ASSESSMENT OF SELECTIVE CONTAMINANTS OF EMERGING CONCERN (CECs) IN THE GANGA RIVER BASIN, INDIA

Dissertation submitted to Jawaharlal Nehru University in partial fulfilment of the requirements for the award of the degree of

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Submitted by

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<u>RECOMMENDATION FORM FOR EVALUATION BY TIDE EXAMINERIS</u>

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This is to ratify that the dissertation/thesis titled "**Assessment of selective Contaminants of Emerging Concern (CECs) in the Ganga River Basin, India** submitted by Ms **Anshula Dhiman** in partial fulfillment of the monuments for and of degree of **M.Phil**/M.Tech/Ph.D of Jawaharlal Nehru University, New Delhi, has not been previously submitted in part or in full for any other degree of this university or any other university/institution.

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Anshula Dhiman

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Acronym List

1. Ace: Acenaphthene
2. Acy: Acenaphthylene
3. AIHA: American Industrial Hygiene Association
4. Ant: Anthracene
5. B.D: Below detection
6. BaA: Benzo (a) anthracene
7. BaP: Benzo (a) pyrene
8. BbF: Benzo (b) fluoranthene
9. BBP: Benzyl butyl phthalate
10. BcF Benzo (c) fluorene
11. BDL: Below detection limit
12. BEHA: Bis(2-ethylhexyl) adipate
13. BEHP: Bis(2-ethylhexyl) phthalate
14. BghiP: Benzo (ghi) perylene
15. BIS: Bureau of Indian Standards
16. BjF: Benzo (j) fluoranthene
17. BkF: Benzo (k) fluoranthene
18. BP: Benzophenone
19. CEC: Contaminant of emerging concern
20. Chy: Chrysene
21. DaeP: Dibenzo (a, e) pyrene
22. DahA: Dibenz (a, h) anthracene
23. DaiP: Dibenzo (a, i) pyrene
24. DBP: Dibutyl phthalate
25. DEP: Diethyl phthalate
26. Df: Detection frequency
27. DMP: Dimethyl phthalate
28. DnOP: Di-n-octyl phthalate
29. EC: Emerging contaminants
30. EP: Ethyl Paraben
31. ERL: Effects range low
32. ERM: Effects range median
33. Fla: Fluoranthene
34. Flu: Fluorene
35. HSDB: Hazardous Substances Data Bank
36. IcdP: Indeno (1,2,3-cd) pyrene
37. ICSC: International Chemical Safety Cards
38. LOD: Limit of detection
39. LOQ: Limit of quantification
40. MCL: Maximum Contaminant Level
41. MDL: Method detection limit
42. MeC: 5-methyl chrysene
43. MP: Methyl Paraben
44. N.D: Not detected
45. OSHA: Occupational Safety and Health Administration
46. PAHs: Polyaromatic hydrocarbon
47. PAE: Phthalate esters
48. PCPs: Personal care products
49. Phe: Phenanthrene
50. Pyr: pyrene
51. RQ: risk quotient
52. SCB: Screening benchmark values
53. SPM: Suspended Particulate matter
54. SQG: Sediment quality guideline
55. TCS: Triclosan
56. TSCA: Toxic Substances Control Act
57. US EPA: United States Environmental Protection Agency
58. WQG: Water quality guideline

Chapter 1

Introduction

With increasing modernization, there has been increase in the use of man-made chemicals all over the world which interferes with the biological systems of animals and human body. Over 80,000 synthetic chemicals are released into natural environment annually as either a part of manufacturing process or as waste water discharge (Naidu et al., 2016). These chemicals, mostly present in very low concentration that are not detected in regular water quality monitoring. The "emerging contaminants" (ECs) or CECs are chemical substances which can be regarded as pollutants that at present are not included in standard monitoring programs at the European level and can be considered for future regulation, depending on research on their ecological toxicity, potential health effects and public view and on examining data based on their occurrence in the various environmental compartments (Norman, 2012). NORMAN network has identified at least 700 comounds categorized into twenty classes (Giessen et al., 2015). These include compounds: PPCPs (pharmaceuticals and personal care product), PAHs (polyaromatic hydrocarbons), pesticides, surfactants, flame retardants, biocides, gasoline and their degradation products, food additives, steroids and hormones, microplastics, nanomaterials and EDCs (endocrine disrupting compounds) (Sharma et al.,2018, Carvalho et al., 2018, Zhang et al., 2009, Limpiyakorn et al., 2009, US EPA, 2014 and NORMAN network). It also includes new chemical products released from the degradation and other chemical processes of the existing emerging contaminants (Geissen et al., 2015). In US, 139 stream water were analyzed for presence of the emerging contaminants and found surfactants concentration to be highest followed by the steroids and plasticizer (Kolpin et al., 2002). These substances may be present from long time but have not been detected until newer and advance technologies were developed. Most of the emerging contaminants are present at concentration ranging from µg/L to ng/L in aquatic environments (Carvalho et al., 2018). Majorly, waste water discharge from point sources like WWTPs (Waste water treatment plants) introduce vast array of organic pollutants in water bodies (Carvalho et al., 2018 and Petrie et al., 2015). A brief overview of different classes of the EC-:

1.1 Pharmaceuticals

These include prescription and non-prescription drugs used in the diagnosis, treatment and prevention of a disease and for restoration and modification of the bodily function. There are many different classes of pharmaceuticals including antipyretics, analgesic, antibiotics, antimicrobial, antiseptics, hormones, stimulants, tranquilizers, anesthetics, blood thinners, anthelmintic, betablockers, contraceptives etc. Pharmaceuticals are reported at very low concentrations in the environment ranging from ng/L to low µg/L, which are much lesser than most of the lowest observed effect concentrations (LOECs) estimated for aquatic organisms. These drugs are released into the environment from sources like industrial wastewater, animal husbandry activities, human excretion, domestic sewage. Human excreta and WWTP effluent are the primary source for the synthetic steroids (17α-ethinyloestradiol, mestranol) and natural endogenous (17β-estradiol, estrone, estriol) (Fan et al., 2011). Common drugs detected in the STP effluents are antibiotics, anti-inflammatory drugs, β-blockers, MRI contrasts media, lipid regulators and hormones (like contraceptives). These are thought to pose high ecological risk for sensitive species for which acute toxicity experiment (such as bacteria, algae and invertebrate) are conducted which are representing the organisms of the food chain. Pharmaceuticals have unknown and unpredicted effects on the biota from the prolonged exposure to the low-level concentration. India now stands at 3rd position with respect to volume and accounts for 10% of the global pharmaceutical production which has expanded in the last few decades (Department of Pharmaceuticals, Government of India, 2018). Among the therapeutic drugs, antibiotics are getting much more attention. Their widespread use has resulted in the selection and promotion of the bacterial pathogens resisting the antibiotic and their potential to significantly impact natural microbial consortia (Kümmerrer, 2001). Hormonal pharmaceuticals, due to their high potency at extremely low concentrations are responsible for endocrine disruption in humans and animals (Goel et al., 2013). Illicit drugs are also the major concern due to their significant deleterious effects on human being impacting the society. Illicit drugs, which are not used for medical purpose and banned according to the international rules includes classes of opiates, amphetamines, cannabis, cocaine, and their byproducts. These subsequently end up in sewage system after illegitimately burying of the drugs in soil, disposing of into the sinks or in public waste management facilities (Thomaidis, 2012). Nevertheless, the considerable information gap on their occurrence, distribution and fate in the aquatic environment make it more difficult to control the spread of pharmaceuticals (Hernando et al., 2006).

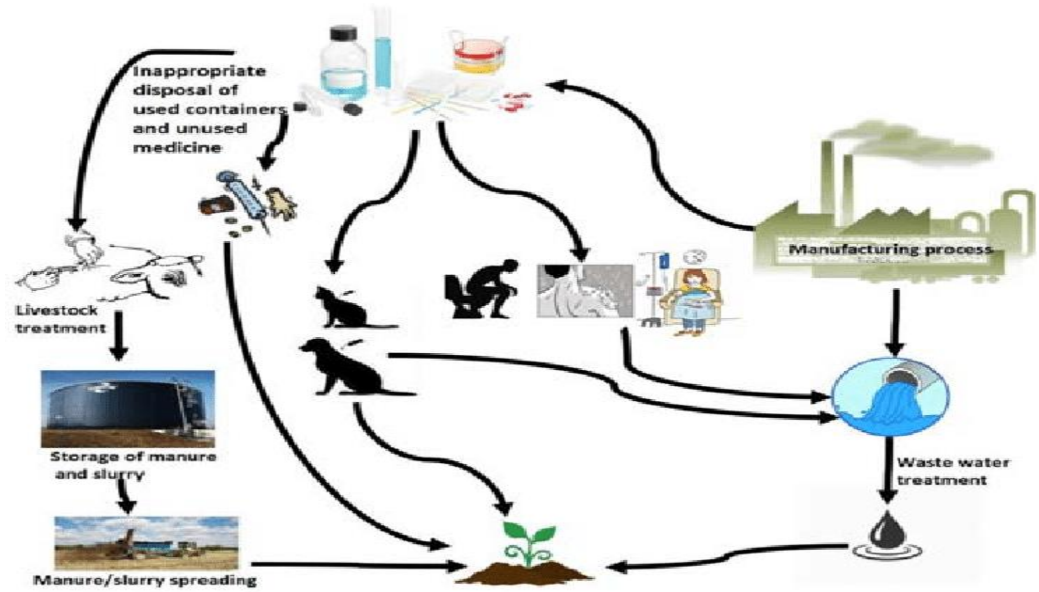


Fig.1.1. Pathways through which pharmaceutical and degraded products re introduced into environment (Kalaji et al., 2017).

