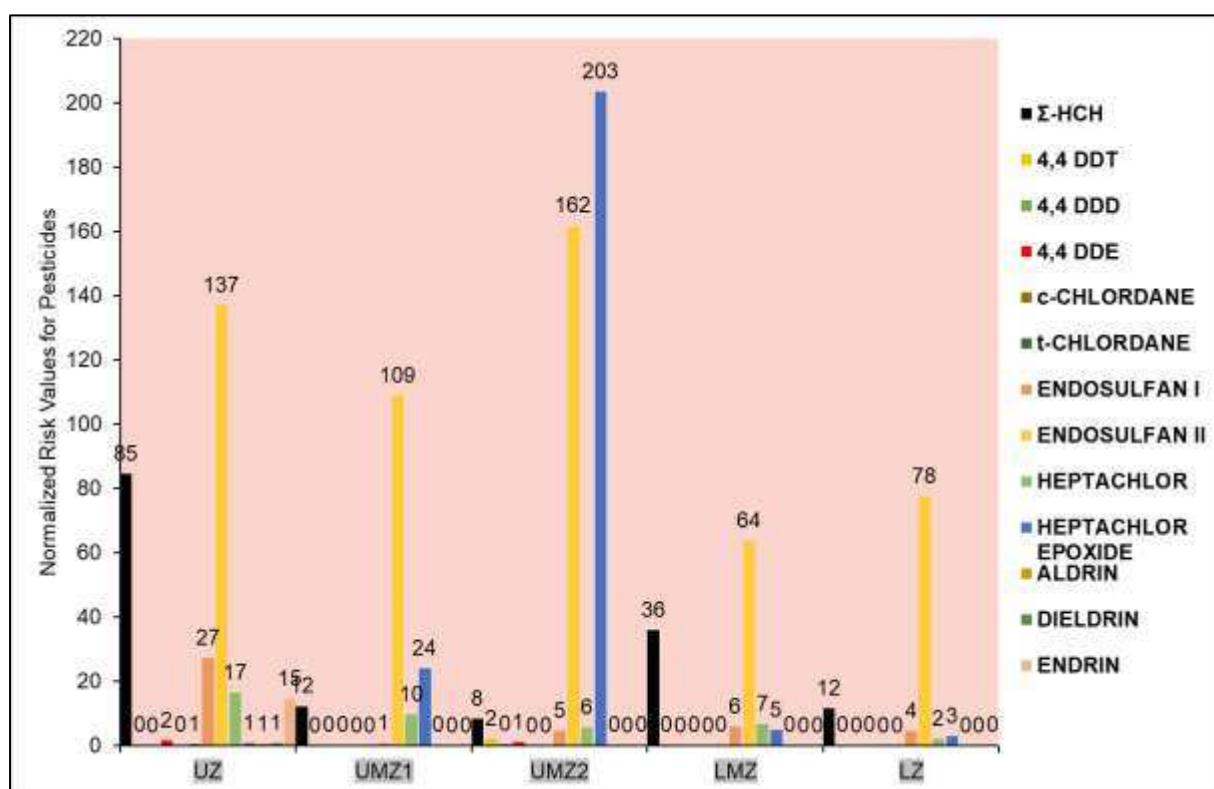
(ii) Sediments

Unlike surface water, there are no ecological risk assessment models available for sediments. Therefore, to estimate the ecological risks posed by pesticides present in riverbed sediments, we have adopted the concept of normalization wherein the values measured on different scales were adjusted to a common scale. Therefore, as per normalization concept, for present study, concentration of each pesticide is divided by its own guideline threshold value as established by USEPA or Canadian ISQG (Interim Sediment Quality Guidelines) for freshwater sediments. Subsequently, the threshold value for all pesticides is converted into common scale of 1 (new threshold value) in order to attain alignment in representation.

Normalization is performed for those pesticides with available threshold guideline values. The normalized threshold value (Figure 3) derived from the seasonal data results revealed a high risk due to majority of target pesticides. The results of zone-wise and site-wise ecological risk posed by individual pesticides present in sediments of Ganga River are presented in Figure 4.2. High Risk was observed in all zones due to T-HCH, Endosulfan (I & II), Heptachlor and Hept-Epoxy. In addition UZ also showed High risk due to p,p'DDE and Endrin, while UMZ2 showed high risk due to p,p'DDT and p,p'DDE. Results indicate that unlike water where LZ was at high ecological risk, the sediment contamination point towards UZ and UMZ2 at more risk from historical contamination. Urgent attention needs to be paid to lower the pesticide load in these segments either by increasing the water flow, introducing detoxification drives or other technological interventions, in addition to immediate ban on illegal use of already banned pesticides.

SEDIMENT

Figure 4.2: Zone-wise ecological risk posed by individual pesticides present in surface sediments of Ganga River



5.2. Heavy Metals

1. Surface Water

The ecological risks posed by heavy metals to aquatic ecosystem were estimated as per the Risk Quotient (RQ) approach. Risk Quotient (RQ) technique, which can be applied in order to determine if measured or predicted levels of environmental parameters are likely to cause harm to environmental/human targets. It can be accomplished by comparing their measured or predicted environmental concentrations (MECs or PECs) with appropriate threshold values or predicted no-effect concentrations (PNECs) to get Risk Quotients (RQs). The PNEC value calculation was made using an assessment factor (AF) of 1000 applied for acute toxicity values–LC50 (96 h) or 10 applied for chronic toxicity values–NOEC/EC 50, which expresses the degree of uncertainty in the actual environmental extrapolation. The risk quotients (RQs) between MEC values and acute or chronic PNECs were calculated, Risk was then categorized as low ($RQ \leq 0.1$), moderate ($0.1 < RQ < 1.0$) and high risk ($RQ \geq 1.0$). The values above 1 (>1) represents high ecological risks to aquatic ecosystem. The results of zone-wise and site-wise ecological risk posed by individual heavy metals present in water of Ganga River are presented in Figure 4.3.

Zone wise comparison shows (Fig 4.3) $LZ > UMZ1 > LMZ = UMZ2 = UZ$, where LZ shows high ecological risk from 5 out of 8 heavy metals studied at most of its sites. Additionally, this was the only zone also that showed high risk from Lead (one of the most toxic metals).

Among the metals, Zinc and Iron were found to pose high risk at all the 43 sites across the zones. Further, high ecological risk was recorded for Nickel, Chromium, Copper, and Lead at sites marked RED in Fig 4.3.

Figure 4.3: Ecological risk posed by individual heavy metals present in surface water of Ganga River

High ecological risk (>1) is indicated in RED while moderate risk is indicated in YELLOW. WHITE cells indicate negligible or no risk.

	UZ				UMZ1												UMZ2								LMZ								LZ												
	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14	S15	S16	S17	S18	S19	S20	S21	S22	S23	S24	S25	S26	S27	S28	S29	S30	S31	S32	S33	S34	S35	S36	S37	S38	S39	S40	S41	S42	S43		
Nickel	Red					Red	Red		Red			Red				Red																						Red	Red	Red	Red	Red	Red	Red	
Arsenic										Yellow						Yellow	Yellow			Yellow	Yellow	Yellow							Yellow																
Cadmium																																													
Chromium						Red	Red		Red			Red				Red	Red																					Red	Red	Red	Red	Red	Red	Red	
Copper						Red	Red		Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red
Lead																																													Red
Zinc (Zn)	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red
Iron	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red

2. Surface Sediments

Håkanson (1980) developed a method to evaluate the ecological risks due to heavy metal pollution in aquatic sediment. The procedure is based on the assumption that the sensitivity of the aquatic system depends on its productivity. The potential ecological risk (E_r^i) was introduced to assess the degree of heavy metal pollution in sediments, according to the toxicity of heavy metals and the response of the environment:

$$E_r^i = T_r^i C_f^i$$

$$C_f^i = C_o^i / C_n^i$$

$$RI = \sum_{i=1}^n E_r^i$$

Where,

E_r^i = potential ecological risk factor,

T_r^i = Toxic-response factor for a given heavy metal, which accounts for the toxic and the sensitivity requirement.

C_f^i = Contamination factor,

C_o^i = Concentration of heavy metals in the sediment,

C_n^i = Background value for heavy metals

RI = Potential Ecological Risk Index due to Total Heavy Metals

Based on the equation, the categorization of ecological risk (E_r^i) is listed in Table 4.1:

Table 4.1: Categorization of E_r^i and RI		
Criterion	E_r^i	RI
Low	<40	<150
Moderate	40–80	150–300
Considerable	80–160	300–600
High	160–320	≥600
Very high	≥320	

The potential ecological risk index (RI) results for heavy metals in sediments revealed low risk (RI<150) in all the zones. The results of zone-wise Potential Ecological Risk Index (RI) from total heavy metal contamination and site-wise ecological risk (E_r^i) posed by individual heavy metals present in sediments of Ganga River are shown in Figure 4.4a & b respectively.

SEDIMENT

Figure 4.4a: Zone-wise Potential Ecological Risk Index (RI) in sediments

**Results for Mercury and Iron not included in RI. Mercury concentration were found below detection limits whereas Iron is considered unsuitable as sediment parameters in a risk index*

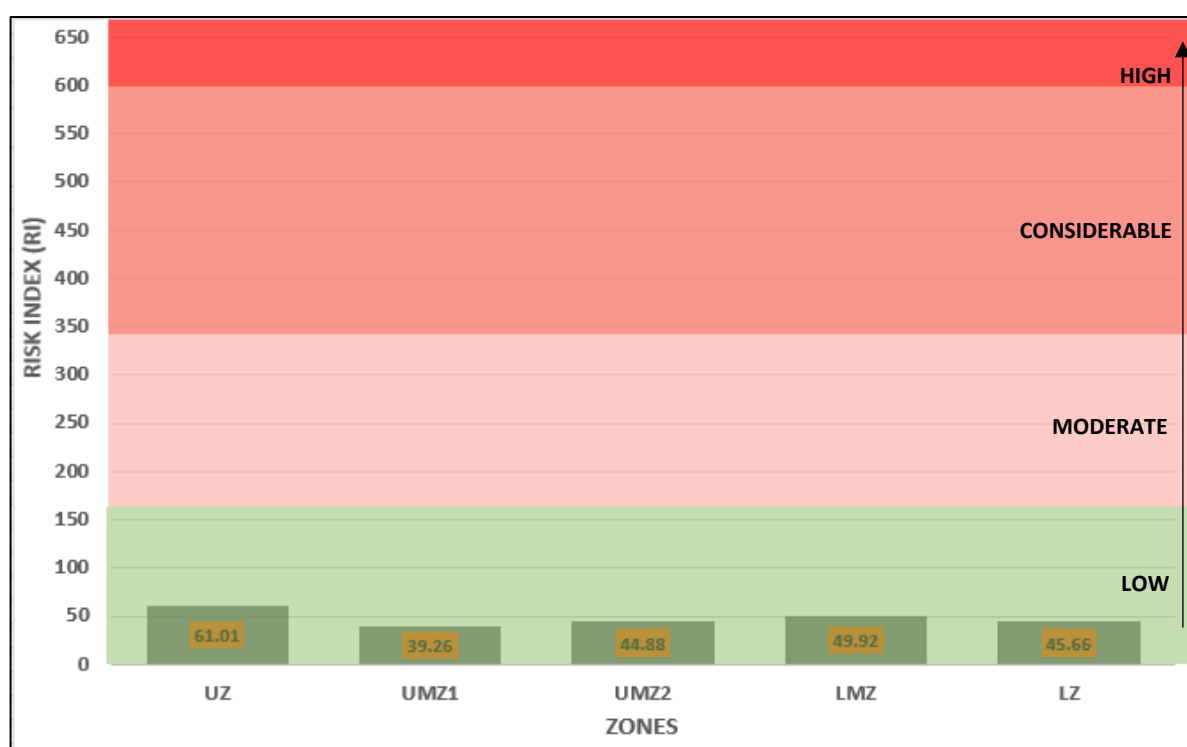
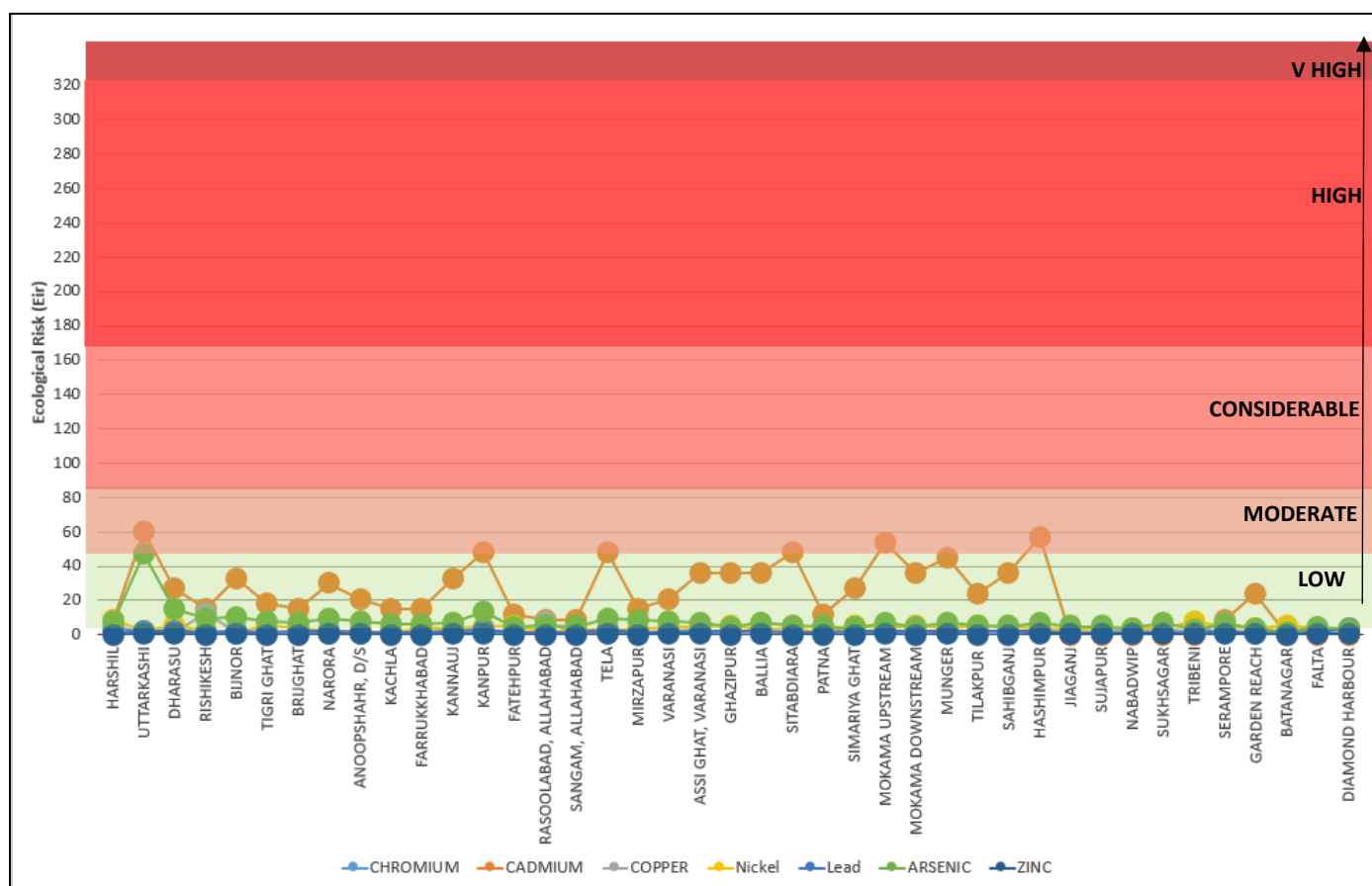


Figure 4.4b: Site-wise ecological risk posed by individual heavy metals present in sediments

Moderate Risk observed due to Cadmium at most of the sites except some sites from LZ



As shown in Figure 4.4b for zone wise contamination in sediment compartment, all the zones showed low risk from total heavy metals. In calculating potential ecological risk due to total heavy metals, risk due to Iron (Fe) was not included. Fe, Mn and P are unsuitable as sediment parameters in a risk index because their appearance is often governed by physical/chemical processes in the sediments, which cannot unambiguously be linked to contamination. These elements often show very complex sedimentological distribution patterns.

Mercury levels were below detectable limits; hence mercury was also not added in the total Risk Index.

Ecological risk due to individual heavy metal (E_{ir}) at each site (Figure 4.4b) showed that moderate risk exists due to Cadmium at almost all the sites except some sites in LZ. Moderate risk is also observed for Arsenic at Uttarkashi in UZ.

5.3. PCBs

An ecological risk assessment associated with PCBs in riverine environment was conducted based on the potential ecological risk index (ERI), established by Hakanson (1980) and followed by other studies (Cui et al. 2016; Lai et al. 2015). This ERI was designed to calculate the extent of water pollution that provides a rapid analysis and simple numerical value for the likely ecological risk of a specific pollution state.

$$E_i^r = T_i^r * C_i^f \quad (1)$$

$$C_i^f = C_i^o / C_i^n \quad (2)$$

Where,

E_i^r = monomial potential ecological risk factor

T_i^r = toxic-response factor for PCBs (here T_i^r for PCBs is 40), obtained from standardized PCBs toxic factor developed by Hakanson (1980).

C_i^f = Contamination factor, calculated with the help of C_i^o (PCB concentration in sediments) and C_i^n reference value for PCBs (0.01 ppm or 10 ng/g).

Hakanson (1980) categorizes the potential ecological risk factors of a particular contaminant into the following categories:

	Very high potential ecological risk ($E_i^r > 320$)
	High potential ecological risk ($E_i^r = 160-319$)
	Considerable potential ecological risk ($E_i^r = 80-159$)
	Moderate potential ecological risk ($E_i^r = 40-79$)
	Low potential ecological risk ($E_i^r < 40$)

Figure. 4.5 shows the Ecological risk posed $\Sigma 11$ PCB Congeners across different zones. Accordingly, UMZ2 emerged as the zone with considerable ecological risk. UMZ 1 and LMZ posed moderate while UZ and LZ posed low potential ecological risk.

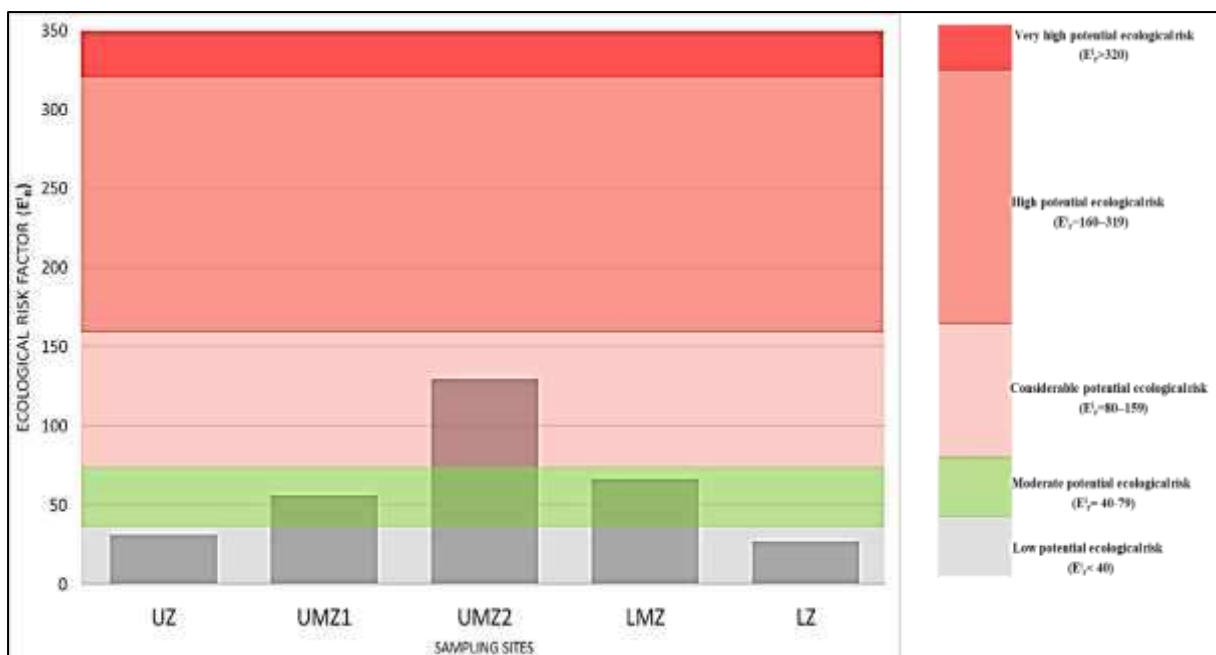


Figure 4.5. Zone wise Ecological Risk Assessment due to Σ_{11} PCB Congeners

Figure 4.6 identifies the ecological risk due to individual PCB congeners. It was observed that PCB 126 posed high potential ecological risk whereas PCB 101 presented moderate potential ecological risk. Rest of the congeners appeared under the low ecological risk category.

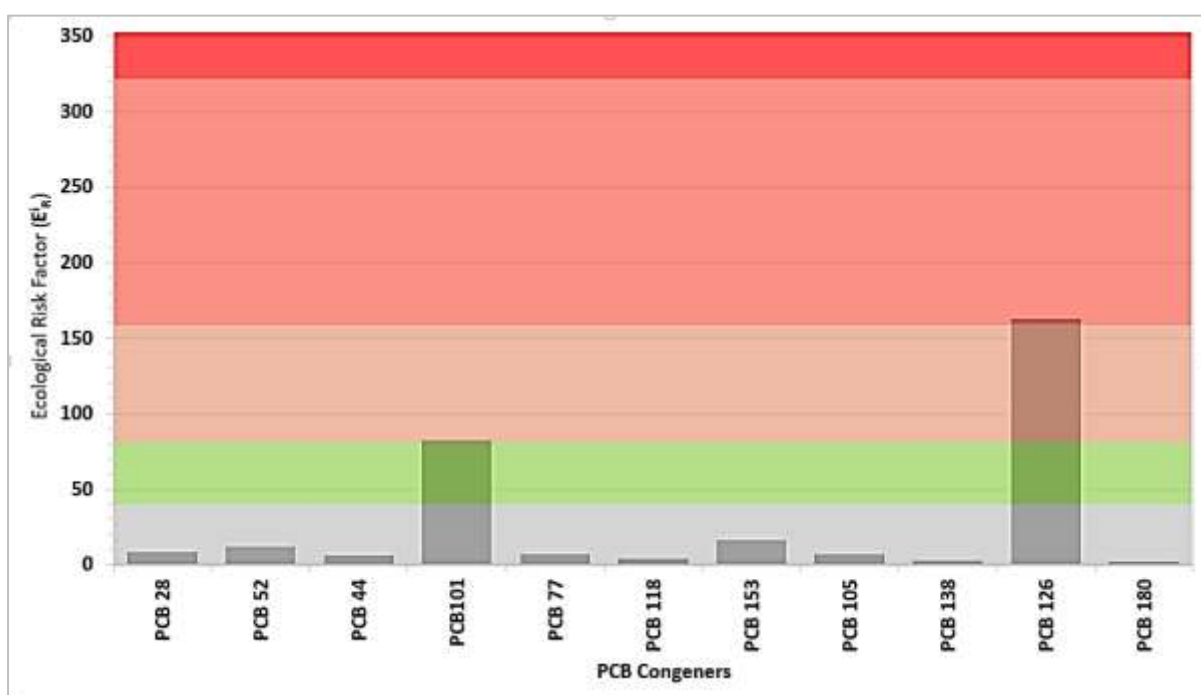


Figure 4.6. Ecological Risk Assessment due to Individual PCB Congener

Based on the ERA, it is recommended that UMZ and LMZ must be prioritized for implementing PCB contamination mitigation strategies. The recent order of NGT imposing ban on open burning of e-waste and dumping of e-waste of the Ganga (NGT, 2019) is a welcome step. At the same time, it is important that this order is implemented not only on Ramganga but in entire Uttar Pradesh so that the direct discharge into Ganga can be prevented. Further, technological intervention is required for removal of heavier PCBs like 126 and 101 from Ganga as they pose moderate to considerable risk and have the potential to break down into lighter PCB and persist in the ecosystem for longer time thus posing risk to the biodiversity at large.

• • • • •

Overview of findings and Priorities for filling information gaps - ERA

Overview of findings

- Ecological risk assessment (ERA) for the Ganga River revealed high ecological risk to the aquatic organisms due to one or more pesticides.
- For Water, LZ (West Bengal) emerged as the high-risk zone. High industrial settlements, high cropping intensity, low river flow due to abstraction of water from dams/barrages, could be the possible reasons for high ecological risks in these zones. *p, p' DDT, p, p' DDE, Heptachlors, Hept-Epoxyde, Drins, Methyl Parathion, Malathion, and Chlorpyrifos were identified as pesticides posing higher risks to aquatic biodiversity.*
- Among individual sites, Mokama downstream (UP) showed high risk from maximum number (14) of pesticides.
- For pesticides, in surface sediments High Risk was observed in all zones due to T-HCH, Endosulfan (I & II), Heptachlor and Hept-Epoxyde. In addition UZ also showed High risk due to p,p' DDE and Endrin, while UMZ2 showed high risk due to p,p' DDT and p,p' DDE.
- ERA for Heavy metals in water exposed LZ as the zone with high ecological risk. Among the metals, high risk was observed for Nickel, Chromium, Copper, and Lead. High risk was also observed for Zinc and Iron at all the 43 sites across the five zones.

Priorities for filling information gaps

- Results indicate that unlike water where LZ was at high ecological risk, the sediment contamination point towards UZ and UMZ2 at more risk from historical contamination. Urgent attention needs to be paid to lower the pesticide load in these segments either by increasing the water flow, introducing detoxification drives or other technological interventions, in addition to immediate ban on illegal use of already banned pesticides.
- Pesticides and heavy metals in aquatic ecosystems usually occur as a mixture of multiple pesticides/heavy metals rather than individually. Therefore, further research on the potential combined eco-toxicological effects (synergistic, additive, or antagonistic) of contaminants mixture is warranted.
- To ensure a healthy ecosystem for the biodiversity of the Ganga, we propose a holistic ecological risk assessment that includes population-level risk assessment at each critical habitat to evaluate the long-term effects of multiple stressors on aquatic populations.
- Aquatic life criteria threshold guidelines values or Sediment quality guideline values are developed considering different approaches/areas such as water/sediment chemistry, controlling factors of bioavailability, and

- The potential ecological risk index (RI) results for total heavy metals in sediments revealed low risk in all the zones. Ecological risk due to individual heavy metal at each site showed that moderate risk exists due to Cadmium at almost all the sites except some sites in LZ. Moderate risk is also observed for Arsenic at Uttarkashi in UZ.
- For PCBs, Ecological risk posed by $\Sigma 11$ PCB Congeners across different zones showed UMZ2 as the zone with considerable ecological risk. UMZ1 and LMZ posed moderate while UZ and LZ posed low potential ecological risk.
- Out of all the 11 PCBs, the congener-PCB 126 posed high potential ecological risk whereas PCB 101 presented moderate potential ecological risk.

in situ biological (acute and chronic toxicity testing) effects to predict the adverse biological effects caused by contaminated water/sediments to aquatic biota. As these approaches may vary spatially (from country to country), therefore it is suggested that India should develop its own Aquatic life criteria threshold guidelines values and Sediment quality guideline values in order to ensure enhanced ecological risk assessment.



Chapter 6

Physico-chemical Quality Parameters

The main pollution parameters that have to be considered for surface water quality management, in general, include water temperature, pH, dissolved solids, dissolved oxygen, compounds of nitrogen (Nitrates and Ammonium), conductivity, etc. For the present study, all of the above parameters have been evaluated by using digital kit **ProDSS and YSI**.

1. pH

pH is the negative logarithm of the hydrogen ion (H^+) concentration of a solution and is a measure of whether the liquid/solid is alkaline or acid. In fresh water bodies, hydrogen ion is governed by the equilibrium between carbonate ions, carbon dioxide and bicarbonate. The pH scale ranges from 1.0 (very acid, when more $[H^+]$), 7 (neutral, when $[H^+] = [OH^+]$) to 14 (very alkaline, when more $[OH^+]$). Atmospheric deposition due to acid rain and wastewater discharges are some of the key contributors that can change the pH. It is likely to increase during the day largely due to the consumption of carbon-dioxide for photosynthetic activity and falls during night due to respiratory processes. pH affects many biological and chemical activities in the water bodies e.g., different organisms flourish within different pH ranges. However, most of the aquatic animals prefers a pH range of 6.5 to 8.5. A pH outside this range could reduce the biodiversity in the water systems as it may stress the physiological systems of many organisms and can reduce their reproduction potential. Additionally, a low pH can result in high mobility and bioavailability of toxic contaminants for uptake by different aquatic plants and animals. This can result in circumstances that are highly toxic to aquatic life, particularly to vulnerable or sensitive species.

Symbol (physical parameter)	pH
Units Used for Analytical Results	pH units
Method(s) used for analysis	Digital calibrated water quality probe meter with pH sensitive probe. Calibrated at 3 point calibration range at 4.0 (acidic), 7.0 (neutral) and 10.0 (basic)
QC/QA	QC (Standards checked) after analysis
Aquatic Life Criteria	6.5-8.5 is preferable

In the present study the range of natural pH, in post-monsoon season, extends from around, **7.49 to over 8.79** between all the five states whereas, in post-winter sampling, the range of pH extends from around, **7.73 to over 8.96**.

Figure 5.1 shows the zone-wise and site-wise seasonal assessment of pH along with the presence of five species of conservation significance in those zones. The relatively higher values of pH in post-monsoon months coinciding with maxima of total rainfall may be attributed to the considerable dilution of water which increases the buffering effects of the systems. The river water seems to possess high buffering capacity as evidenced by pH fluctuation within a narrow range. However, high pH values in post winter season may be attributed to discharge of unregulated and untreated industrial and sewage effluents. High fluctuation in pH values (above the aquatic life criteria range of 6.5-8.5 were recorded at many sites in LZ, and some sites in LMZ and UMZ.