1.2 Personal care Products (PCPs)

PCPs are the synthetic group compounds used in every day product. They are primarily used on the human body (mainly dermal contact) and not supposed to be ingested or injected. The age of modern font cosmetics emerged in the 1940s with the widespread use of synthetic surface-active agents (Wilmott et al., 2005). PCPs are primarily classified into groups-: disinfectants (e.g., triclosan), fragrances (e.g., synthetic musk), insect repellants (e.g., DEET), preservatives (e.g., parabens), UV filters (e.g., methyl benzylidene camphor) and flame retardants. These are used in the cosmetic products, for e.g., organic UV filters have been used in various kinds of cosmetics such as shampoos and hair coloring products that shield the skin or hair against sun. Antimicrobials like triclosan (TCS) and triclocarban (TCC) are biphenyl ethers used in soaps, deodorants, moisturizers, toothpaste and plastics. PCPs are among the most frequently discovered organic substances in surface water worldwide due to their extensive use in today's modern world (Peck, 2006). This uncontrolled introduction of these contaminants is the reason why they bypass the sewage treatment system. Unlike pharmaceuticals personal care products are directly discharged into receiving environments (air, surface and ground water, soil, sediment, sewage, sludge and bio-solids, landfills) through regular use, such as bathing, excretion, spraying or discarding of expired or used products.

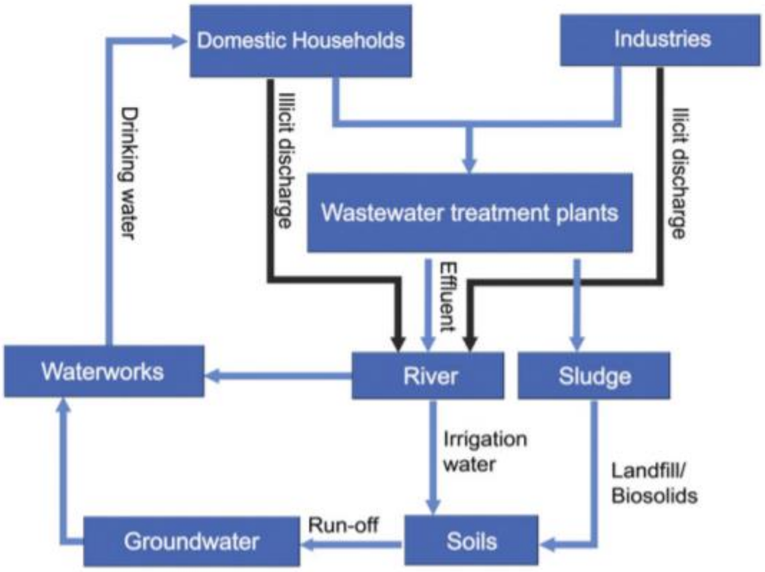


Fig. 1.2. Sources and passage routes of PCPS. Adapted from (Ellis, 2006).

They don't undergo any metabolic transformations so enter the environment unaltered. Because of the PCP's active ingredients are bioactive chemicals, they effect the flora and fauna and also have the tendency to bioaccumulate in non-target aquatic organisms and are environmentally persistent (e.g., U.V filters, fragrances and disinfectants) (Ternes et al., 2004). The subtle immediate effects of the PCPs can go undetected and also the long- term cumulative effects can cause irreversible changes to the receiving ecosystem by the time they are known. (Daughton and Ternes, 1999). They can potentially cause estrogenic effects at relatively low concentrations. Endocrine active compounds present in U.V filters and preservatives (Routledge et al., 1998;

Schlumpf et al., 2001) and triclosan can cause endocrine effects (Foran et al., 2000). Because of the broad chemical classes of the PCPs, their effects and environmental fate are difficult to investigate.

1.3 Pesticides

Pesticides are the synthetic organic compounds that are used in agricultural to prevent, destroy and mitigate pest, as plant regulators defoliants or desiccants (USEPA, 2007a). Currently, the most widespread pesticides being used as herbicides, fungicides, insecticides, and bactericides. These also comprise of nematicides for managing microscopic parasites that lives in soil, molluscicide for common mollusks species such as snails and slugs, avicide for birds, rodenticides, piscicide for fish, miticides, and algicides. (Plan, 2011). Chemically they can be classified as- organophosphates, organochlorine, carbamates, pyrethroids, phenoxyalkonates and triazines. Extensive use of pesticides in agriculture has led to pollution of water, sediment, soil and air. In a study by Pimentel (1995), it was shown that only a small percentage (0.3%) of the pesticide applied on plants attack the pest and the major part (99.7%) of it is released into the environment. Pesticides contributing to the air come from sprayed pesticides or fumigated soil which gives off volatile organic compounds, they can volatilize in the air. Surface run off from agricultural fields pollute the water bodies, soil and sediment. Through seepage and leaching, it causes contamination of the groundwater. Point sources include seed treatment, spray filling and cleaning (Plan, 2011).

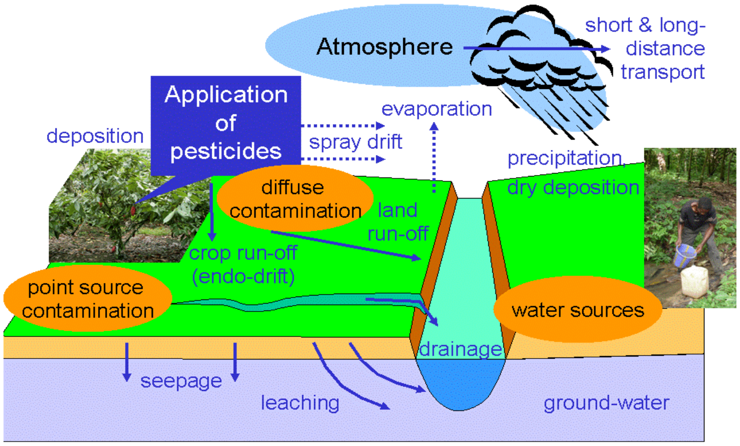
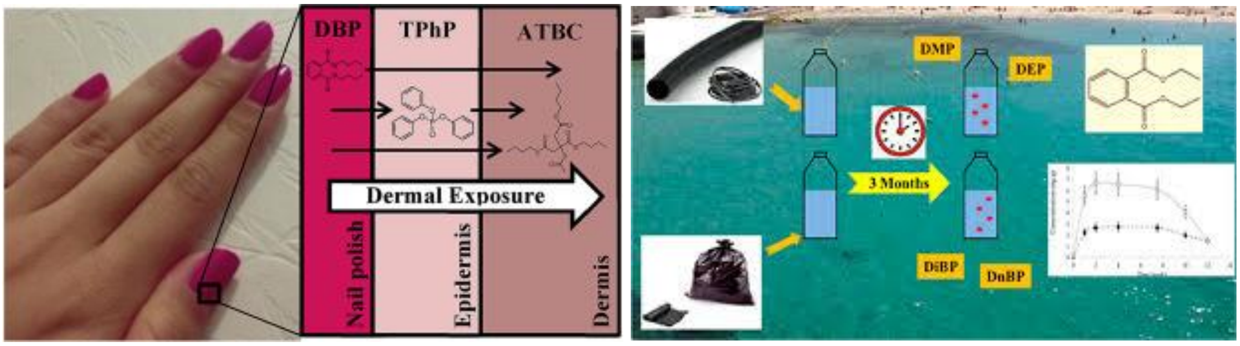


Fig 1.3. Pathways for pesticide

1.4 Industrial compounds and solvent

This category includes a wide range of organic compounds that are potential contaminants. It includes plasticizers, flame retardants,

1.4.1 Plasticizer-: These compounds are nonvolatile organic colorless and odorless liquids used for increasing the elasticity of the polymers such as plastics and rubber. Their application makes the material softer and more flexible, enhances the plasticity, reduces the viscosity and friction. They are usually added to PVC to make them soft and pliable which would otherwise be hard and brittle. They are classified based upon their chemical compositions. The most commonly used are phthalate esters, aliphatic dibasic acid esters, benzoate esters, trimellitate esters, polyesters, citrates bio-based plasticizers and others include phosphates, chlorinated paraffins, alkyl sulfonic acid esters and more (Gilbert, 2012). Plasticizer contamination occurs due to their synthesis of plastic products and usage of such products. Aerial concentration of phthalates from urban air is reported to be more than rural areas (1-2 µg/m^3 and 1-5 ng/m^3 respectively). Main sources contaminating the environment are landfill leachate from aged plastic, industrial discharge and marine plastic waste. Indoor concentration normally ranges in ng/ m^3 but depends on boiling point of the compound. They are persistent and accumulate in organic matrices. Their bioaccumulation depends on octanol–water partition coefficient K_{OW}. Plasticizers PCBs readily metabolizes by particular enzymes. Humans are exposed by inhalation of dust laden with plasticizers, non-dietary ingestion resulting from leached material from food and drink containers (e.g., well-known plasticizer bisphenol-A), dermal penetration (Chen et al., 2010; Thomaidis, 2012). Endocrine disruption by phthalates (e.g., (2-ethylhexyl) phthalate (DEHP), dibutyl phthalate (DBP), di-isobutyl phthalate (DIBP), and n-butyl benzyl phthalate (BBP)) have been reported in experiments carried on certain animals. Detrimental effects in male vertebrates such as defects in reproductive tract, decrease in phallus size and sperm count due to impaired sperm production, feminization during fetal development and altered uterus development in female may be caused due to phthalate esters (PAEs) and bisphenol A (BPA) (Rosenfeld and Feng, 2011; Roark, 2020).



(a) **(b)**

Fig 1.4. (a) Dermal exposure to plasticizer in nail polish (b) Phthalates release from breakdown and degradation of plastic fragments (Tokumura et al., 2019; Paluselli et al., 2019).

1.4.2 Flame retardants-: The term itself expresses the compounds that prevent or slow down the start of a fire. They are incorporated chemically inserted or physically blended in consumer and industrial products like furnishing and building material, textiles, plastics, electrical devices and coatings of transport parts. Diverse types of flame retardants are halogenated hydrocarbons (chlorine and bromine containing compounds), inorganic compounds (antimony oxides, boron compounds, aluminum hydroxide, oxides of heavy metals such as zinc and magnesium), organo-phosphorous retardants (halogenated phosphorus substances, organic phosphate esters) and salts of inorganic phosphorus. Most of them due to their toxicity have been banned for use but still are found due to persistence in environment. They degrade into compounds which are also found to be toxic to biota, like dioxins are produced as degradation product of halogenated compounds when heated for recycling or incinerated. These organic chemicals are released in air and lodged onto the dust particle, water and soil during their manufacturing or leaked from finished products. E-wastes, leaching from landfills and recycling of plastic and other material result in their contamination. They are known to affect animals and humans and cause endocrine disruption, compromise immune system and neurological functions, cancer, reproductive toxicity and impairs fetal and child development (Speight, 2017; Aken and Bhalla, 2011; Aznar-Alemany and Eljarrat, 2020).

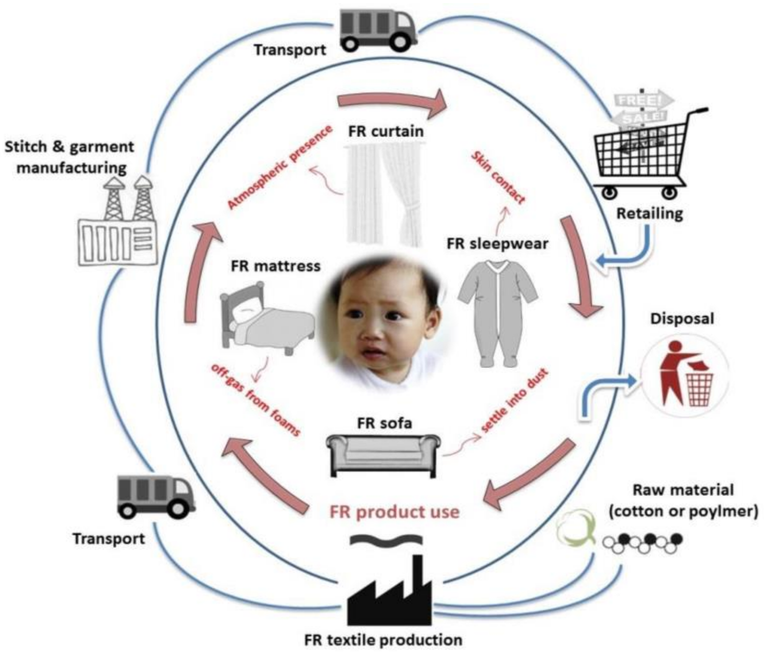
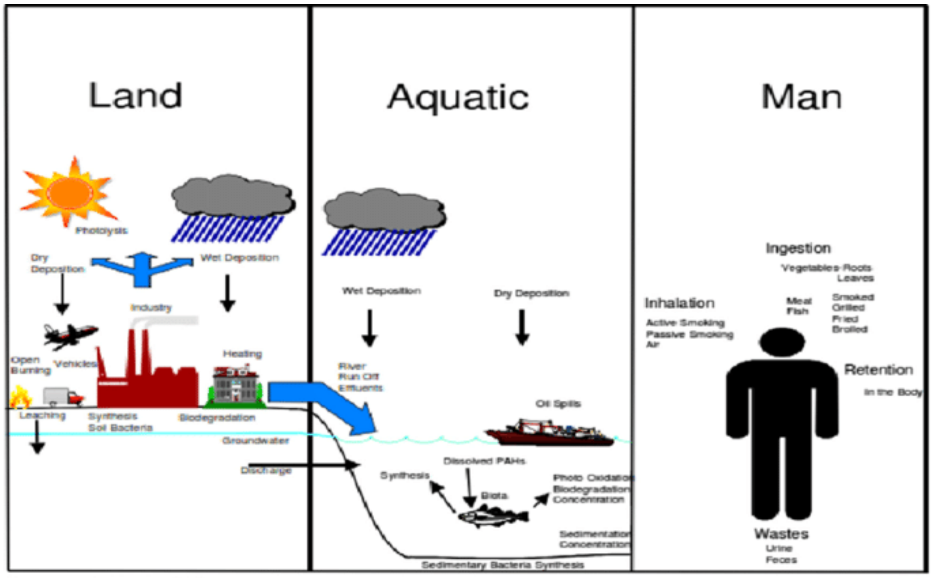


Fig 1.5. Life cycle of flame retardants (FR) textile products (Yasin et al., 2016).

1.4.4 Polycyclic Aromatic Hydrocarbons (PAHs)-: PAHs are semi-volatile hydrocarbons made of multiple fused or condensed aromatic rings and are non- polar uncharged compounds. PAHs are combination of hundred different chemicals and are naturally found in coal and tar deposits, and are also released from petroliferous shale erosion, oil seepages, forest fires (due to incomplete combustion of biomass and wood), volcanic eruptions. These are consisted in products that are usually derived from fossil fuels, including creosote, coal-tar pitch, and asphalt. Anthropogenic sources include combustion of biofuels, burning of polystyrene products, accidental petroleum spillage, municipal and industrial wastewater discharge (Boehm, 2005; Crawford and Quinn, 2017; Sörensen and Wichert, 2009). PAH s are generally not soluble in water, but some smaller molecules are found as contaminants in drinking water. PAHs are found adsorbed on fine-grained particles in organic rich sediments and in aquatic systems concentrations are highest in the suspended sediments (WHO, 1998; Wenning and Martello, 2014; Walker et al., 2014). These are also bound to air-borne particles or present as vapors and can undergo photo-oxidation in the presence of sunlight or react with other pollutant in the air. PAHs in the air can precipitate in an oily matter and contaminate soil and water (Das et al., 2014). The levels of PAHs vary in distinct environmental matrices for e.g., in marine water varied from non-detected to 11 µg/L and concentration in sediment range from µ/Kg to g/Kg depending upon the proximity of the area to source. Sediment cores have high concentration in the past 100-150 years and peaking in 1950. Unlike other POPs, PAHs do not undergo biomagnification in food chains and animals at higher trophic level like fish, birds, marine animals, have lower level of PAHs residue in their tissue compared to those at lower trophic level (Wenning and Martello, 2014). Out of all, 16 PAHs are considered to be toxic pollutants by the USEPA which are highly hydrophobic and adsorb onto the sediments. Many PAHs are believed to be toxic, carcinogenic and mutagenic. Because of it is lipophilic nature, gastrointestinal tract easily absorbed these compounds which further bioaccumulate into the fatty tissues of animal.

PAHs are proven to be more toxic to aquatic animals in the presence of ultraviolet light. Terrestrial invertebrates are prone to highly contaminated soil or sediment and can cause tumors, reproduction, development, and immunity. Mammal can be exposed to PAHs by inhaling tobacco smoke, wood smoke, ingestion of contaminated food or dermal contact (Dong et al., 2014; Veltman et al., 2011; Beyer et al., 2010). The short-term effects are not clear but occupational exposure to asphalt production plants, coal tar production plants, coking plants, smoke houses, coal-gasification sites, aluminum production plants, and trash incinerators at municipal facilities have shown to cause symptoms such as eye irritation, nausea, vomiting, diarrhea and confusion (Unwin et al., 2006). Chronic exposure possibly decreases the immunity, cataracts, detrimental effects to liver and kidney (e.g. jaundice), asthma-like symptoms, breathing problems, and function abnormalities in lungs. PAHs like naphthalene can cause skin irritation and cause damage to red blood cell due if inhaled or ingested in large amounts (Diggs et al., 2011; Bach et al., 2003).



Source: Suess, 1976

Fig. 1.6. Dispersal of PAHs in the air, land and aquatic environment (Suess et al., 1976).

1.4.5 Surfactants-: These chemicals are the ‘surface active agents’ that works to lower the interfacial surface tension between two liquids. They can be used as detergents, wetting agents, emulsifier, foaming agents and dispersants. Based on head group polarity surfactants can be classified into four categories: anionic, cationic, nonionic and amphoteric. Anionic forms are the most common and ancient type which has been used for washing and have various other application (Ivanković and Hrenović, 2009). These include Linear alkyl benzene sulfonates (LASs) which is the most popular type used in household detergents and shampoos type and Per fluorinated compounds (PFCs) such as perfluoro octane sulfonate (PFOS), and perfluorooctanoate (PFOA). Cationic surfactants are quaternary ammonium compounds (QACs) that are widely used in textile and cosmetic industry (Jardak et al., 2016; Zhang et al., 2015). Most common non-ionic and amphoteric surfactants are alcohol and alkylphenol ethoxylates (AEOs and APEOs) and amine oxides (AOs) respectively. Zwitterionic (amphoteric) surfactants have cores with both cations and anions attached to the same molecule. The main sources for the surfactants include domestic discharge from urban (after treatment) and non-urban areas (without treatment), industries like pharmaceuticals, textiles, tanneries, food, cosmetic, paint and pigment, paper and pulp, mining, petro-chemical, and as fertilizers and other formulations in agricultural fields. The concentrations can reach from micrograms to milligrams in wastewater while grams in soil corrections for agriculture (Jardak et al., 2016) Usually anionic and nonionic surfactants have LD_{50} equivalent to sodium chloride that are not toxic. Prolonged exposure may result in irritation and damage to skin due to distortion of lipid membrane of skin cells (Shao et al. 2005). They affect pathological, physiological, biochemical functioning of aquatic animals (Koparal et al. 2006). Surfactants are also capable of toxic effect on aquatic plants and can cause break-up the chlorophyll-protein complex delaying the metabolism and the growth (Larson et al. 1993).

1.5 Life style compounds and food additives

Life style compounds are substances that are usually consumed in modern day to day life. These include caffeine, nicotine and its metabolite cotinine. Caffeine is a natural stimulant and also a diuretic present tea, coffee, cacao plants, some fruits and added to the energy drinks. Nicotine is natural alkaloid also used a stimulant.

Food additives are compounds used to preserve, enhance the taste, smell, appearance and other properties that include artificial sweeteners (sucralose, aspartame), stabilizers (triethyl citrate), preservatives (butylated hydroxy anisole) are recognized as emerging contaminants. Other food additives are emulsifier, antioxidants, acidity regulators, foaming agents, fortifying agents and flavor, bulking and gazing agents, etc. (IFIC 2010; Awuchi et al., 2020).