As seen in Figure 5.1, the water quality from **Bijnor to Narora** (post-monsoon and post – winter), is within the permissible range (6.5-8.5) and biodiversity of this stretch in UMZ1 is the highest of the total river with presence of all the five species of conservation significance.

pH Permissible range for aquatic life criterion = 6.5-8.5

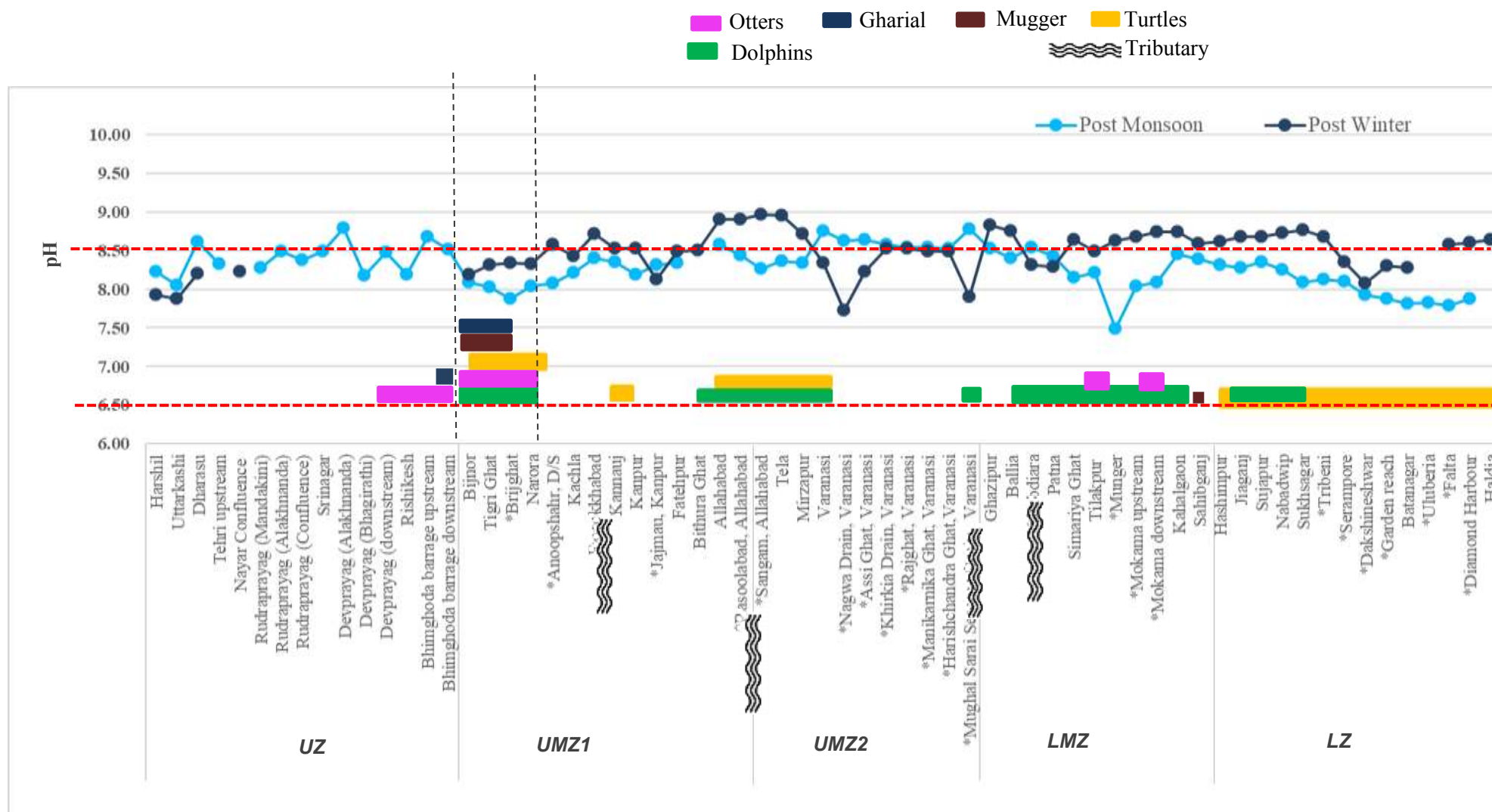


Figure 5.1: pH range recorded in five zones along the bank of river Ganga in Post-Winter & Post-Monsoon

2. Dissolved Oxygen (DO- mg/L)

Dissolved oxygen (DO) is measure of oxygen in its dissolved form. DO levels decline if more oxygen is consumed than is produced, and some sensitive and vulnerable animals may weaken, diverge, or die. Different biological and chemical processes can result in decline of DO, for example biological decomposition of effluents from wastewater and sewage treatment plants, that contains high amount of organic materials, by microorganisms. The levels of dissolved oxygen can fluctuate seasonally or within a period of 24-hour. They also fluctuate with altitude and water temperature as warm water reportedly holds less oxygen than cold water and also at higher altitudes water holds relatively less oxygen.

Symbol (physical parameter)	DO
Units Used	mg/L O ₂
Method(s) used for analysis	Digital calibrated water quality probe meter with DO sensitive probe
QC/QA	QC (Standards checked) after analysis
Aquatic Life Criteria	>5 mg/L is preferable

Figure 5.2 shows the zone-wise and site-wise seasonal assessment of DO along with presence of five species of conservation significance.

DO values during the post-monsoon were higher than post-winter season. Dilution factor post the rainy season is responsible for increasing the levels of oxygen as compared to post winter season. However, the dramatic fluctuations in DO levels during post-winter sampling, in sites representing the industrial and urbanized belts of UMZ1 (Jajmau, Kanpur to Rasoolabad, Allahabad), UMZ2 (Drains and Ghats of Varanasi) and LZ (Serampore to Batanagar) is indicative of untreated or partially treated industrial wastes and municipal sewage, organic discharges, and anoxic discharges which use up DO. As seen in Figure 5.2, the DO levels from **Bijnor to Narora**, in both the sampling season (post-monsoon and post-winter), is well above

the minimum level for aquatic life criteria (≥ 5 mg/L) and presence of all the five species of conservation significance was also recorded in this stretch.

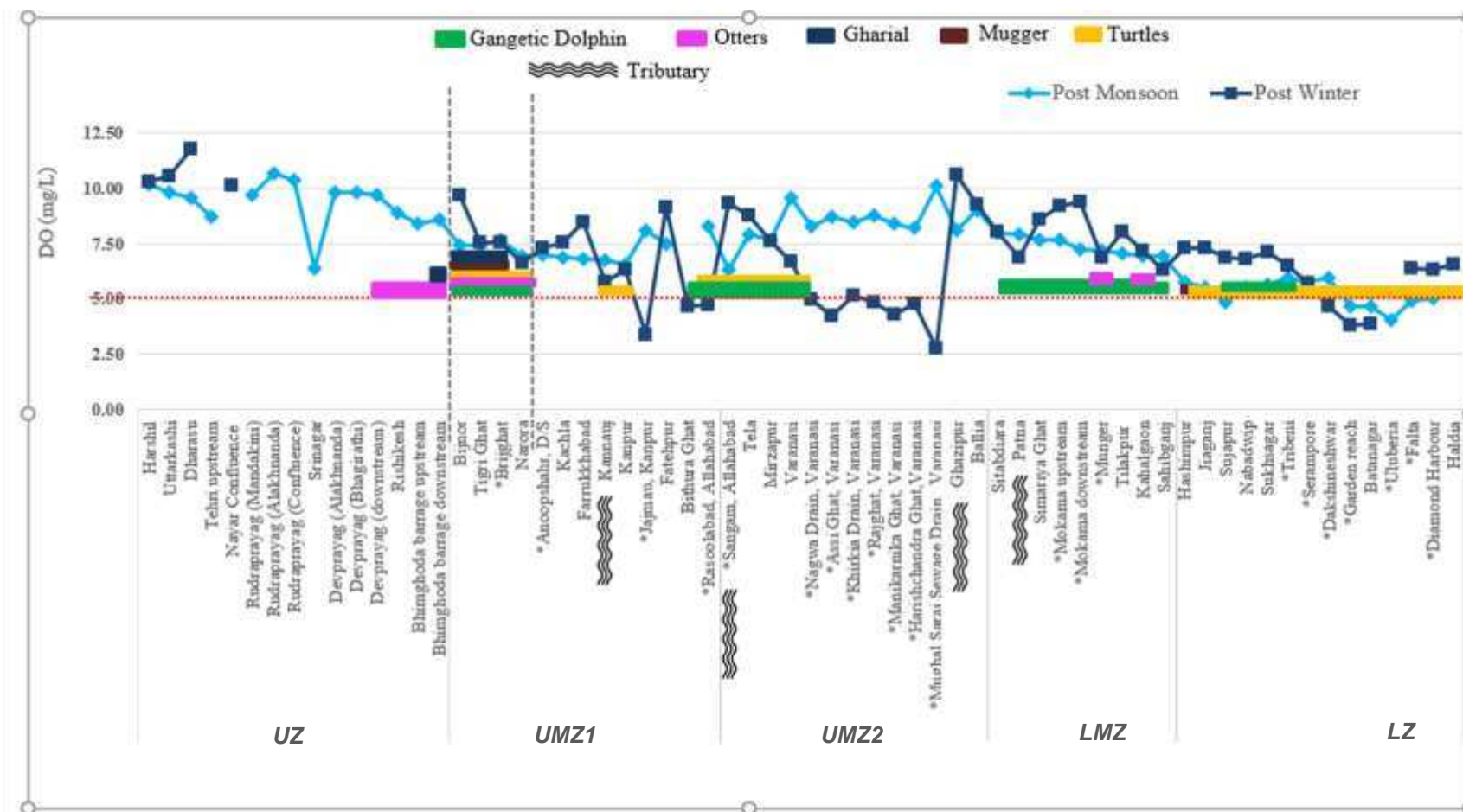


Figure 5.2: DO range in five zones along the bank of river Ganga in Post-Winter & Post-Monsoon

3. Total Dissolved Solids (TDS, mg/L)

In water bodies, total dissolved solids (TDS) consist of different ions (chlorides, calcium, nitrate, phosphorus, iron, sulphur, etc.,) that traverse through a 2 µm filter paper. The levels of TDS can affect the water equilibrium in the cells of aquatic species which in turn can disturb their cell density and eventually the ability to maintain their position in the water system. Elevated levels of TDS can serve as transporters of toxicants, which can readily adhere to suspended particles. This is particularly problematic areas such as in agricultural belts where high amount of pesticides is being used and areas where there is high discharge of untreated industrial effluents.

Symbol (physical parameter)	TDS
Units Used	mg/L Dissolved Solids
Method(s) used for analysis	Digital calibrated water quality probe meter with TDS sensitive probe
Occurrence/Origin	Agricultural runoffs, industrial and sewage discharge
QC/QA	QC (Standards checked) after analysis
Aquatic Life Criteria	<500 mg/L is preferable

In the present study, the range of TDS, in post-monsoon season, extends from around **52.75 mg/L** to over **378.58 mg/L** between all the five zones whereas, in post-winter sampling, the range of TDS extends from around, **110.15 mg/L** to over **9642 mg/L**.

The mean values (Figure 5.3) for the total dissolved solids (TDS) were higher in low precipitation season (post-winter) than in the high precipitation season (post-winter). The lower values of this parameter in post-monsoon season suggest that the runoff water contributes to its dilution in the rainy season. As seen in Figure 5.3, the TDS level in all zones, in both the sampling season (post-monsoon and post-winter),

were recorded to be well above the minimum permissible level for aquatic life criteria (≥ 500 mg/L).

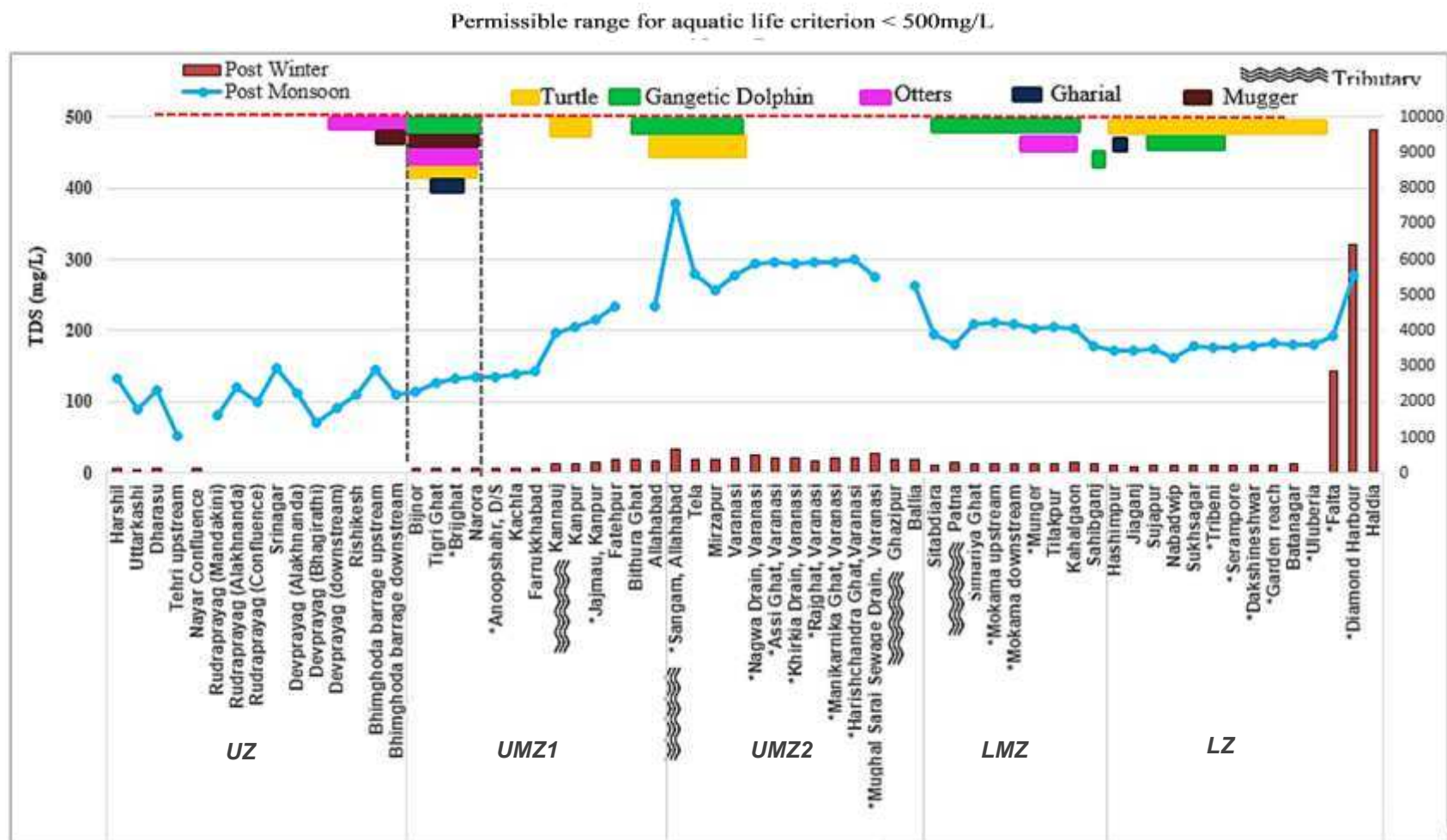


Figure 5.3: TDS range in five states along the bank of river Ganga in Post-Winter & Post-Monsoon

*Additional Sites

4. Nitrates (NO_3^- , mg/L)

Nitrates are essential plant nutrients that are present in several different forms in aquatic and terrestrial ecosystems. Some of these forms of nitrogen include nitrites, ammonia, and nitrates. Mineral origin nitrates (NO_3^-) in water bodies are relatively little. Though, microbacterial oxidation and nitrogen fixation by plants can also produce nitrates, most of the nitrates found in rivers is from organic and inorganic sources, like agricultural runoffs and waste discharges. In excess amount Nitrates can cause substantial water quality problems like enhanced eutrophication, and variations in the different plants and animals that inhabits the water systems. This sequentially can affect the other important water quality parameters and indicators like temperature and dissolved oxygen.

Excessive levels of NO_3^- may result in hypoxia due to low levels of dissolved oxygen and under specific conditions it may result in toxicity to animals at levels >10 mg/L. The natural level of nitrate and ammonia in fresh water systems is usually at low concentration of < 1 mg/L, however with untreated wastewater effluents, it can shoot up to 30 mg/L.

Symbol (physical parameter)	NO_3^-
Units Used for Analytical Results	mg/L of N or mg/L of NO_3^-
Method(s) used for analysis	Digital calibrated water quality probe meter with NO_3^- sensitive probe
Occurrence/Origin	Oxidation of ammonia, Agricultural fertiliser runoffs, industrial and sewage discharge
QC/QA	QC (Standards checked) after analysis
Aquatic Life Criteria	<10 mg/L is preferable

In the present study the range of nitrates, in post-monsoon season, extends from around, **0.05 mg/L to over 12.08 mg/L**. However, in post-winter sampling, the range of nitrates extends from around, **0.27 mg/L to over 550 mg/L**. The high and

concentrated nitrate levels recorded during post-winter season may be attributed to high evaporation (low water level), and lower flow volume. The reason for the high nitrate values at some sites in LMZ and LZ could be attributed mainly to agricultural fertiliser runoffs. In LZ, the nitrate concentration exceeded at 5 out of 13 sites sampled. Diamond Harbour and Haldia showed exceptionally high levels of nitrates, which is reflective of the eutrophic condition of the water. Effluents from industries adjacent to Diamond Harbour and Haldia and domestic sewage from upstream Kolkata add nutrients including reactive nitrogen to the system. The area is also rich in ground water nitrate.

As seen in Figure 5.4, nitrate levels from **Bijnor to Narora**, in both the sampling season (post-monsoon and post-winter), are well below the minimum permissible level for aquatic life criteria (<10 mg/L) and the presence of all the five species of conservation significance indicates that aquatic biodiversity of this stretch is the highest of the total river.

Permissible range for aquatic life criterion < 10 mg/L

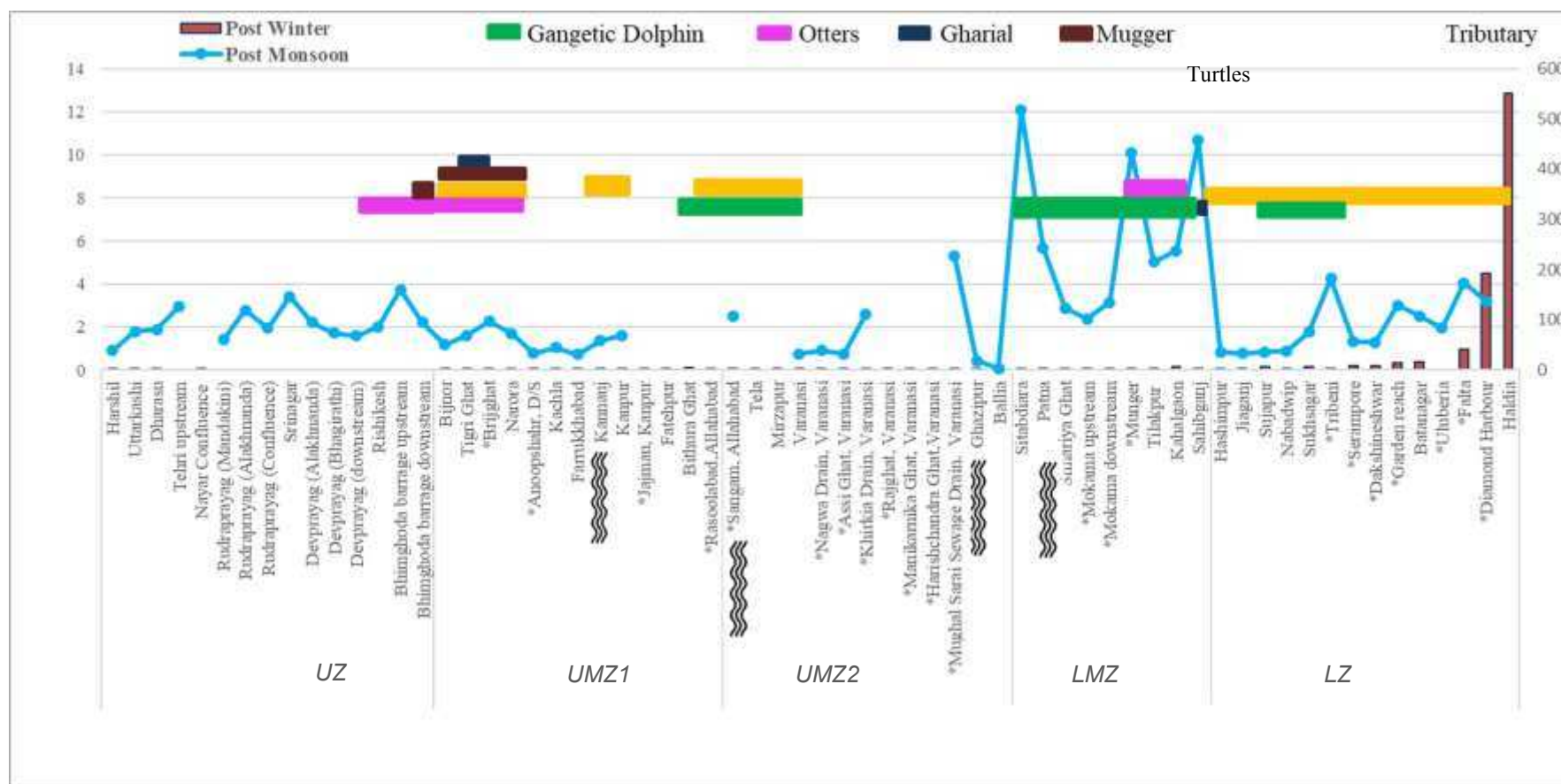


Figure 5.4: Nitrate concentration range recorded in five states along the bank of river Ganga in Post-Winter & Post-Monsoon

*Additional sites

5. Specific Conductivity ($\mu\text{S}/\text{cm}$)

The ability of water to pass an electrical current is defined as conductivity and it is measured in micro siemens per centimetre ($\mu\text{S}/\text{cm}$) or micromhos per centimetre ($\mu\text{mhos}/\text{cm}$). The temperature affects the conductivity measurements therefore the standard method for reporting conductivity is the measurement of conductivity recorded at or corrected to 25°C and is defined as specific conductance ($\mu\text{S}/\text{cm}$). One of the important factors that can affect specific conductivity (SPC) in water is the presence of dissolved solids or ions. Similarly, conductivity is directly proportional to change in temperature i.e., elevated water temperatures results in higher the conductivity. Industrial, agricultural and sewage discharges to streams can change the conductivity due to the presence of ions. The aquatic life criteria suggest that fresh water systems that have conductivity in the range of **150 to 500 $\mu\text{S}/\text{cm}$** support good mixed fisheries **whereas** conductivity (USEPA, 2017).

Symbol (physical parameter)	Specific Conductivity (SPC)
Units Used for Analytical Results	$\mu\text{S}/\text{cm}$
Normal method(s) used for analysis	Digital calibrated water quality probe meter with conductivity sensitive probe
QC/QA	QC (Standards checked) after analysis
Aquatic Life Criteria	150 to 500 $\mu\text{S}/\text{cm}$ is preferable

In the present study the range of specific conductivity (Figure 5.5) in post-monsoon season extends from around, **25.90 $\mu\text{S}/\text{cm}$** to over **582 $\mu\text{S}/\text{cm}$** . However, in post-winter sampling, the range of specific conductivity extends from around **171.80 $\mu\text{S}/\text{cm}$** to over **14820 $\mu\text{S}/\text{cm}$** .

Due to the dilution of the water source in post-monsoon season, at almost all the sites, the conductivity was found to be within the prescribed or permissible range

of $<500 \mu\text{S/cm}$. However, in post-winter sampling, at most of the sites (especially those located along the industrial and agricultural belt) the specific conductivity exceeded the prescribed or permissible range of $<500 \mu\text{S/cm}$ for aquatic life criteria. The reason for sudden high increase in specific conductivity could be attributed to continuous inflow of agricultural runoff, domestic and industrial discharge accompanied with high evaporation, low water level and lower flow volume in dry seasons. As the water level lowers, the ions present become concentrated, contributing to higher conductivity levels.

It was observed that specific conductivity at three sampling points in LZ (West Bengal), namely Falta ($4424 \mu\text{S/cm}$), Diamond Harbour ($9851 \mu\text{S/cm}$) and Haldia ($14820.00 \mu\text{S/cm}$) far exceeded the permissible value of $500 \mu\text{S/cm}$ for aquatic life criteria. The reason for such higher value is attributed to the nearness of industrial sector to these belts and discharge of highly polluted inorganic and organic load into the stream.

As shown in Figure 5.5, conductivity ranges in both the sampling seasons (Post-Monsoon and Post – Winter), from **Bijnor to Narora**, are well below the minimum permissible level for aquatic life criteria ($<500 \mu\text{S/cm}$) and the presence of all the five species of conservation significance indicates that aquatic biodiversity of this stretch is the highest of the total river.

Permissible range for aquatic life criterion = 500 $\mu\text{S}/\text{cm}$

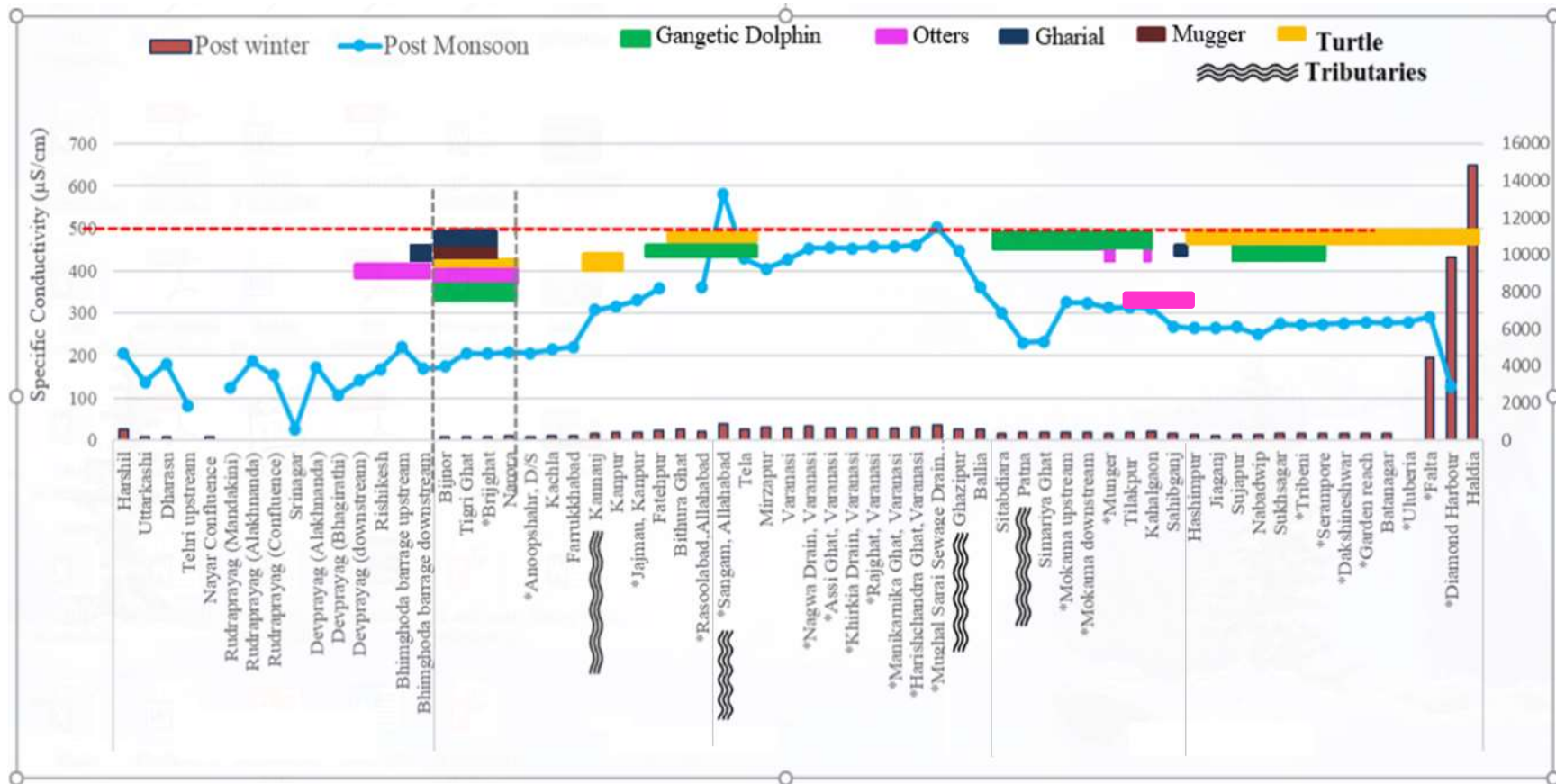


Figure 5.5: Specific Conductivity range in five states along the bank of river Ganga in Post-Winter & Post-Monsoon

*Additional site

6. Ammonium (N-NH₄, mg/L)

Discharges from wastewater treatment plants, industrial effluents and agricultural runoff can result in elevated ammonium levels. It also utilizes and exerts pressure on oxygen levels in water as it is converted to oxidised forms of nitrogen. Elevated concentrations of ammonium may act as important source of nitrogenous fertilizer for aquatic plants resulting in eutrophication and reduced oxygen concentration due to increased biological oxygen demand. Additionally, toxicity of ammonium to aquatic life at certain concentrations is directly related to pH, salinity, and water temperature, e.g., at elevated pH levels in water, ammonium hydroxide is extremely toxic to aquatic life.

Symbol (physical parameter)	N-NH ₄
Units Used for Analytical Results	mg/L
Normal method(s) used for analysis	Digital calibrated water quality probe meter with ammonium sensitive probe
QC/QA	QC (Standards checked) after analysis
Aquatic Life Criteria	0.5 mg/L is preferable

In the present study, due to technical issues sampling assessment of ammonium was done post monsoon in some sites in UZ, UMZ1 and UMZ2 whereas post-winter from sites LMZ and LZ. The range of ammonium, in post-monsoon sampling, extends from around, **0.02 mg/L** to over **0.45 mg/L** whereas in post-winter the ammonium levels range from **0.09 mg/L** to over **5.52 mg/L** (Figure 5.6).

Permissible range for aquatic life criterion ≤ 0.5 mg/L

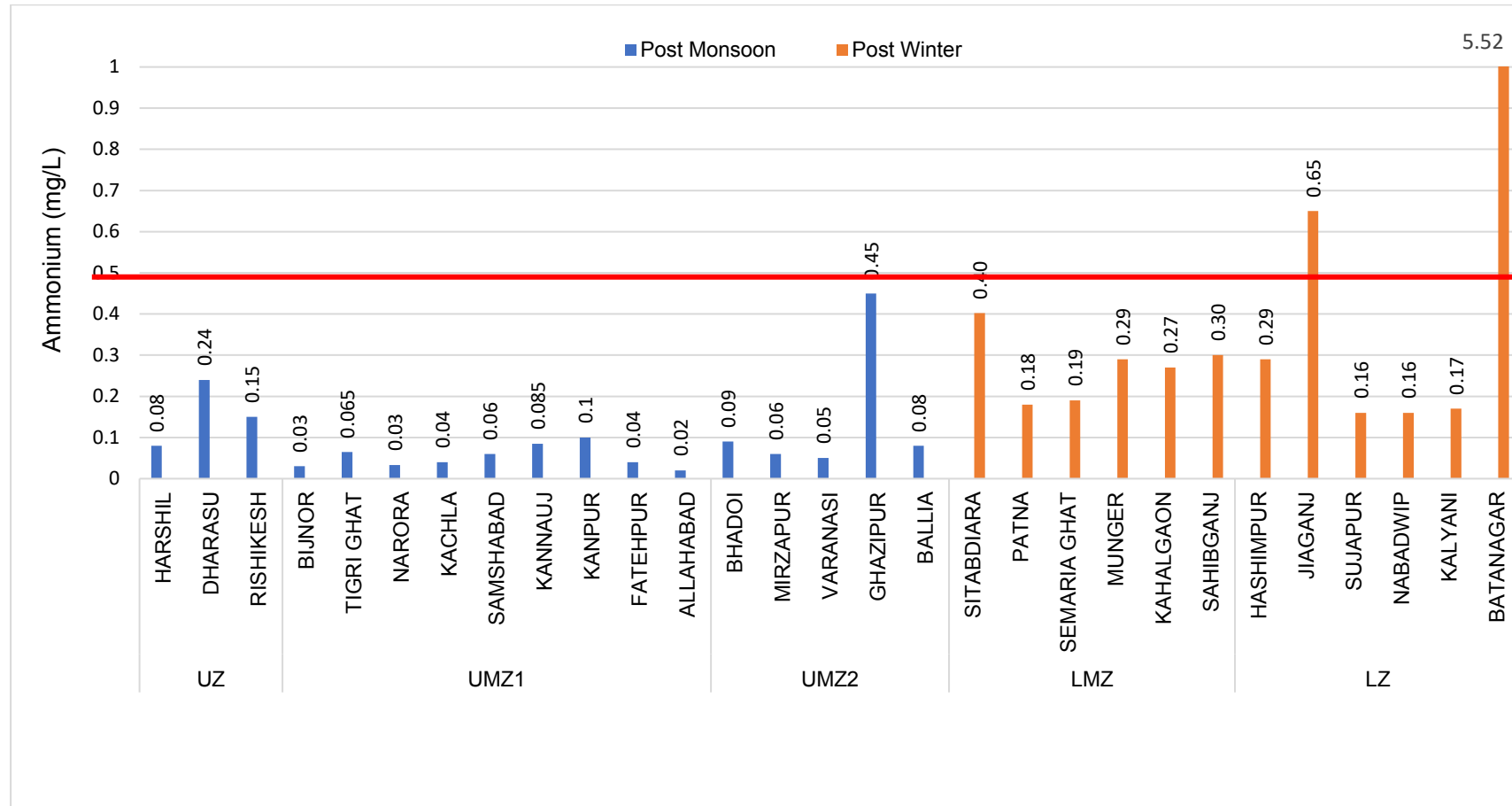


Figure 5.6: Ammonium range in five zones along the bank of river Ganga in Post-Winter & Post-Monsoon

Overview of findings and Priorities for filling information gaps - Physico-chemical Parameter

Overview of findings

- There were significant seasonal and spatial variations in water quality parameters of Ganga River and demonstrated the effects of environmental flow, precipitation, agriculture activity and industrial settlements. The levels of water quality parameters recorded were generally higher than the acceptable limits in some downstream stretches, particularly after Narora, which indicate that downstream stretches are heavily influenced by flow conditions, high agriculture, industrial, and urban settlements.
- The aquatic community in rivers integrates all impacts - the effects of pollution as well changes in hydro-morphology. The results, of the present study, show that the **appearance and distribution** of aquatic organisms in rivers is significantly influenced by flow conditions, and water quality status of the aquatic environment.
- Of all the sites studied, the water quality parameters from **S5 to S7 (~175 Km)** in UMZ2 were within permissible range and the presence of five species (Gangetic Dolphin, Turtles, Smooth Coated Otter, Mugger and Gharial) of conservation significance were also recorded **within** this stretch indicating that aquatic biodiversity of this stretch of the river is the highest.