Concentrations of both have been compound groups have been reported in wastewater effluent, surface and groundwater and higher than other emerging contaminants like pharmaceuticals and personal care products (Stuart et al., 2012 and 2013). Food additives like artificial sweeteners are released directly from food industries, households, animal farming; WWTP effluents as excretion without any alteration after consumption by human bodies. Sucralose is reported to be very persistent in environment so proposed to use as a marker of domestic wastewater contamination and caffeine as indicator of human-derived waste in surface water (Richardson and Ternes, 2017; Buerge et al., 2009; Oppenheimer et al., 2011). Deleterious effects of caffeine include behavioral alteration in mice, modifies central nervous system (CNS) processing like memory in insects and rodents, effects embryonic development of zebra fish, death from intoxication in humans (Rah et al., 2017; Castellano, 1976). ASs can cause inflammatory bowel disease, a multipotent carcinogen (cyclamate), inflammation of liver in mice, cytogenic and mutagenic for plants, neurological and oxidative alterations in daphnids (Wiklund et al., 2014; Oliveira et al., 2017; Qin et al., 2012; Bian et al., 2017)

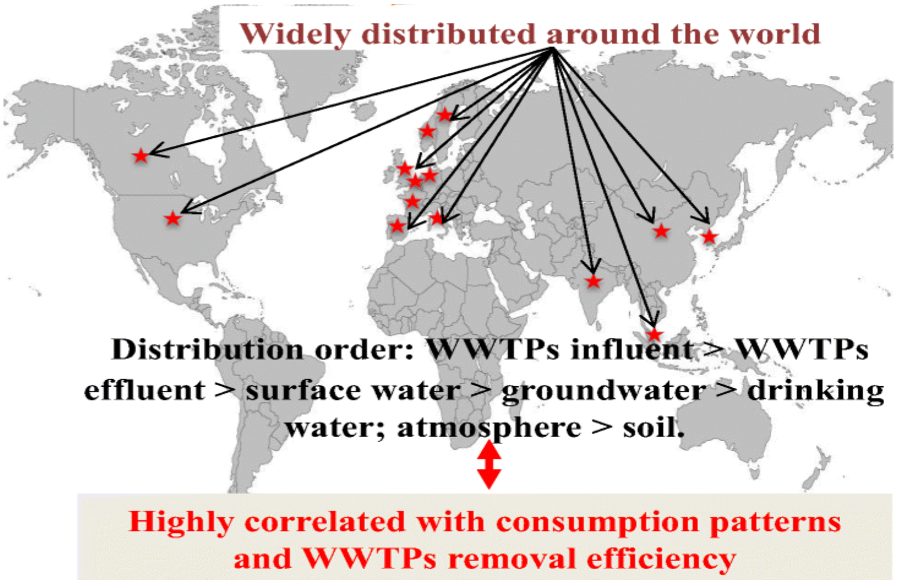


Fig. 1.7. Distribution of ASs worldwide (Luo et al., 2019)

There is still lack of understanding on how the ECs interact with each other and various other contaminants (Naidu et al., 2016) and the potential health effects of many EC's have not been recognized till now.

1.6 Regulation and Risk Assessment of CECs

The regulation and risk assessment of emerging contaminants is a vast topic in itself. This is due to the diversity and complexity associated with emerging contaminants. Source identification is not enough, chemical processes like dilution, adsorption, and transformation may impact their concentration and original structure. Indicators and tracers can help to find the sources of ECs in the groundwater (Lamastra et al., 2016). The major sources of EC contamination in groundwater is via WWTPs landfills, manure application, industrial runoff, urban run-off, etc. Widely spread and well-studied ECs are used as indicators for contamination. For example, PPCPs and ASs widely used for domestic purposes, contaminate groundwater which shows contamination from domestic wastewater. Yang et al. (2018), observed that sucralose can be used as a tracer for groundwater contamination. These studies are quite a few, mostly done in developed countries. Very few studies and regulations are there for ECs in developing countries. There is a poor understanding of their sources, pathways, and human and ecological risk. The concentrations of most of the ECs are found very low often in the studies but the bioaccumulation and biological activeness made these compounds a topic of contention in research. A basic approach followed for the management of the contamination is given below.

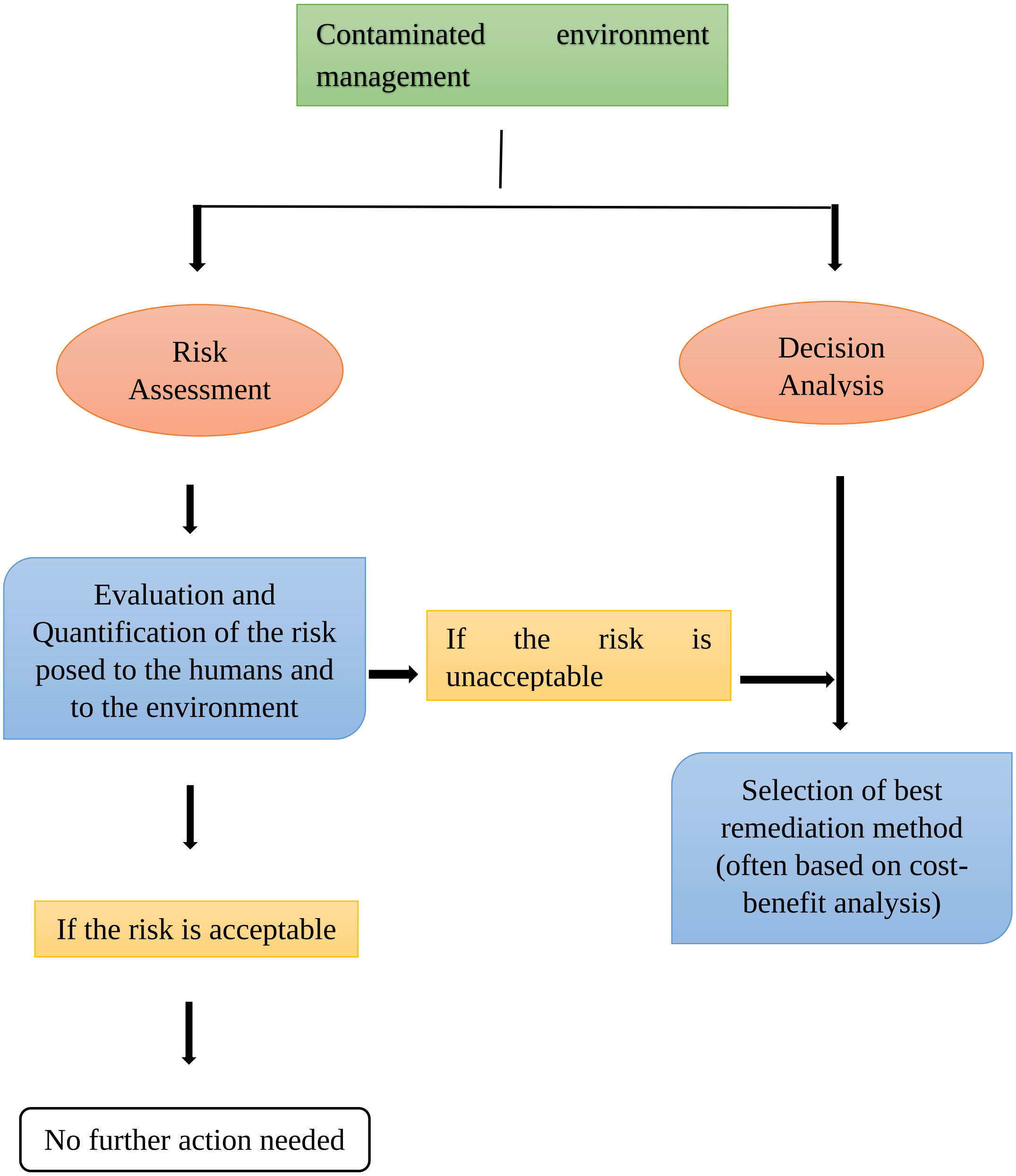


Fig. 1.8. Representation of basic approach for the management of the contamination. Adapted from (Khadam and Kaluarachchi, 2003)

Known toxic effects of pharmaceuticals in the Indian sub-continent include a sharp decrease in the number of vultures due to the consumption of diclofenac from the remains of livestock, renal failure in humans. Some studies also showed the toxic effects of emerging contaminants on aquatic fauna. Emerging contaminants show various toxic effects on the environment and human beings. Studies show, emerging contaminants show a toxic effect on bacteria, algae, fungi, wildlife, fishes, invertebrates, and arthropods. Emerging contaminants have a drastic impact on the aquatic ecosystem as compared to humans. Toxic effects on humans include cytotoxicity, oxidative stress, affecting the cardiovascular system, reproductive system, kidneys, lungs, and adverse effect on the neural system (US EPA, 2014; Frye et al., 2012; Vandenberg et al., 2013)

1.6.1 Risk assessment of ECs:

Risk assessment is a very significant step to regulate the ECs contamination in environment. This process helps to find priority compounds for regulation. Risk assessment is a scientific procedure to evaluate the adverse effects of a known or potentially harmful compound to human well-being and the natural environment. It has four steps; hazard identification, exposure assessment, toxicity assessment, and risk characterization (US EPA, 1989b). Studies are very scarce and this scarcity of data makes all the risk estimates uncertain to some extent. Due to various categories of ECs, it will a big task to produce risk assessment methods and databases for emerging contaminants. Also, the transformation of ECs after the interaction with the environment is a challenge in risk assessment. There is a need to focus on the single compound toxic effect as well as joint toxic effects of ECs as it can be synergistic or antagonistic (Di Poi et al., 2018).

The two most widely methods applied are 1) Risk Quotient (RQ)and 2) Hazard Quotient (HQ). Other than that, new methods have been developed for risk assessment of ECs. RQ is the ratio of a point estimate of exposure and a point estimate of effects while HQ is the ratio of a measured environmental concentration (MEC) and an effect concentration (EC). Risk assessment can be performed for acute exposure(short-term), for chronic(long-term) exposure, or the combination of both. Chonattu et al. (2016), studied the gaps by developing a water quality index, using physicochemical and biological parameters to study the potential threats caused by landfill leachates on groundwater quality in Njelianparamba, India. The above-described studies are vulnerability studies, a supporting step for risk assessment. Cooper et al. (2008) used physicochemical and toxicological data, in addition, the degree and extent of transport, fate, and toxic effects in the environment were used to produce a risk assessment database for pharmaceuticals. The European Commission gave guidelines for the environmental risk assessment (ERA) of human drugs which is compulsory for all medicine manufacturing establishments. ERA comprise three stages: first is initial screening, second is fate evaluation of the medicinal product, and finally identifying potential effects in aquatic ecosystem. Molander et al. (2009), created ecotoxicological data for most common ECs. Most of the studies are done in Europe. Also, a handful of studies are done in the USA and some other countries (China, Iraq South Africa, Korea and Lebanon).