Priorities for filling information gaps

Further studies, on correlation of physical-chemical parameters and bioavailability of contaminants (pesticides, heavy metals, PCBs, Microplastics, and other priority emerging contaminants) are warranted for enhanced assessment of ecological risks.



ANNEXURES

ANNEXURE I - Publications/Key Outputs

2021	
1.	State Report- Eco toxicological study of Ganga and its environment, UTTARAKHAND
2.	State Report - Eco toxicological study of Ganga and its environment, UTTAR-PRADESH
3.	State Report – Eco toxicological study of Ganga and its environment, WEST BENGAL
2020	
4.	Book Chapter
	Eco toxicological study of Ganga River and its environment, In Book. Biodiversity Conservation and Ganga Rejuvenation. Hussain, S.A. and Badola, R. (eds). (2020). Summary report. Ganga Aqualife Conservation Monitoring Centre, Wildlife Institute of India, Dehradun. 137 pp.
5.	Flyer
	Eco toxicological Profile of the Ganga River
6.	Scientific Publication
	Sah, Ruchika, Anju Baroth, and Syed Ainul Hussain. 2020 . “First Account of Spatio-Temporal Analysis, Historical Trends, Source Apportionment and Ecological Risk Assessment of Banned Organochlorine Pesticides along the Ganga River.” <i>Environmental Pollution</i> . https://doi.org/10.1016/j.envpol.2020.114229 .
2019	
7.	Conference presentation (International)
	“Spatiotemporal trends of Microplastics loading in the sediments of River Ganga: First observation on occurrence, identification and quantification” at SETAC Europe 29 th Annual Meeting, Helsinki, Finland. May 2019
8.	Seminar presentation (National):

An ecotoxicological perspective towards biodiversity conservation in Ganga River: A study on habitat contamination and potential risks” at Annual Research Seminar, Wildlife-Institute of India, Dehradun, India. August 2019

9.	M.Sc Dissertation
	Spatial Analysis Of Polychlorinated Biphenyls (PCBs) In The Sediments From River Ganga Across Uttar Pradesh, Submitted to FRI (Deemed to be) University
10.	Book Chapter:
	Assessment of Physico-Chemical Parameters and Organochlorine Pesticides in Water And Sediment Of River Ganga: Preliminary Status And Trends. In book: BIODIVERSITY PROFILE OF THE GANGA RIVER, 2019.
2018	
11.	Technical Report
	Eco-Toxicological Survey Report: An Assessment Of Seasonal Variations In Surface Water Quality Of River Ganges
12.	Conference presentation (Oral)
	Evaluating spatial distribution and ecological risk of pesticide burden in middle stretch of river ganga” at International Conference to Water: From Pollution to Purification”, Kerala, India. December 2018
13.	Conference presentation (Poster – Best Poster – III Prize)
	Assessment of physico-chemical parameters and organochlorine pesticides in water and sediment of river Ganga: Preliminary status and trends” at International Conference to Water: From Pollution to Purification”, Kerala, India. December 2018
2017	
14.	Technical Manual
	Technical Guidance Manual on collection of water, sediments, plants, and fish samples from Ganga River (2017)

ANNEXURE II – Supplementary Information

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Physico-chemical Properties

Table A1: Key physical chemical properties and legal status of target Organochlorine Pesticides (OCPs) and Organophosphorous Pesticides (OPPs)

Target Analyte	Molecular formula	CAS no	Molecular Weight (g mol ⁻¹)	Solubility in water (mg/L)	Log K _{oc}	Log K _{ow}	Half-life Water (days)	Half-life Soil (days)	Legal Status in India ^{d,e} (Effective dates)
α-HCH	C ₆ H ₆ Cl ₆	319-84-6	290.83	10	3.57	3.8	77d	328.5 ^a	#
β- HCH	C ₆ H ₆ Cl ₆	319-85-7	290.82	5	3.57	3.78		4599 ^a	#
γ- HCH	C ₆ H ₆ Cl ₆	58-89-9	290.82	17	3.57	3.72	3-300	460 ^a	Banned* (25/03/2011)
δ- HCH	C ₆ H ₆ Cl ₆	319-86-8	290.82	10	3.8	4.14			#
p,p'-DDT	C ₁₄ H ₉ Cl ₅	50-29-3	354.49	0.025	5.18	6.91	56-4380	1095-7665 ^b	Restricted** (26/03/1989)
p,p'-DDD	C ₁₄ H ₁₀ Cl ₄	72-54-8	320.04	0.090	5.18	6.02	45-10220	730-5694 ^b	
p,p'-DDE	C ₁₄ H ₈ Cl ₄	72-55-9	318.02	0.12	4.70	6.51	690-43800	>7300 ^b	
Aldrin	C ₁₂ H ₈ Cl ₆	309-00-2	364.9	0.25	-	6.50	-	20-100	Banned (20/09/1996)
Dieldrin	C ₁₂ H ₈ Cl ₆ O	60-57-1	380.9	0.195	3.87	5.40	-	2555	Banned (17/07/2001)
Endrin	C ₁₂ H ₈ Cl ₆ O	128-10-9	380.9	0.25	-	5.20	8 and 89	1460-2920	Banned 1990

Endrin aldehyde	C ₁₂ H ₈ Cl ₆ O	7421-93-4	380.9	0.024	-	4.80	>1460	5110	-
Endrin ketone	C ₁₂ H ₈ Cl ₆ O	53494-70-5	380.9	-	-	4.99	-	-	-
Heptachlor	C ₁₀ H ₅ Cl ₇	76-44-8	373.3	0.18	-	6.10	0.25-9	263 to 730	Banned (20/09/1996)
Heptachlor epoxide	C ₁₀ H ₅ Cl ₇ O	1024-57-3	389.3	0.350	4.34	5.40	~1460	730	-
c-Chlordane	C ₁₀ H ₆ Cl ₈	5103-71-9	409.8	0.056	5.5	6.0	238-1398.5	835-2190	Banned (20/09/1996)
t-Chlordane	C ₁₀ H ₆ Cl ₈	5103-74-2	409.8	0.850	5.5	6.0			
Methoxychlor	C ₁₆ H ₁₅ Cl ₃ O ₂	72-43-5	345.65	0.1-0.25	4.90	4.68	50-370	40-365	#
α-Endosulfan	C ₉ H ₆ Cl ₆ O ₃ S	959-98-8	406.93	0.53	3.46	4.74	30	10-39°	Banned (13/05/2011)
β- Endosulfan	C ₉ H ₆ Cl ₆ O ₃ S	33213-65-9	406.93	0.28	3.53	4.78	45	108-264°	
Endosulfan Sulfate	C ₉ H ₆ Cl ₆ O ₄ S	1031-07-8	422.92	0.48	-	6.1		100-150 °	
Methyl Parathion	C ₈ H ₁₀ NO ₅ PS	298-00-0	263.21	0.006	3.85	2.86	3-6	0.5	Restricted***
Malathion	C ₁₀ H ₁₉ O ₆ PS ₂	121-75-5	330.4	143	-	2.36	1-17	1.65	Permitted
Chlorpyrifos	C ₉ H ₁₁ Cl ₃ NO ₃ PS	2921-88-2	350.6	1.4		4.96	24.5	14 to ~365	Permitted

*Complete ban on manufacture, use, import, and export | [Directorate of Plant Protection, Quarantine & Storage | GOI](#);

**Banned for agricultural use; restricted use in health sector

*** Methyl Parathion 50 % EC and 2% DP formulations are banned for use on fruits and vegetables. (S.O.680 (E) dated 17th July, 2001). The use of Methyl Parathion is permitted only on those crops approved by the Registration Committee where honeybees are not acting as a pollinators. (S.O.658 (E) dated 04th Sep., 1992.) <http://www.spices.res.in/pages/pesticides-restricted-use-country>

Presently India does not have any legislation, laws or policy for these OCPs

Log K_{oc}= The sorption coefficient or K_{oc} is the ratio between the sorption coefficient (K_d), and the organic carbon content of the sorbent and is commonly used to assess the extent to which an organic chemical is sorbed. (<http://www.ecetoc.org/report/estimated-partitioning-property-data/computational-methods/log-koc/>).

Log K_{ow}= The n-octanol-water partition coefficient or K_{ow} is used for assessing the partitioning behaviour of chemicals in the environment in different abiotic matrices. It is the ratio of a particular compound in the water and the octanol phases after a period of mixing. (<http://www.ecetoc.org/report/estimated-partitioning-property-data/computational-methods/log-koc/>).

PCBs Congener	Molecular formula	CAS No.	Molecular Weight (g mol ⁻¹)	Degree of Chlorination	K _{ow}	Half-life (Months)	TEF*
28	2,4,4'-Trichlorobiphenyl	7012-37-5	257.5	3	5.68	35.6 (~2.96 yrs)	Not found
44	2,2',3,5'-Tetrachlorobiphenyl	41464-39-5	292	4	6.00 ± 0.30	Not found	Not found
52	2,2',5,5'-Tetrachlorobiphenyl	35693-99-3	292	4	5.81	120(~10 yrs)	Not found
77	3,3',4,4'-Tetrachlorobiphenyl	32598-13-3	292	4	6.1	120(~10 yrs)	0.0001
101	2,2',4,5,5'-Pentachlorobiphenyl	37680-73-2	326.4	5	6.38	120(~10 yrs)	0.43
105	2,3,3',4,4'-Pentachlorobiphenyl	32598-14-4	326.4	5	7	120(~10 yrs)	0.0001
118	2,3',4,4',5'-Pentachlorobiphenyl	31508-00-6	326.4	5	7.1	82.2(~6.85 yrs)	0.0001
126	3,3',4,4',5-Pentachlorobiphenyl	57465-28-8	326.4	5	6.89	120(~10 yrs)	0.1
138	2,2',3',4,4',5-Hexachlorobiphenyl.	35065-28-2	360.9	6	6.32	226(~18.8 yrs)	1.1
153	2,2',4,4',5,5'-Hexachlorobiphenyl	35065-27-1	360.9	6	6.7	226(~18.8 yrs)	1.1
180	2,2',3,4,4',5,5'-Heptachlorobiphenyl	35065-29-3	395.3	7	6.56	456.2	0.00001

Table A2: Key physical chemical properties Polychlorinated Biphenyls (PCBs)

**TEF is based on the recognition that there is a common mechanism of action involving binding to the AhR, and that the toxicity of substances assigned a TEF value is relative to toxicity of 2,3,7,8- tetrachlorodibenzo-p-dioxin, which is assigned a TEF value of 1.*

Van den Berg M , Birnbaum L , Bosveld ATC , Brunstrom B , Cook P , Feeley M, et al. (1998). Toxic equivalency factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife . Environ Health Perspect , 106 , 775 – 92 .

Toxicity Profile

Table A3: Toxicological Profile* of target OCPs, OPPs, heavy metal, and PCBs in aquatic organisms

S.No	Chemical Name	Organism	Life Stage	Endpoint	Effect Conc.	Research/ Toxicological Findings
1	Endosulfan	<i>Cichlid Fish</i>	Adult (n = 90)	Median lethal concentration (LC50) Sublethal effects	17.7 l µg/L 3.4 and 6.8l µg /L	<ul style="list-style-type: none"> • Increase hemoglobin concentration, neutrophils, lipid peroxidation (gills, hepatopancreas, and brain) and WBC count after 96 h in exposed fish. • Decrease in aspartate aminotransferase and alanine aminotransferase and an increase in alkaline phosphatase.
2	DDT	<i>Lake Trout</i>	Adult females	Bioaccumulation and Mortality		<ul style="list-style-type: none"> • Mass of the fry shows a relatively closer relationship between ppm. of DDT and the mortality
3	o,p -DDT	<i>Paralichthys dentatus</i> (summer flounder)	juvenile male (1.5–2 years)	Reproductive Histopathological	30 or 60 mg/kg	<ul style="list-style-type: none"> • <i>o,p</i> -DDT elicited altered gonadal development • Cause liver to produce an estrogen inducible substance and inhibited testicular maturation. This may have induced hepatocytic hypertrophy and kidney function impairment.
4	DDT	<i>Oreochromis mossambicus</i> (Mozambique tilapia)		Histopathological changes in the reproductive system	sub-lethal = 5 µg /L	<ul style="list-style-type: none"> • Posthatch survival significantly lower, and prevalence of larval skeletal deformities significantly higher • Incomplete axial development was the common gross deformity in posthatch larvae, caused by failure to develop chondroblasts posterior to the buccopharyngeal cavity • Increased oocyte atresia in the ovaries and disorganization of seminiferous lobules in the testes of adults. • DDT exposure reduced survival and increased deformities in larvae, at levels that did not cause severe histopathological changes to parental gonads

		<i>Oreochromis mossambicus</i> <i>Clarias gariepinus</i>	Adult male	Reproductive system	0.1–1.2 µg /L (Environment relevant conc.)	<ul style="list-style-type: none"> • Alterations to testis tissue • Decrease in sperm motility
5	HCHs (HCH isomers), DDTs (DDT and its metabolites)	<i>B. Bagarius</i> Catfish				<ul style="list-style-type: none"> • Inhibits the reproductive physiology at receptor level