Ranking and scoring systems (RSSs) determines the capability of a chemical compound to cause environmental effects based on the information about its perseverance, bioaccumulation, and toxicity and help to prioritize compounds (Mitchell et al., 2002). The scoring method encompassed categorizing and linking scores for exposure and hazard. There are various ways to determine the ranking system. Indicators and tracers can be helpful to develop these models. Environmental tracers provide the information on the time scales of the solute transport and maximum concentration of a contaminant at the discharge area, which can support the development of conceptual models (Lamastra et al., 2016).

There are hundreds of known ECs presently and remediating each of them will not be feasible. So, selecting the most harmful compounds will make the ECs regulation practical and easier. This is where risk assessment is useful.

1.6.2 Regulation of ECs

The monitoring and regulation of emerging contaminants from their point sources are much easier compared to their diffused sources. Also, the diffuse sources can pose a greater risk of contamination (Jurado et al., 2010) There are many regulations and rules are made by developed countries like the USA, UK, Japan, and some European countries. It cannot be denied that economic development and human greed made it tough to set strict regulations for these contaminants. The regulatory authorities choose priority compounds based on their toxic effect, information gap, and lack of monitoring data. The regulation for specifically selected compounds is due to the high cost of monitoring and remediation methods, and the scarcity of data on the effect and behavior of ECs.

In the USA Environment protection agency (EPA) regulate and protect the groundwater. EPA defined the primary standards to control the contaminants in drinking water. EPA made a contaminant candidates list (CCL) for priority compounds and also decides whether to regulate these compounds or not through regulatory determination. The CCL3 list includes pesticides, pharmaceuticals, chemicals used in commerce, pathogens, and biological toxins. CCL4 list includes 97 chemicals from industrial use, pesticides, disinfection by-products and pharmaceuticals. Preliminary regulations are taken for PFOS and PFOAs in CCL4 list (US EPA, 2021). Drinking water directives defined the quantities of organic pollutants in European drinking water. Most of the European countries implement the rules of the European Water Framework Directive (2000; 2000/60/EC) and the Groundwater Daughter Directive (2006; 2006/118/EC). The main aim of this directive is to regulate the priority compounds, which are updated with time. There is a group called Endocrine Disrupters Expert Advisory Group of the European Commission to deal with EDCs. Japan and China don't include pharmaceuticals in their targeted compounds. Environmental quality standards (EQS) were first issued in Japan in 1997. It is revised from time to time. The compounds included are heavy metals, chlorinated organic compounds, and volatile organic carbons. The Indian government has proposed some set of rules for pharmaceuticals (antimicrobial-resistant). There has been revision for their rules from time to time. A National Policy was designed in 2011. Chennai Declaration was proposed in 2012 to manage antimicrobial drugs in the country.   A new schedule (schedule H1) was added to the Drugs and Cosmetic Rules,1945, including 46 drugs. It was implemented in 2014 by the Central Drug Standard Control Organization. Recently a Nation Action Plan on antimicrobial resistance 2017-2021, launched with six strategic priorities to effectively curd antimicrobial resistance in India (Philip et al., 2018).

An interdisciplinary approach combining science-policy and advocacy can be helpful for the regulation of ECs. The coordination between jurisdictions to exchange data and information can fill the knowledge gaps as regulation strategies need a level of information.

1.7 Study Area

1.7.1 Geology

The Ganga River Basin encompasses Himalayan in north, peninsular India in the south and the Gangetic plain occupying the middle, accounts for 21.6%, 55.4%, and 23.0% of the total basin area, respectively. The Himalayan zone comprise of four sections separated by main thrust systems. The sections are Tethyan sedimentary zone with Palaeozoic –Mesozoic carbonates and clastic sediments, the higher Himalayan crystalline constitutes of orthogneisses, paragneisses, migmatites and highly metamorphosed marbles, the lesser Himalaya consists of metamorphosed and un-metamorphosed Precambrian sequences and the outer Himalayan belt having uplifted Siwaliks of Mio-Pliocene detrital sediments, namely, coarse sandstones, clays and conglomerates. The peninsular system which is Indian Craton region comprise of major geological structures such as Aravalli Range, the Bundelkhand crystalline ranges (made from granite), the Vindhyan (with sandstones, shales and carbonates), the Malwa Plateau and the Chotanagpur Plateau, that are predominantly comprising of different rock types of particularly of Archean and Proterozoic times (Pandey and Singh, 2017). The Ganga alluvial plains are formed by the erosion from the Higher and Lesser Himalaya creating of beds of clay, sand and gravel (Singh et al., 2005). The alluvial plain and peninsular drainage consist of locally formed evaporites from river floodwater and subsurface water capillary action. Tributaries of Ganga, Ramganga, the Ghaghara, and the Gandak rivers drains the Himalaya’s orogenic belt region, the Gomti drains the Ganga alluvial plains and the Son and Tons rivers drains the northern Indian craton region. The tributaries of the Yamuna (Chambal, Sind, Betwa and Ken) and the Son flows through the peninsular region with distinct lithologies such as Deccan Traps, the Vindhyan and Vindhyan–Bundelkhand plateau, respectively. Rivers arising from Himalayan orogenic belt are characterized by the high proportion of fine and very fine sand. Rivers that drain northern Indian craton region mainly transport coarse and medium- grained sand (Rai et al., 2010; Singh et al., 2007).

1.7.2 Geography

The GRB is located between 77’- 88’ E longitudes and 24’- 30’ N latitudes. The river originates from high altitude Himalayas, the Gangotri Glacier with a height of 4100 m (Singh et al., 2003) and total area of approximately 8,61,452 km^2 occupying 26.3% of the country's overall geographical area (Bera, 2017). At Devprayag, Bhagirathi and Alaknanda merge and is called as Ganga. The river Ganga is 2525 km in length (Singh et al., 2003). After entering West Bengal, at

Farakka Barrage, Ganga divides into its distributaries 1) Hooghly, which runs south through the West Bengal and empties at Sagar Island 2) Padma, the major distributary, meets Jamuna and Meghna river before joining the Bay of Bengal, Bangladesh (Allison, 1998). The river can be divided into three main stretches i.e., upper stretch (from origin to Haridwar), middle stretch (Haridwar to Varanasi), and lower stretch (Varanasi to Ganga Sagar) (Action Plan, 2010). Ganga River Basin is highly populated with mean population density of 520/km^2 (Rahaman, 2009). The Ganga basin has a water potential of 695 km^3, which includes surface water and groundwater (Misra, 2011). The area of the Ganga basin that is culturable estimates about 58.0 M. Ha can be divided into 19 sub-basins (Misra, 2011; Bera, 2017). Ganga basin has a humid subtropical climate (Singh et al., 2003). This climate has four seasons classified as winter (January–March), summer (April–May), monsoon (June–September), and post-monsoon (October–December). These can be broadly categorized as (June to September) and dry season (November to March). Ganga basin has a significant impact from summer monsoon from which the eastern part receives more precipitation compared to the west part of the basin. The dry season has little rainfall (Mishra et al., 2013) and wet season witnesses 80% of the annual discharge (Nepal and Shrestha, 2015). High flow at this time is responsible for erosion, transportation, and accumulation processes in the river (Singh et al., 2003). The onset of monsoon usually appears in early June at the mouth of the delta region. By the end of July, the monsoon establishes itself over the entire basin.

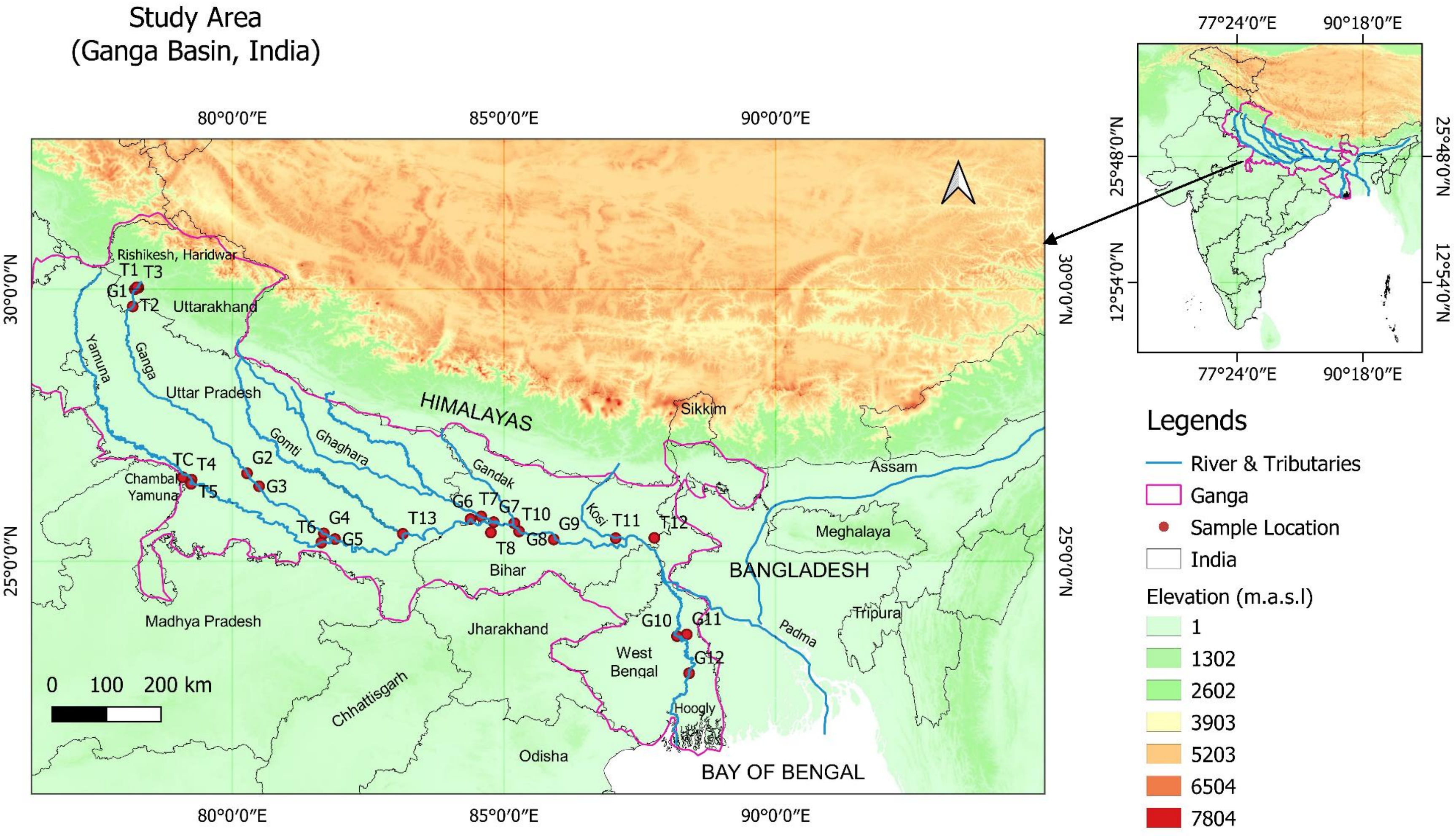


Fig. 1.9. Location map and sampling locations along the Ganga River basin

(G1-G12: Ganga River samples, T1-T12 and TC: Tributaries to Ganga and Yamuna, respectively).

1.8 Aims and objectives

Ever increasing indiscriminate anthropogenic activities during the past decades have delivered bulk quantities of CECs in natural environment. In the present scenario, methodology only for certain classes of ECs are harmonized and for majority of the compounds the detection limits are very low to detect. The presence of vast variety of pharmaceuticals and personal care products have reported from particular stretch or from entire Ganga River (Chakraborty et al., 2019; Sharma et al., 2019). The influence of its tributaries on concentration of ECs in Ganga have not been evaluated in the previous studies. Although presence of the emerging compounds studies in this research have been reported in theses study but still there is lack of data on few ECs such as benzophenone and BcF.

There is need for understanding on how ECs interact with each other, behavior in various environmental matrices and their potential health effects. This will require identification of contaminants, their concentration levels in the environment together with their harmful impacts on the organisms for achieving better management of risk associated with aquatic organisms and humans. The present study aims to determine the concentration and distribution of the CECs along the entire Ganga River basin with understanding the influence of its tributaries, water and bed sediment physicochemical parameters and urban settings. Further, assessment of risk will provide information to the regulatory authorities for proper management of the release of wastewater.

Objectives

1. To determine the concentration of different types of CECs in three environmental receptors (river water, bed sediment and suspended particulate matter (SPM)).
2. To evaluate the influence of tributaries of Ganga to the river contamination.
3. Preliminary assessment of the ecological risk.

Chapter 2

Material and methods

2.1 Sampling locations, sample collection and storage

The sampling was done in month July (from 5th July'19 to 21st July'2019) and a total of twenty-six location were sampled as shown in Fig. 1.9. The monsoon had arrived to the middle stretch. The first sample was collected from Rishikesh during pre-arrival of the monsoon. Three types of samples were collected, namely, river water, bed sediment and SPM.

- River water samples: Twenty-five samples were collected in 2 L amber glass bottle to protect it from direct sunlight. One location (T2) was dry river bed. The samples were transported in ice-box with dry ice and were refrigerated at 4ºC in laboratory until further analysis. Total number of samples were twenty-five.
- Bed sediment: Twenty-six samples were collected in 500 ml amber glass bottles and were kept in ice-box during transportation. These were also stored at 4ºC in laboratory until further analysis. Total number of samples were twenty-six.
- SPM: Twenty-six samples of 40 L were collected in two 20 L polypropylene bottles from each location. The samples were transported at ambient temperature and was processed after reaching the laboratory. Total number of samples collected were twenty-five but only ten samples were used as there was not enough amount of suspended sediment for analysis.

Picture 1: Song river (T1)

Picture 2: Chambal river (TC)

Picture 3: Yamuna river (T6) in Prayagraj

Picture 4: Ganga river (G4) upstream Prayagraj

Picture 5: Gandak River (T10)

Picture 6: Hooghly (G12) in Bansberia, West Bengal

Pictures of sampling locations.

2.2 Sample processing, extraction and analysis

2.2.1 Pre-processing of bed sediment

Homogenized the wet sediment sample in a stainless-steel tray

↓

Air dried the sediment sample

↓

Crushed the samples in a mortar and pestle

↓

Sieve the samples through 0.063 µm sieve

2.2.2 Pre-processing of SPM

The suspended particles in the 20 L polypropylene bottles were allowed to settled by physical process of sedimentation following Stoke’s law. After settling of the particles to the bottom, overlying water was removed using tube. The final volume of water is collected in glass trays to evaporate the residual water.

2.2.3 Sediment Sample Extraction procedure and calculation

Bed sediment samples and SPM (suspended particulate matter) were extracted using United States Environmental Protection Agency (US EPA) 3540c method (US EPA, 1996) for Soxhlet extraction. The summary method is as follows-:

Blended 10 grams of the sample with 10 g of anhydrous sodium sulfate

↓

Homogenized paste was then transferred to an extraction thimble and protected with glass wool

↓

Soxhlet apparatus consisting of the extraction thimble was set-up and connected to a 500-mL round bottom flask containing 300 ml hexane: acetone mixture (1:1)

↓

Heating temperature was adjusted on the heating mantle to obtain a cycling rate of 4-6 cycles/h

↓

The samples were extracted for a period of 16-24 hrs.

↓

Extract was dried with sodium sulfate to remove any water traces

↓

Concentrated the sample by rotary evaporator and stored in GC-vials

Calculation for determination of concentration in sediment using EPA 610 (US EPA, 1984; McDonald et al., 2000)

$$\boldsymbol{Concentration} = \frac{(\boldsymbol{A}) \times (\boldsymbol{V^t}) \times (\boldsymbol{Dlf})}{\boldsymbol{V_i} \times \boldsymbol{W_s}} \qquad \textbf{(2.1)}$$

where:

Dlf = the dilution factor applied to the extracts

$$\boldsymbol{Dlf} = \frac{\boldsymbol{Volume\ of\ extract\ used\ to\ make\ dilution}\ (\mu\mathbf{L})}{\boldsymbol{Volume\ of\ extract}\ (\mu\mathbf{L})} \tag{2.2}$$

W_s = the sample weight (g)

A = Amount of material injected (ng) which calculated using calibration curve plotted using areas vs concentration for external standard for each compound.

V_i = Volume of extract injected (µL).

V_t = Volume of total extract (µL).

2.2.4 Sample preparation, extraction procedure and calculation for water samples

Water samples were filtered using 0.45 micron filter paper.

SD-DLLME in water (Beldean-Galea et al., 2020**)**

6 mL of Milli-Q water was taken in a 10.0-mL conical glass tube

↓

An amount of 0.5 g of NaCl was added to the sample

↓

Subsequently a mixture containing 100 µL of acetonitrile and 75 µL chloroform was rapidly injected to the sample and gently hand shook for 2.0 min.

↓

Extract was then separated from the samples by centrifuging for 5 min at 2264×g

↓

The aqueous part was discarded very carefully and 2.0 μL of the extract was stored and injected into GC for analysis.

Calculation for determination of concentration in water (EPA 610)

$$\boldsymbol{Concentration} = \frac{(\boldsymbol{A}) \times (\boldsymbol{V_t})}{(\boldsymbol{V_i}) \times (\boldsymbol{V_s})} \tag{2.3}$$

where:

A = Amount of material injected (ng).

V_i = Volume of extract injected (μL).

V_t = Volume of total extract (μL).

V_s = Volume of water extracted (mL).

2.3.4 Standard and reagents

For extraction of CECs from sediment and water, HPLC grade hexane, acetone, chloroform, acetonitrile. Analytical standards such as PAHs in toluene, EPA 506 phthalates mix, benzophenone, methyl paraben, ethyl paraben and triclosan from Sigma-Aldrich. HPLC-grade methanol and toluene were used in preparation of the standards for calibration.

2.3.5 Instrumentation

Sample analyses for PAHs and phthalates were carried out on a Shimadzu (Kyoto, Japan) QP2010 GC system equipped with a Shimadzu AOC-20is auto sampler. The following conditions were deployed for analysis.

AOC-20is condition

Injection volume-: 2µL; *No. of rinse with solvent (pre-run)*-:5; *No. of rinse with solvent (post-run)*-:6; *No. of rinse with sample*-: 2; *Viscosity component time*-: 0.2 seconds

SPL1 Injector condition

Temperature-: 280^o C; *Injection mode*-: *Split; Sampling time*-: 1 min; *Carrier gas*-: Nitrogen; *Flow rate*- 1.21 ml/min; *Linear velocity* -:32.7 cm/sec

Column condition

RXi Silica MS column; *Length*-: 30m; *Inner Diameter*-: 0.25 mm ID

The GC column oven was initially held at 110 ◦C for 2 min and then programmed to 250◦C at 10 ◦C/min. After being kept at 250 ◦C for 5 min, the oven was programmed to 280 at 15 ◦C/min. FID1 detector was kept at 290◦C

GC-MS condition for Personal Care Products (PCPs)

Sample analyses for PCPs and PAEs were carried out on a Shimadzu (Kyoto, Japan) GCMS-TQ8050 system equipped with a Shimadzu AOC-20i+s auto sampler.

AOC-20i+s condition

Injection volume-: 2µL; *No. of rinse with solvent (pre-run)*-:4; *No. of rinse with solvent (post-run)*-:5; *No. of rinse with sample*-: 2; *Viscosity component time*-: 0.2 seconds

SPL1 Injector condition

Temperature-: 260^o C; *Injection mode*-: Split; *Sampling time*-: 1 min; *Carrier gas*-: Helium; *Pressure*- 85.7 kPa; *Total Flow*- 15.7 ml/min; *Column flow*- 1.15 ml/min; *Linear velocity* -:39.9 cm/sec; *Purge flow*- 3 ml/min; *Split ratio* -10

Column condition

Sh-RXi Column; *Length*-: 30m; *Inner Diameter*-: 0.25 mm ID; *Total Run time*-: 30 min

The GC column oven was initially held at 100 ◦C for 2 min and then programmed to 250◦C at 10 ◦C/min. After being kept at 250 ◦C for 2 min, the oven was programmed to 290 at 15 ◦C/min.

MS condition

Ion Source Temperature-: 220◦C; *Interface temperature*- 270◦C; *Solvent cut time*- 4 minutes.

2.3 Quality Control

For quality control blanks and five standards were analyzed for each analyte. The retention time, chromatograms, calibration curves for the analytes and LOD calculation were as follows -:

2.3.1 PAHs

Retention time for different compounds is mentioned in table 2.1.