S.No	Chemical Name	Organism	Life Stage	Endpoint	Effect Conc.	Research/ Toxicological Findings
6	Lindane	<i>Cyprinus carpio</i>		Haematological and biochemical responses	Acute and Sub-lethal Median lethal concentration (24 h) = 0.38 ppm	<ul style="list-style-type: none"> Decreased hemoglobin (Hb), hematocrit (Hct) and erythrocyte (RBC) values and increased leucocyte (WBC) count Hematological indices like mean cellular volume (MCV), mean cellular hemoglobin (MCH) and mean cellular hemoglobin concentration (MCHC) were decreased <ul style="list-style-type: none"> plasma glucose and protein levels were increased
7	DDT & HCH	Catfish <i>Heteropneustes fossilis</i> (Bloch)	Pre-spawning phase	Reproductive	DDT, 5.0 ppm HCH, 0.025 ppm	<ul style="list-style-type: none"> Gonado somatic index (GSI) and plasma levels of estradiol-17(E2) declined in response to exposure of HCH and DDT
		Catfish <i>Heteropneustes fossilis</i> (Bloch)	pre-spermiating stage male	Reproductive	lethal dose	<ul style="list-style-type: none"> 1 ppm of c-HCH, DDT and chlorpyrifos was lethal dose on sperm motility
8	Lindane	<i>S. aurata</i>	Eggs/embryos and larvae	Behavioural and morphological changes	Eggs (Mortality, 10 mg/L) = 81.98% Larvae Mortality 1 mg/L = 76.38%	<ul style="list-style-type: none"> Myoskeletal defects, skin opacity, exophthalmia, weak swimming, depigmentation, behavioral changes
		<i>Oncorhynchus mykiss</i>	developmental stages	livers	1 mg/L	<ul style="list-style-type: none"> Hepatocytic alterations (glycogenic depletion, RER and dictyosome changes, secondary lysosome accumulation)
		<i>zebrafish</i>	Fertilized eggs		40 mg/L	<ul style="list-style-type: none"> Hatching, abnormalities in development (external deformations, edema, etc.)
9	Endosulfan	<i>Esomus Danricus</i> (Hamilton-Buchanan)		Behaviour	LC50 (96 hours)	<ul style="list-style-type: none"> Decline in body weight accompanied by a dose and exposure dependent increase in hepato-somatic index and decline in brain and kidney- somatic indices
		<i>Monopterus albus</i> (Asian swamp eel)		behavioural and some hematological parameters	96 h-LC50 0.42 µg /L	<ul style="list-style-type: none"> Abnormal behavioural responses included imbalanced position, restlessness of movement, erratic swimming, tremor, flashing and lethargy. When the swamp eels were exhausted, they were laterally recumbent on the bottom and had no opercula movement. erythrocyte cell showed an increasing trend in size <ul style="list-style-type: none"> Severe blood loss through the gill capillary and hematemeses

				eters		
		<i>Oncorhynchus mykiss</i> (rainbow trout)	Juvenile	histopathological lesions	0.6 and 1.3 µg/L	<ul style="list-style-type: none"> Lesions were observed in gills, liver, spleen, and trunk kidney and changes observed during exposure were reversible

Adams BA , Cyr DG, Eales JG . 2000. Thyroid hormone deiodination in tissues of American plaice, *Hippoglossoides platessoides* : characterization and short-term responses to polychlorinated biphenyls (PCBs) 77 and 126 . *Comp Biochem Physiol C Pharmacol* 127 , 367 – 78.

Nakayama K , Oshima Y, Hiramatsu K , Honjo T .2004 . Alteration of general behavior of male medaka, *Oryzias latipes*,exposed to tributyltin and/or polychlorinated biphenyls. *J Fac Agr Kyushu Univ* ,49 , 85 – 92

Schimmel, S. C., J. M. Jr. Patrick, and J. Forester. 1976. Heptachlor: Toxicity to and uptake by several estuarine organisms. *J. Toxicol. Environ. Health* 1:955-965

S.No	Chemical Name	Organism	Life Stage	Endpoint	Effect Conc.	Research/ Toxicological Findings
	Endosulfan	<i>Betta splendens</i>	male	survival, growth and reproduction	1,400 ng/L	<ul style="list-style-type: none"> • Reduce significantly the cumulative progeny production from 760 to 144 • Reduced number of spermatogonia with increased vacuolar cavities • 21% mortality • Reduced number of vitellogenic oocytes with increased vacuolar cavities
		<i>Cichlasoma dimerus</i>	Adult fish	reproductive	0.1, 0.3 and 1 µg/L	<ul style="list-style-type: none"> • Inhibited the LH-stimulated steroidogenesis in gonads • Decrease in FSH pituitary content and GT activity in the testes • Endocrine disruptive action on the reproductive axis of, causing disruption at the pituitary and/or at the gonad level.
		<i>Danio rerio</i> (zebra fish)	Hatchlings	Reproduction	240 day experiment 44- 1400 ng/L Dose dependent effects	<ul style="list-style-type: none"> • Growth suppressant and magnitude of suppression increased in order of female>male>juveniles • Reduced spawning frequency • Affect the processes of maturation of eggs and vitellogenesis • Delayed sexual maturity • Reduced fertilizability by reducing the motility duration of sperm
10	PCB-126	<i>Danio rerio</i>	embryos	Teratogenic effects	7.5 µ g/L	<ul style="list-style-type: none"> • Abnormal embryonic development
11	PCB-77 PCB-126	<i>Hippoglossoides platessoides</i>		Hormonal effects	5 – 500 ng/g (I.P)	<ul style="list-style-type: none"> • Increased deiodination activity of thyroid hormones in some tissues (Adams et al.,2000)
12	PCBs	<i>Oryzias latipes</i>		Behavioral effects	1 – 125 µ g/g (dietary)	<ul style="list-style-type: none"> • Abnormal swimming behavior (Nakayama et al., 2004)
13	Chlordane	<i>Oncorhynchus mykiss</i>			LC50 = 0.09 mg/L	
14	Heptachlor	<i>Sheepshead minnow</i>		Mortality	20 mg/kg ww (96 hr)	Schimmel et al. 1976
15	Heptachlor Epoxide				6.7 mg/kg ww	
16	Dieldrin	<i>Pseudopleuronectes americanus</i>	Eggs		1.21 mg/kg	Associated with 100% mortality (Smith and Cole 1973)

Smith, R. M., and C. F. Cole. 1973. Effects of egg concentration of DDT and dieldrin on development in winter flounder (*Pseudopleuroneets amerieanus*). *Fish Res. Board Can.* 30:1894-1898

S.No	Chemical Name	Organism	Life Stage	Endpoint	Effect Conc.	Research/ Toxicological Findings
17	Methyl Parathion	<i>Labeo rohita</i>		Oxidative stress, Neurotoxic, Hepatotoxic	1.0 mg/L	<ul style="list-style-type: none"> Changes in antioxidant enzymes system, induction of oxidative stress, increased peroxidation and inhibition of AChE activity
		<i>Danio rerio</i>	Adult	Genotoxicity	1, 1.5, 3 mg/L (96 h)	<ul style="list-style-type: none"> MP has a short-time genotoxic effects
		<i>Catla catla</i>	Adult	metabolic and antioxidant activities	acute (0.09 ppm) sublethal (0.009 ppm)	<ul style="list-style-type: none"> Organel damage: gill is the most sensitive organ to MP toxicity Significant increase of LDH activity indicates severe cellular damage in organ/tissues of MP treated fish
		<i>Brycon cephalus</i>	Adult	Oxidative stress	2 mg /L	Oxidative-stress-inducing potential as MP exposure resulted in a significant induction of SOD, CAT and GST activity in all tissues.
18	Methyl Parathion and Chlorpyrifos	<i>Aphanius Dispar</i>	Juveniles	Tissue enzyme activity	LC50 (24 hr) 0.039 ppm 0.0025 ppm	<ul style="list-style-type: none"> Decreased activity AChE and ALP levels decrease significantly ALT activity elevated and Increase ACP activity (chlorpyrifos)
19	Chlorpyrifos	<i>Oreochromis niloticus</i>	Juvenile and adult	Reproductive , stress antioxidant enzyme activities and lipid peroxidation	96 h LC50 98.67 µg/L (juvenile) 154.01 µg/L (Adult) Sub-lethal - 5 ppb, 10 ppb, 15 ppb (adult fish)	<ul style="list-style-type: none"> Serum estradiol, testosterone and cortisol levels in fish exposed to chlorpyrifos were lower decreased GST activity, and increased SOD enzyme activity by up to 215–446% Compared with the control, suggesting there was a oxidative stress. Acetylcholinesterase activity decreased (45.83–77.28%) in gonad tissues.
		<i>Oreochromis Niloticus</i>	Juvenile	oxidative stress	12 µg/L and 24 µg/L (96 h)	<ul style="list-style-type: none"> Lipid peroxidation (LPO) was elevated in brain Glutathione peroxidase (GSH-Px) activity in liver and brain tissues was significantly elevated Catalase (CAT) activity was significantly increased (P<0.05) in liver Superoxide dismutase (SOD) activity increased in brain
20	Malathion	<i>Cyprinus carpio carpio</i>	Adult	hematological and immune responses	0.5 and 1 mg/L for 14days (sublethal)	<ul style="list-style-type: none"> Alterations in the haematological profiles and immune responses lead to increased reactive oxygen species formation, resulting in oxidative damage and inhibition of the antioxidant capacities.
		<i>Labeo Rohita</i>	Adult	Mortality and biochemical changes	LC100 (25 mg/L, lethal) and LC0 (5 mg/L, sublethal)	<ul style="list-style-type: none"> Gradual decrease of nucleic acids, protein, free amino acids (FAA) and glycogen (Defective Metabolic processes leading to increase rate in mortality) Increased antioxidant enzyme activity (Catalase and Glutathion-S- transferase), in the liver, muscle and gill

		<i>Cyprinus carpio carpio</i>	Adult	Hematological, immune, and the oxidative status	0.5 and 1 mg/L	<ul style="list-style-type: none"> Negative effect on the haematological parameters, immune response, and antioxidant enzyme activities of the fish.
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S.No	Chemical Name	Organism	Life Stage	Endpoint	Effect Conc.	Research/ Toxicological Findings
21	Methyl parathion and Cadmium (Cd)	<i>Danio rerio</i>	Adult	neurotoxicity	(96 h) 5 mg/L MP and 5 mg/L Cd	<ul style="list-style-type: none"> Proteomics revealed neurotoxicity induced by joint stress
22	Chromium	<i>Channa punctatus</i> (Bloch)	Adult female	Histopathology (Ovary)	4 mg/L (10% of 96 h LC50, 1 month, sublethal chronic exposure) 20 mg/L (50% of 96 h LC50, 4 days acute exposure)	<ul style="list-style-type: none"> Atretic oocytes were increased (acute exposure) A decrease in percentage of vitellogenic oocytes (chronic exposure) indicating impairment of vitellogenesis
		<i>Channa punctatus</i> (Bloch)	Adult	Histopathology & Behaviour	LC50(96 hr) = 41.75 mg/L	<ul style="list-style-type: none"> Results showed acute chromium toxicity severely affects the vital organs (liver, gills, kidney) and normal behavior (hyperactivity, Loss of balance, rate of swimming, rate of opercular activity, convulsions which may be deleterious for fish populations)
		<i>Channa punctatus</i> (Bloch)	Adult	Growth and behaviour	2 and 4 mg/L (chronic exposure, 2 months)	<ul style="list-style-type: none"> Dose and duration-dependent affects histopathology of gill, kidney (including interrenal tissue) and liver as well as abnormal behavioral patterns and reduced growth rate which may in the long-run may pose serious threat to fish health and affect their population
		<i>Channa punctatus</i> (Bloch)	Adult	Growth and Behaviour	2 and 4 mg/L (chronic exposure, 1 & 2 months)	<ul style="list-style-type: none"> Chromium impaired the pituitary-ovarian axis affecting at the sites of both pituitary and ovary
		<i>Danio rerio</i>	Adult	Behaviour	0.7 mg/L (Cr) 3.5 mg/L (Zn)	<ul style="list-style-type: none"> Behavioral responses under metal exposures were time dependent Alterations in swimming speed and turning times and decreased average distance and dispersion
		<i>Labeo bata</i> , <i>Puntius sarana</i> <i>Catla</i>	Adult	Acute toxicity	96h LC50 7.33 (<i>Labeo bata</i>), 10.37 (<i>Puntius sarana</i>)	<ul style="list-style-type: none"> Acute toxicity assessed

		<i>catla</i>			31.61 (<i>Catla catla</i>)	
		<i>Clarias batrachus</i>	Adult	oxidative stress and antioxidant enzymes	96 hr LC50 (28 days)	<ul style="list-style-type: none"> Increased level of lipid peroxidation and decreased level of reduced glutathione (GSH), glutathione peroxidase (GPx), catalase (CAT), superoxide dismutase (SOD) in the Gill and Kidney tissue of fish
		<i>Oncorhynchus tshawytscha</i>	Eggs Posthast adult	Histological and morphological variations	$\geq 120 \mu\text{g/L}$	<ul style="list-style-type: none"> Reduced growth and survival Kidneys of fish exposed to the greatest concentrations of chromium had gross and microscopic lesions and suggested chromium accumulates and enters the lipid peroxidation pathway where fatty acid damage and DNA damage ($24 \mu\text{g/L}$ expressed as chromosome changes) occur to cause cell death and tissue damage.
S.No	Chemical Name	Organism	Life Stage	Endpoint	Effect Conc.	Research/ Toxicological Findings
23	Arsenic	<i>Catla catla</i>	Adult	Biochemical parameters	96 h = 43.78 mg/L	<ul style="list-style-type: none"> Hematological, biochemical and liver transaminases activity are altered in arsenate exposed group
24	Lead	Invertebrates			EC50 = 26.4-202,530 $\mu\text{g/L}$ EC10 or NOEC = 2.4-963 $\mu\text{g/L}$	<ul style="list-style-type: none"> Lead damages nerve cells and ganglia, and alters cell structure and enzyme function. Axonal degenerative changes, especially in neuronal cell bodies, were recorded In Pb-poisoned freshwater snails leading to altered protein synthesis
		<i>Cyprinus carpio</i>			EC50 = 52-3,598 $\mu\text{g/L}$ EC10 or NOEC = 18-1,559 $\mu\text{g/L}$ LC50 = 0.44 mg/L in small fish and 0.80 mg/L in large fish)	<ul style="list-style-type: none"> Oxidative stress due to excessive ROS production. Oxidative stress by Pb exposure induces synaptic damage and neurotransmitter malfunction in fish as neurotoxicity. Exposure to lead also influences immune responses in fish as an immune-toxicant.
25	Mercury	<i>Cyprinus carpio</i>		Mortality	LC50 = 0.16 mg/L in small fish and 0.77 mg/L in large fish	
26	Copper	<i>Cyprinus carpio</i>		Mortality	LC50 = 0.30 mg/L in fish (<i>Cyprinus carpio</i>)	

27	Cadmium	<i>Rainbow trout and Cyprinus carpio</i>				<p>Cadmium is an endocrine disrupter. Cadmium has been shown to interfere with the formation of steroids, eggs, and sperm, in rainbow trout, and it alters hormone synthesis in testes.</p> <p>In carp (Cyprinus carpio) it inhibits steroid formation and ovarian maturation. Extensive (1.8 and 3.4 µg/L) cadmium exposure in trout causes delayed egg formation, and it has been shown to inhibit egg development into the fry. Direct exposure of rainbow trout embryos to cadmium induces premature hatching, mortality, and developmental abnormalities. Exposures to low levels of cadmium can cause DNA damage and stress in common carp`</p>
28	Nickel					

*Toxicity profile values, if otherwise mentioned, were extracted from ECOTOX database (<https://cfpub.epa.gov/ecotox/explore.cfm?sub=Chemicals>) or PPDB (<https://sitem.herts.ac.uk/aeru/ppdb/en/atoz.htm>)

LC50= Lethal concentration or LC50 is statistically derived dose at which 50% of the test animals will be expected to die.

EC50= The Acute toxicity is expressed as the median effective concentration (EC 50) for immobilization. This is the concentration which immobilizes 50% of the Daphnia in a test batch within a continuous period of exposure which is usually 48hrs.