Compound	Molecular weight (g/mol)	Retention time
Benzo(c)fluorene	216.2772	**9.908**
Benz[a]anthracene	228.2879	12.795
Cyclopenta[cd]pyrene	226.2720	12.868
Chrysene	228.2879	12.945
5-methylchrysene	242.3145	14.636
Benzo[b]fluoranthene	252.3093	17.487
Benzo[k]fluoranthene	252.3093	17.685
Benzo[j]fluoranthene	252.3093	17.880
Benzo[a]pyrene	252.3093	18.536
Indeno[1,2,3-cd] pyrene	276.3307	19.325
Dibenz[a,h]anthracene	278.3466	20.377
Benzo[ghi]perylene	276.3307	22.080
Dibenzo[a,l]pyrene	302.3680	22.490
Dibenzo[a,e]pyrene	302.3680	24.272
Dibenzo[a,i]pyrene	302.3680	25.536

Table 2.1. Standard mix solution of PAHs in toluene with molecular weight (g/mol), retention time and octanol/water partition coefficients

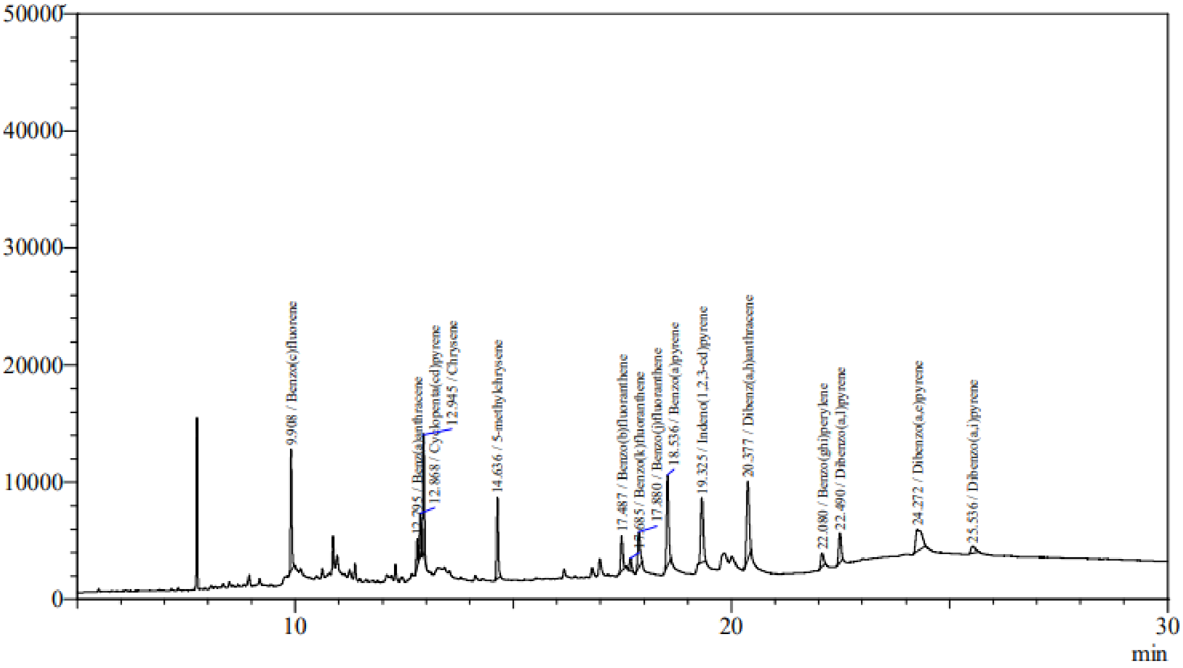
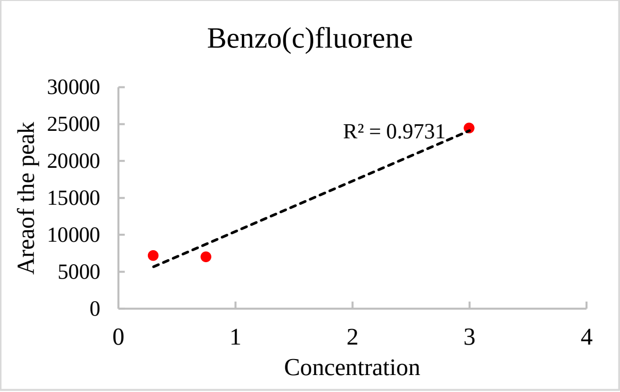
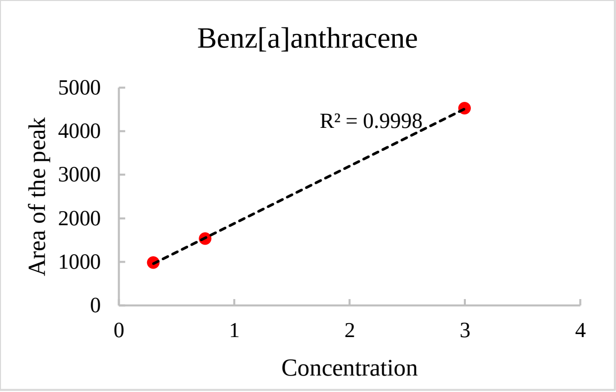
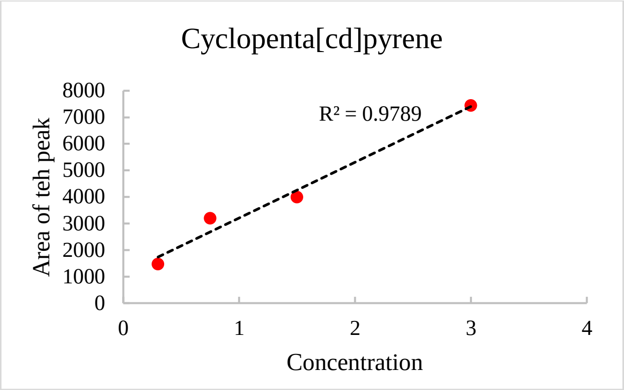


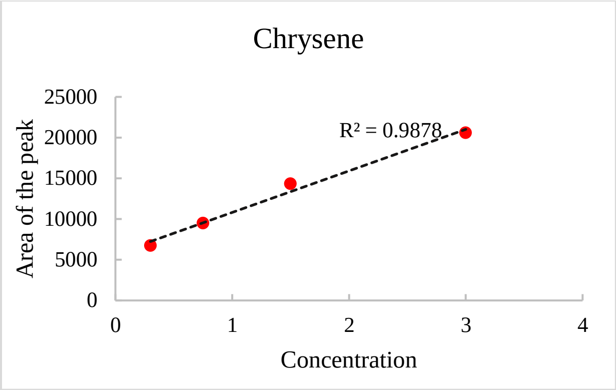
Fig. 2.1. Chromatogram for PAHs standard

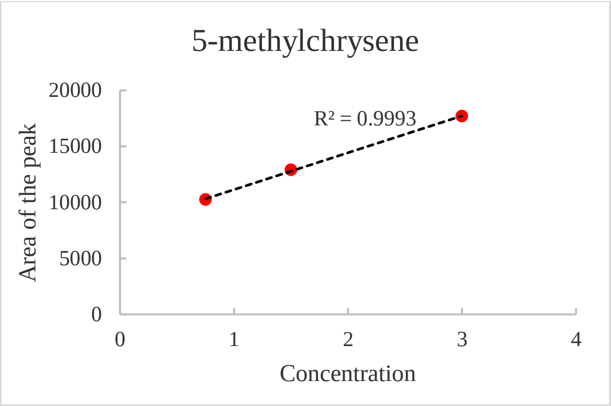
Calibration curves

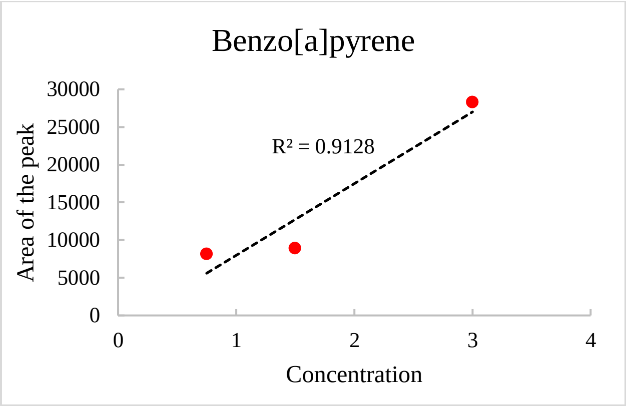


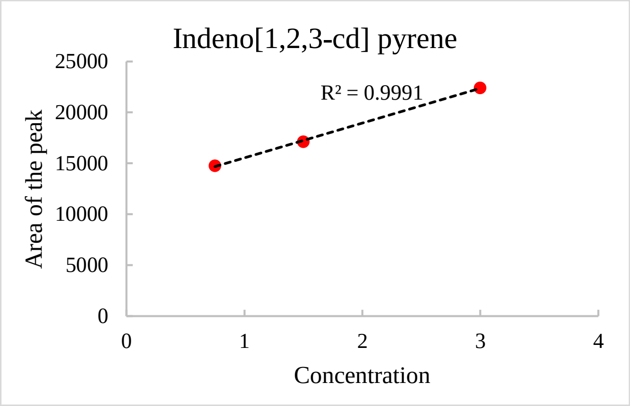


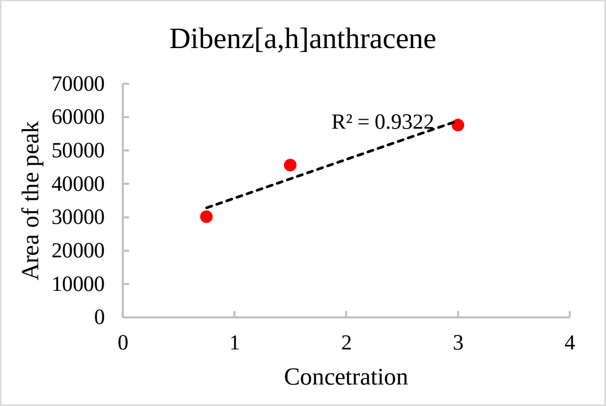

Cyclopenta[cd]pyrene
R² = 0.9789
Area of teh peak
8000
7000
6000
5000
4000
3000
2000
1000
0
0
1
2
3
4
Concentration