NOEC= The chronic toxicity is expressed as No observed effect concentration (NOEC) that is the concentration in water which below an unacceptable effect is unlikely to be observed.

https://www.chemsafetypro.com/Topics/CRA/ecotox_aquatic_toxicity.html

Table A4: OCP contamination Comparison with other rivers in India

River	UNIT	Season	T-HCH	T-DDT	T-CHL	Methoxychlor	T-ES	Endosulfan Sulfate	Reference
Thamirabarani River	µg/L		ND-0.037(↓)			0-0.034(↓)	0.009-34.433(↓)	0-0.005(↑)	Arisekar et al. (2018)
Mahi River	µg/L	Summer	369.25-1133.93(↑)	135.00-270.69(↑)					Alam et al. (2015)
		Monsoon	465.36-915.92(↑)	148.67-274.39(↑)					
Tamiraparani River	ng/L	Summer	<0.01–0.12(↓)	<0.01–0.10(↓)	<0.01–0.42(↓)				Kumarasamy et al. (2012)
		Post-monsoon	ND-<0.06(↓)	<0.01–0.38(↓)	<0.01–0.49(↓)				
Yamuna River			<0.1-165(↓)	<0.1-239(↓)					Kumar et al. (2012)
Ghaggar River	ng/L	winter season	BDL–241.66(↓)	27.33–367.51(↓)					Kaushik et al. (2010)
Gomti River	ng/L		BDL–301.44(↓)	BDL–15.57(↓)	BDL–23.21(↓)	BDL(↓)	BDL–92.00(↓)	BDL–92.00(↑)	Malik et al. (2009)
Yamuna River	ng/L	Post-Winter	12.76–593.49(↓)	66.17–722.94(↓)					Kaushik et al. (2008)
Kaveri River	ng/L	Pre-Monsoon	3.2-182(↓)	0.75-4.17(↓)					Babu Rajendran et al. (1997)
River Kali	ng/L	Summer	ND-11.49(↓)				2.30-12.61(↓)		Maurya et al., (2016)
		Monsoon	ND-13.37(↓)				3.23-14.22(↓)		

River Ganga	µg/L	Post Monsoon	0.112-9.304	0.004-0.465	0.010-0.486	ND-0.034	ND-0.084	ND-0.028	Present Study
		Post Winter	0.050-1.877	0.002-0.568	0.001-0.298	ND-0.066	ND-0.144	ND-0.057	

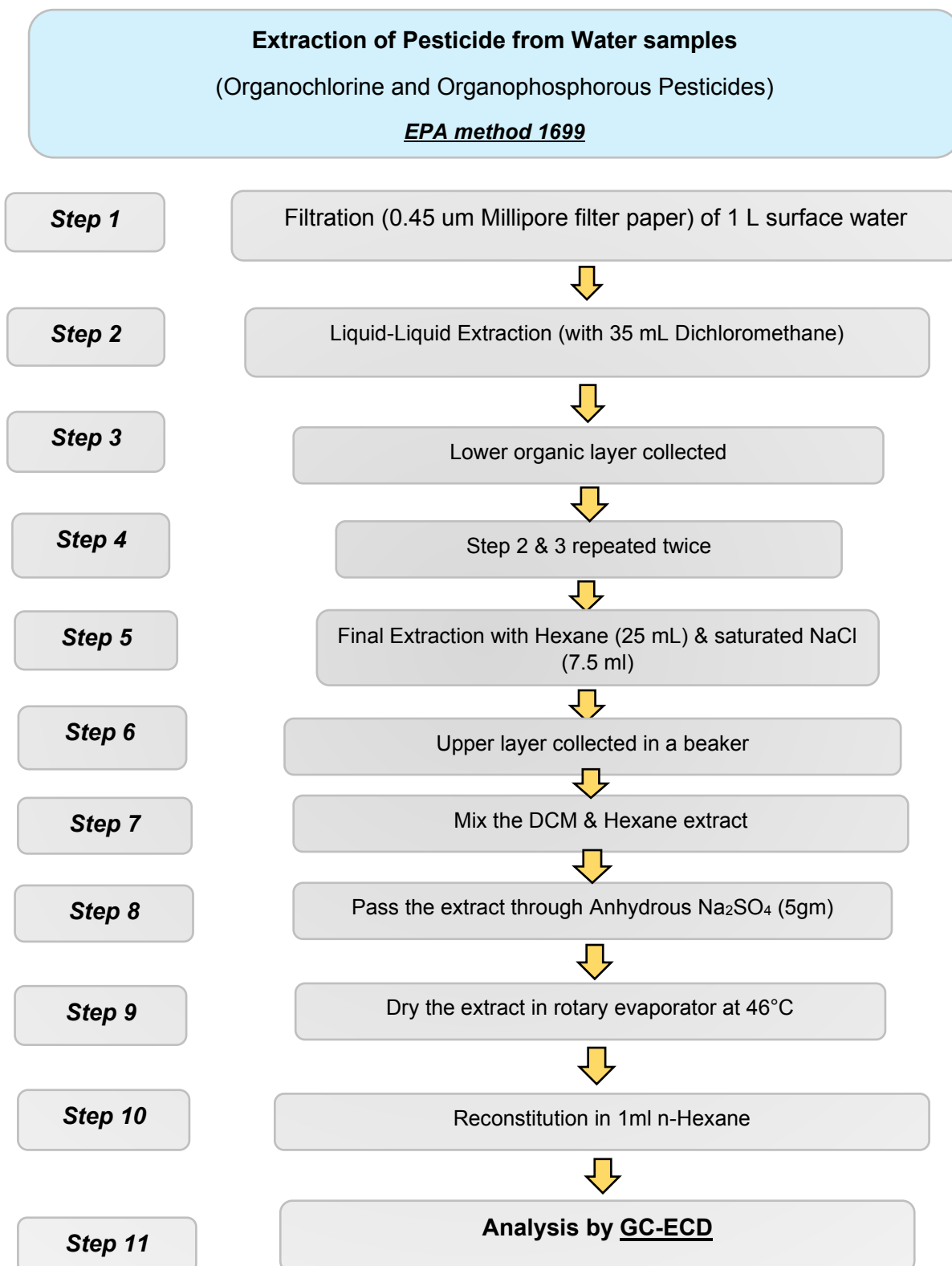
(↑) = Values higher than present study

(↓) = Values lower than present study

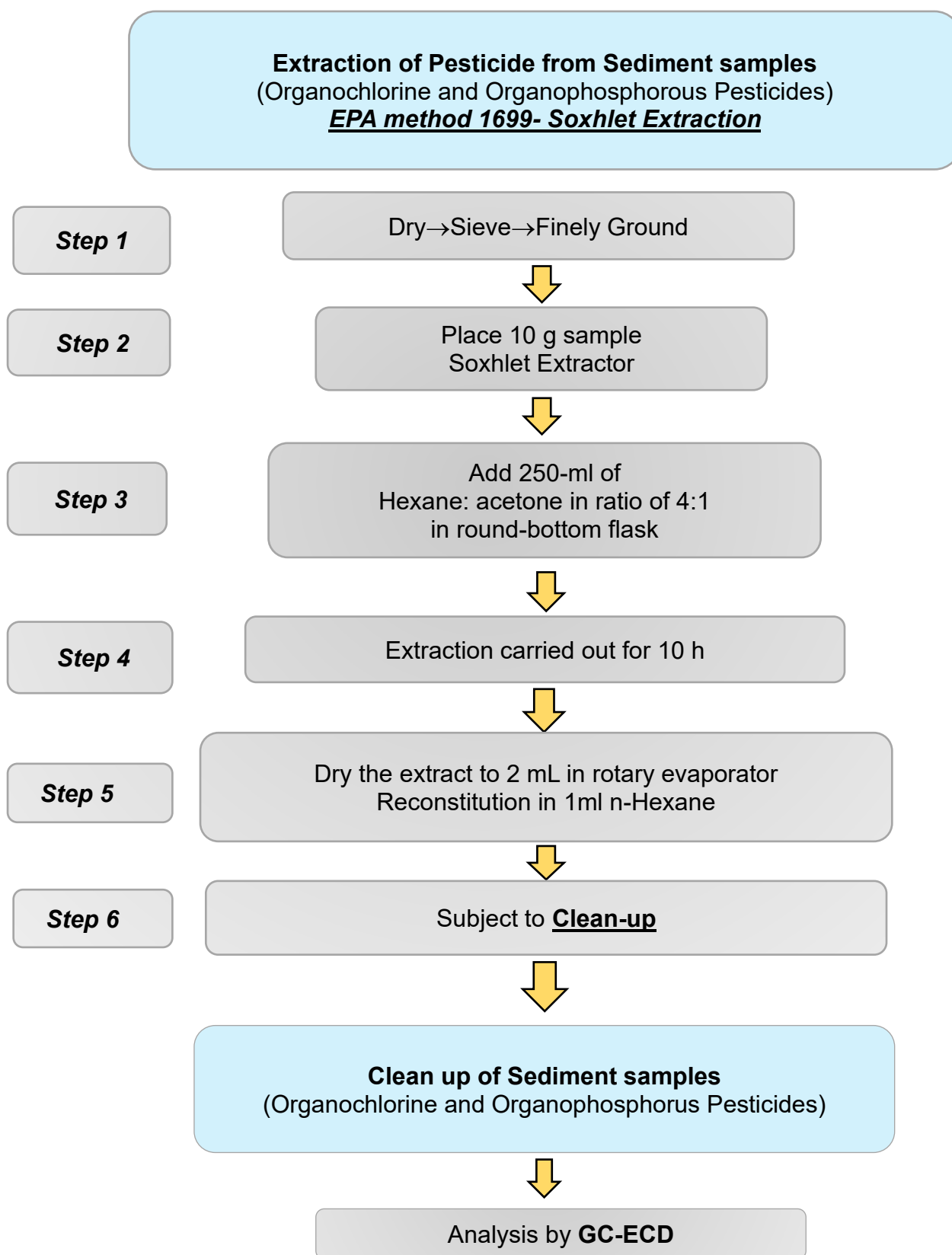
Sample Preparation Methodology - Extraction of target analytes:

a) Pesticides (OCPs and OPPs)

Extraction of pesticides from Water samples

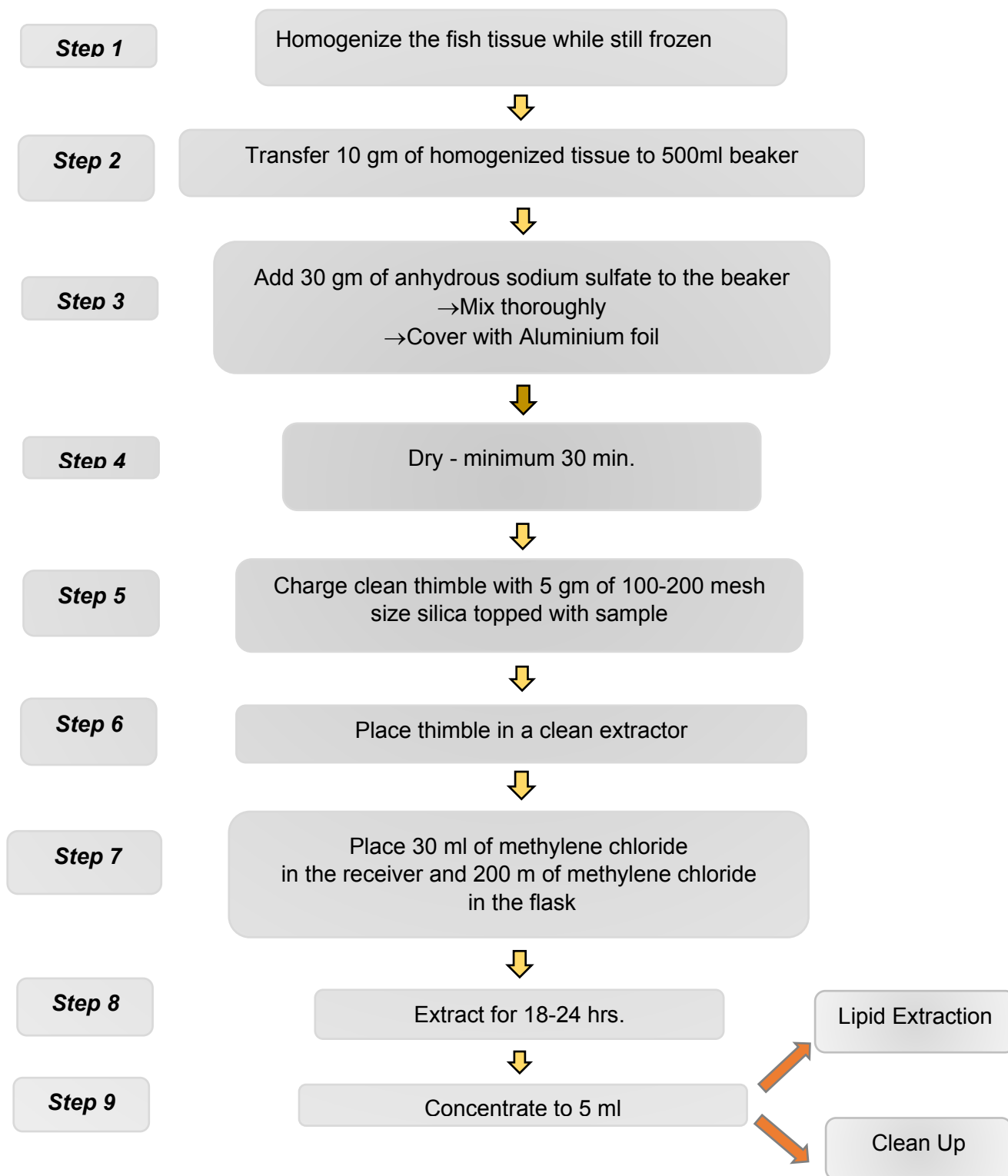


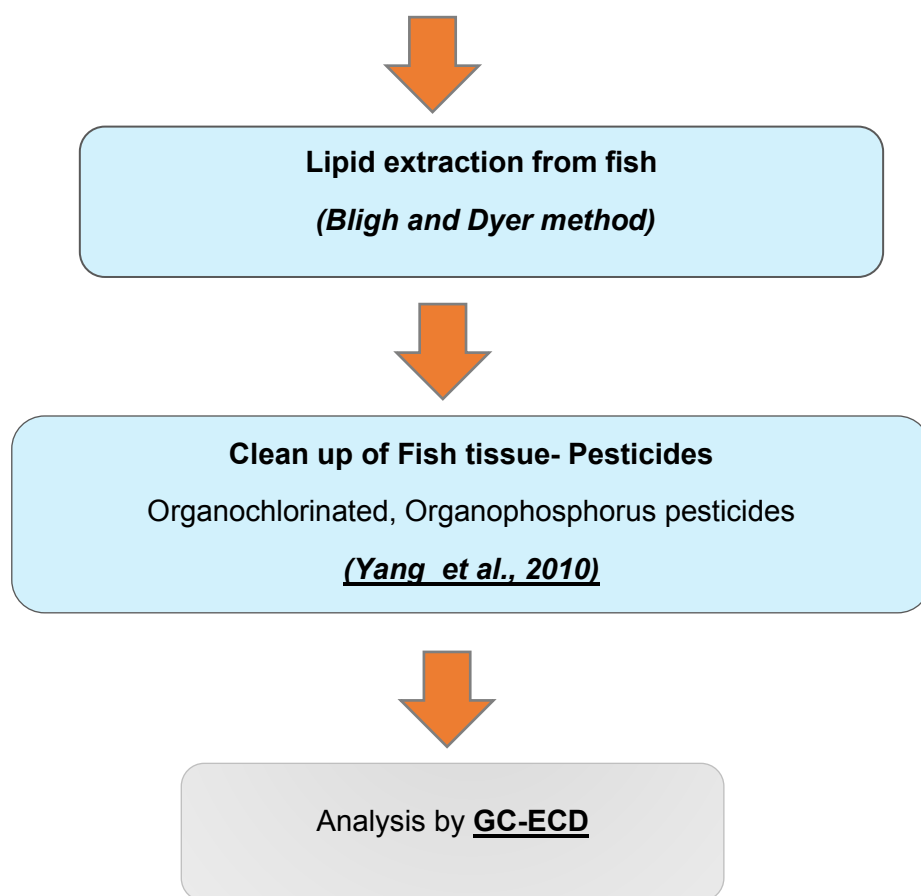
Extraction of pesticides from Sediment samples



Extraction of pesticides from Fish samples

Extraction of Pesticides from fish
Organochlorinated Pesticides, Organophosphate pesticides
EPA method 1699 (Soxhlet method)





b) Heavy Metals

The samples were sent to external laboratory for heavy metals. The lab have followed there in-house method for extraction of heavy metals from water, sediment, and fish samples.

i. Water

Briefly, 100 mL water sample was taken in a pre-cleaned 100 mL volumetric flask and 0.5 mL of suprapure nitric acid was added and mixed properly to ensure that $\text{pH} < 2$. After that 0.2 mL of 5 mg/L of Yttrium internal standard and 0.4 mL of 5 mg/L of gold standard was added so that the final aspirated concentration is 10 $\mu\text{g/L}$ and 20 $\mu\text{g/L}$ respectively in the sample. The samples were then injected into ICP-MS for analysis.

ii. Sediment

Accurately $0.5 \text{ g} \pm 0.05\text{g}$ of sample was weighed in a clean, dry microwave vessel. To this sample, 7 ml of HNO_3 (Trace Metal Grade) was added and allow it to react for 5 mins. After the reaction subsides, the vessel with lid was closed and fix it in the rotor. Finally, the rotor was placed in the Microwave Reaction System (MRS) and the samples were digested and administered under optimized run conditions. The samples were then injected into ICP-MS for analysis.

iii. Fish

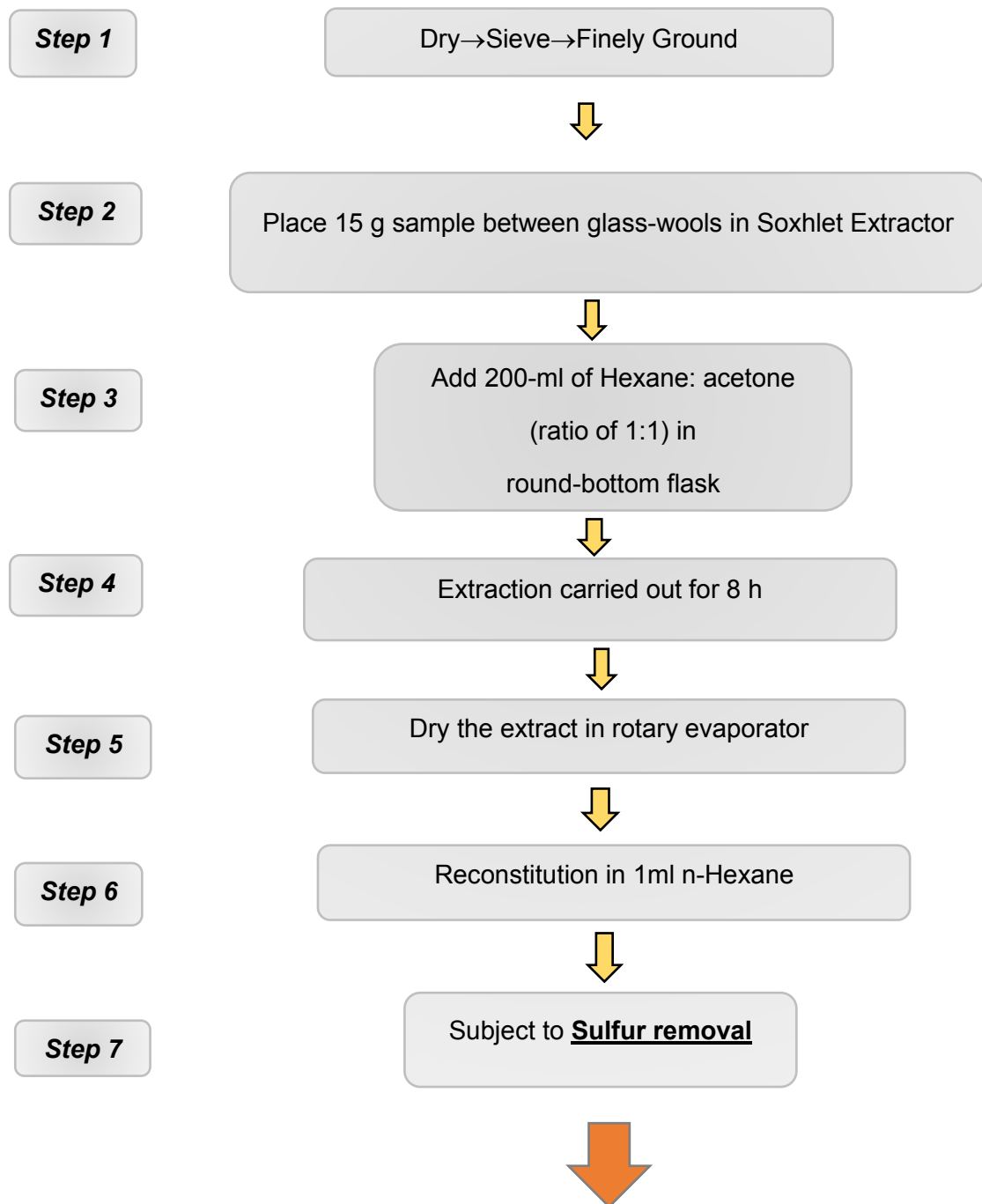
Accurately $2.5 \pm 0.1\text{g}$ of sample was weighed in a clean, dry microwave vessel. To the sample 7 ml of HNO_3 (Trace Metal Grade) was added and allow it to react for 10 minutes. After that, 2.0 ml of Hydrogen peroxide (30%) was added to the sample mixture and was the reaction was allowed to subside. Thereafter, the vessel was closed with lid and fixed in the rotor. Finally, the rotor was placed in the Microwave Reaction System (MRS) and the samples were digested and administered under optimized run conditions. The samples were then injected into ICP-MS for analysis.

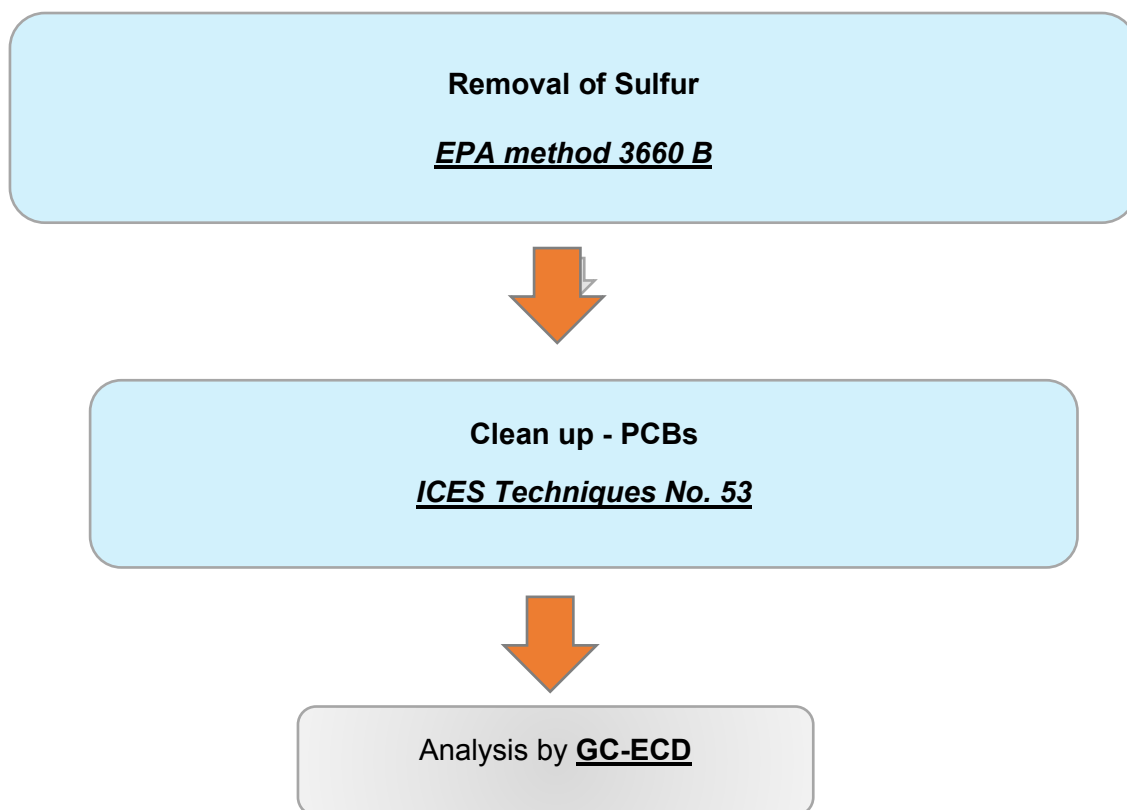
c) PCBs

Sediment

Extraction of Polychlorinated Biphenyls (PCBs) from sediment

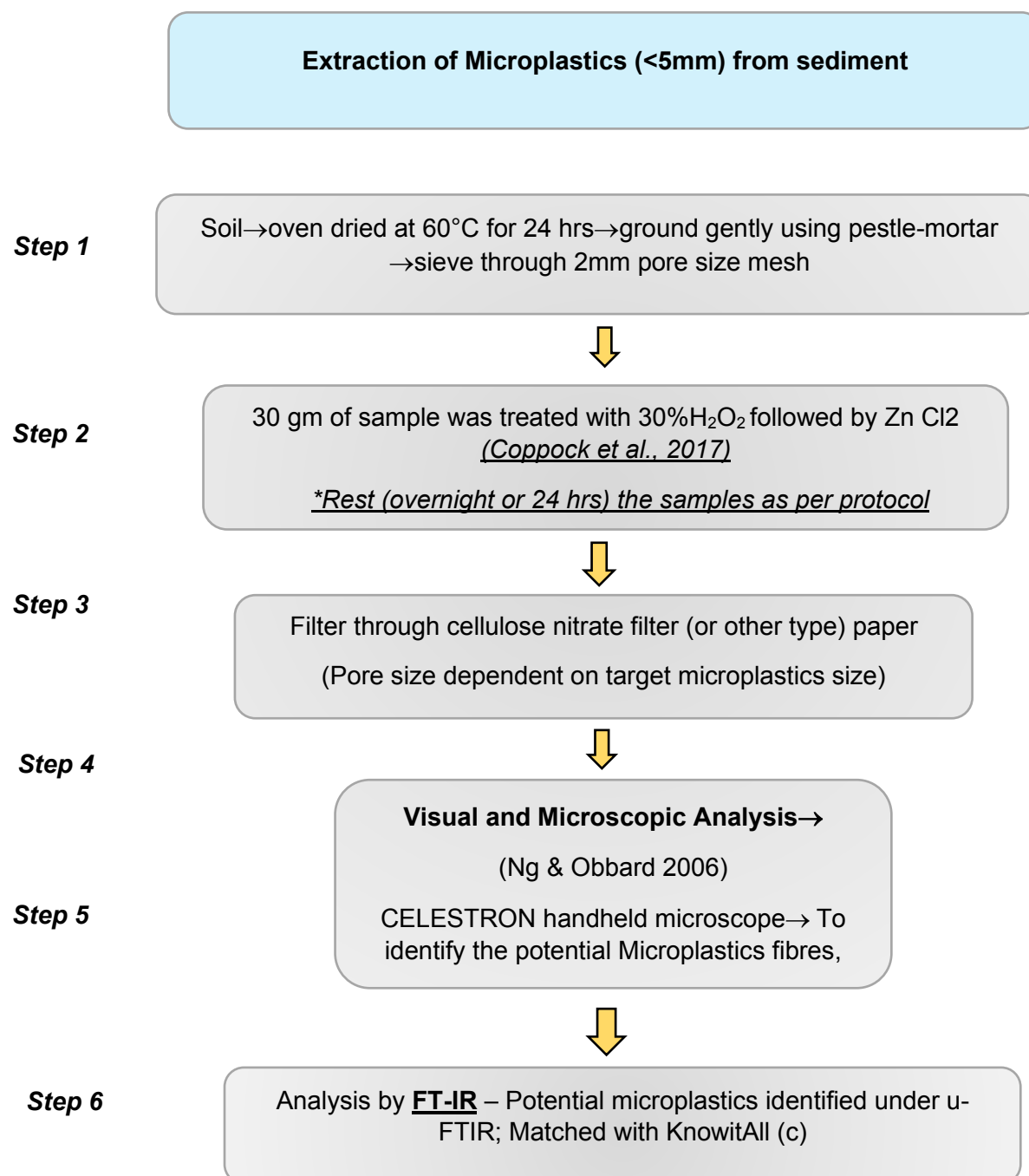
EPA Method SW-846 Method 3540C





d) Microplastics

Sediment



Quality assurance and quality control (QA/QC)

QA/QC was performed according to the requirements of ISO/IEC 17025 and USEPA guidelines. A Field, laboratory blank and solvent blank were run routinely to check for interferences and cross contamination. The blank concentrations were <MDL (method detection limit). Relative Standard deviation of random duplicate sample analysis was $<\pm 5\%$. Linear calibration curves were obtained with the r^2 value of 0.995-0.999 and calibration verification standard deviation was $<\pm 5\%$. The target compound concentrations were quantified by an external standard method using the peak height and area of the standards at five level calibration curves. Matrix spiked recovery study was undertaken by spiking the known working standard solutions of OCPs/PCBs/Heavy Metals with samples which were extracted and analyzed in the same way as the real samples. The matrix spiked recoveries were in the range of 78-124% for studied compounds. After every 10 samples, the standard quality check was performed. Method detection limits (MDL) and Limit of quantification (LOQ) were assessed based on USEPA guidelines. Any target analyte detected below MDL was considered as not detected (ND).

International Thresholds - ALC

**Table A5: International Aquatic Life Criterion[#] guideline values for surface water* and sediments*
OCPs, OPPs, PCBs, and heavy metal**

Analytes	WATER		SEDIMENT
	CMC	CCC	USEPA (TEL) or Canadian ISQG
α-HCH	0.95	-	0.94
β- HCH		-	
γ- HCH		-	
δ- HCH		-	
p,p'-DDT	1.1	0.001	1.19
p,p'-DDD	-	-	3.54
p,p'-DDE	-	-	1.42
Aldrin	1.5		
Dieldrin	0.24	0.056	2.85
Endrin	0.086	0.036	2.67
Endrin aldehyde	-	-	-
Endrin ketone	-	-	-
Heptachlor	0.52	0.0038	0.6
Heptachlor epoxide	0.52	0.0038	0.6
c-Chlordane	2.4	0.0043	4.5
t-Chlordane	2.4	0.0043	4.5
Methoxychlor	-	0.03	-
α-Endosulfan	0.22	0.056	-
β- Endosulfan	0.22	0.056	-
Endosulfan Sulfate	-	-	-
Methyl Parathion	0.065	0.013	-
Malathion		0.1	-
Chlorpyrifos	0.083	0.041	-
PCBs		0.014	34.1
Arsenic (As)	340	150	5.9
Cadmium (Cd)	1.8	0.72	0.596
Chromium (Cr)	16	11	37.3
Copper (Cu)	4.8	3.1	35.7
Lead (Pb)	82	3.2	35
Mercury (Hg)	1.4	0.77	0.174
Nickel (Ni)	470	52	18
Iron(Fe)	-	1000	-
Zinc (Zn)	-	120	123
Iron (Fe)	-	1000	-

[#]Aquatic life criteria for toxic chemicals are the highest concentration of specific pollutants or parameters in water that are not expected to pose a significant risk to the majority of species in a given environment

CMC= *Criterion maximum concentration (CMC)* is an estimate of the highest concentration of a material in the water column to which an aquatic community can be exposed briefly without resulting in an unacceptable effect

CCC=*Criterion continuous concentration (CCC)* is an estimate of the highest concentration of a material in the water column to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect

TEL= Represents the concentration below which adverse effects are expected to occur only rarely.

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