Chrysene
R² = 0.9878
Area of the peak
25000
20000
15000
10000
5000
0
0
1
2
3
4
Concentration


5-methylchrysene
R² = 0.9993
Area of the peak
20000
15000
10000
5000
0
0
1
2
3
4
Concentration


Benzo[a]pyrene
R² = 0.9128
Area of the peak
30000
25000
20000
15000
10000
5000
0
0
1
2
3
4
Concentration


Indeno[1,2,3-cd] pyrene
R² = 0.9991
Area of the peak
25000
20000
15000
10000
5000
0
0
1
2
3
4
Concentration


Dibenz[a,h]anthracene
R² = 0.9322
Area of the peak
70000
60000
50000
40000
30000
20000
10000
0
0
1
2
3
4
Concetration

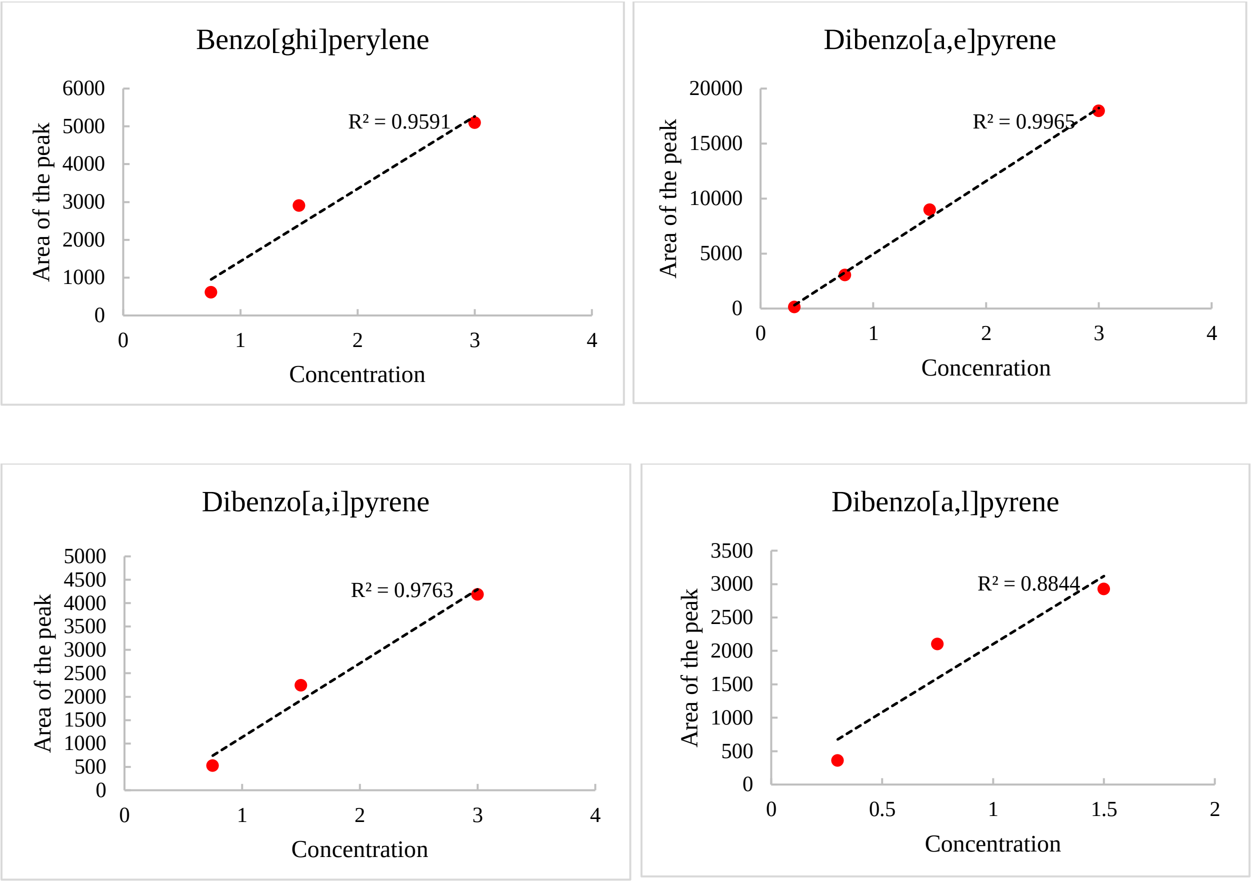


Fig. 2.2. Calibrations curves for PAHs

Limit of detection (LOD) calculation

$$\boldsymbol{LOD = 3.3 \times \frac{S_y}{S}} \qquad \textbf{(2.4)}$$

where,

S_y= Standard deviation of the intercept

S= Slope of the Calibration curve

PAHs	**LOD (ng/L)**
Benzo(c)fluorene	0.30
Benz[a]anthracene	0.12

Cyclopenta[cd]pyrene	0.70
Chrysene	0.27
5-methylchrysene	1.50
Benzo[b]fluoranthene	0.59
Benzo[k]fluoranthene	1.94
Benzo[j]fluoranthene	1.01
Benzo[a]pyrene	0.32
Indeno[1,2,3-cd] pyrene	0.27
Dibenz[a,h]anthracene	0.49
Benzo[ghi]perylene	1.05
Dibenzo[a,l]pyrene	0.46
Dibenzo[a,e]pyrene	0.06
Dibenzo[a,i]pyrene	0.96

Table 2.2. LOD calculated for PAHs

2.3.2 PAEs

Retention time of the compounds for the standard are-:

Compound	**Molecular weight**	**Retention time**	**Log K_{oc}**
Dimethyl Phthalate	194.18	8.178	1.6
Diethyl Phthalate	222.24	9.888	1.84
Di-N-Butyl Phthalate	278.34	13.903	3.14
Benzyl Butyl Phthalate	256.25	17.834	3.8
Bis(2–Ethylhexyl) Phthalate	390.5561	18.178	4.94
Bis-2-Ethylhexyl Adipate	370.57	20.308	4.2
Di-N-Octyl Phthalate	390.56	23.172	4.38

Table 2.3. Standard mix solution of PAEs with molecular weight (g/mol), retention time and octanol/water partition coefficients

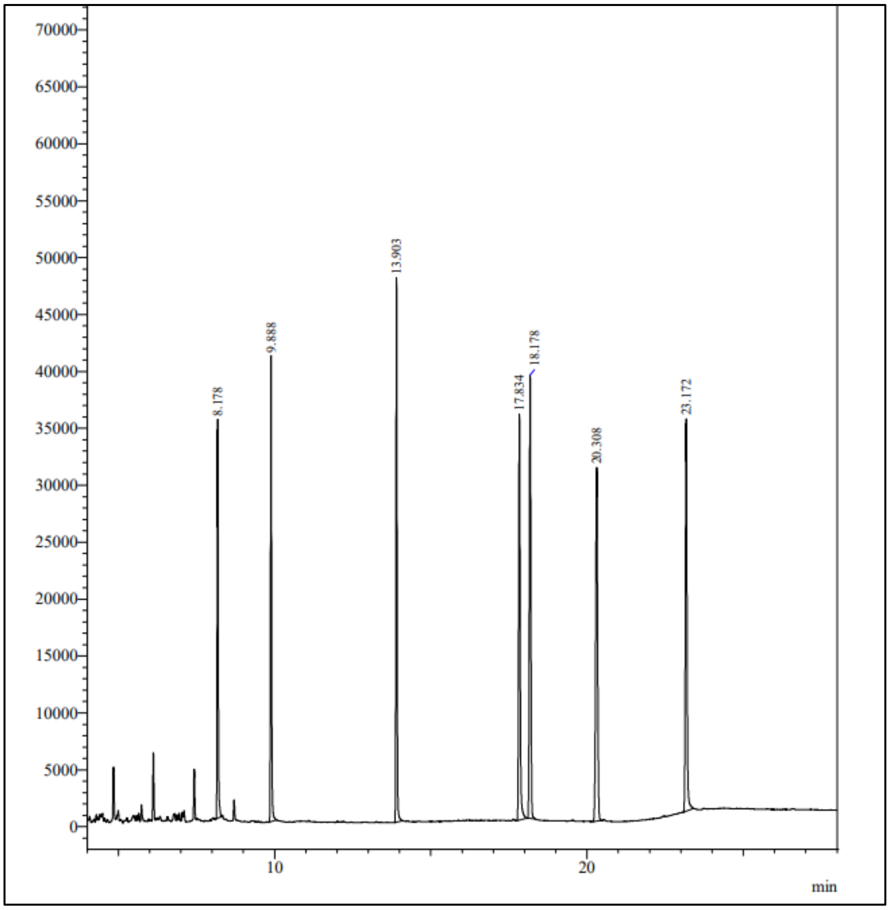
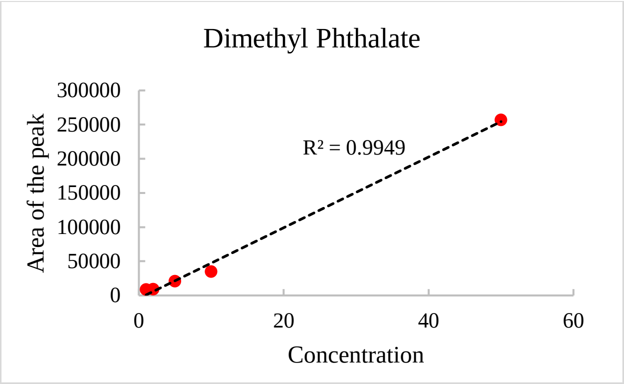
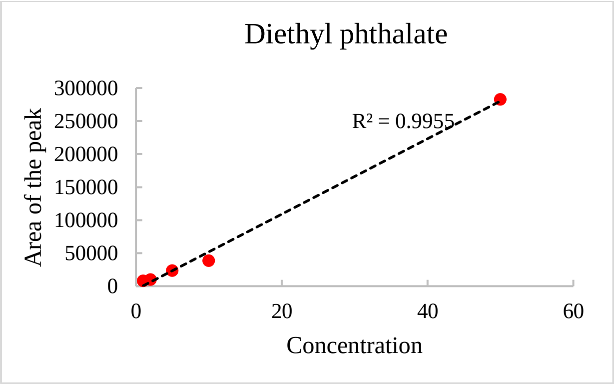


Fig. 2.3. Chromatogram for PAEs standard

Calibration curves





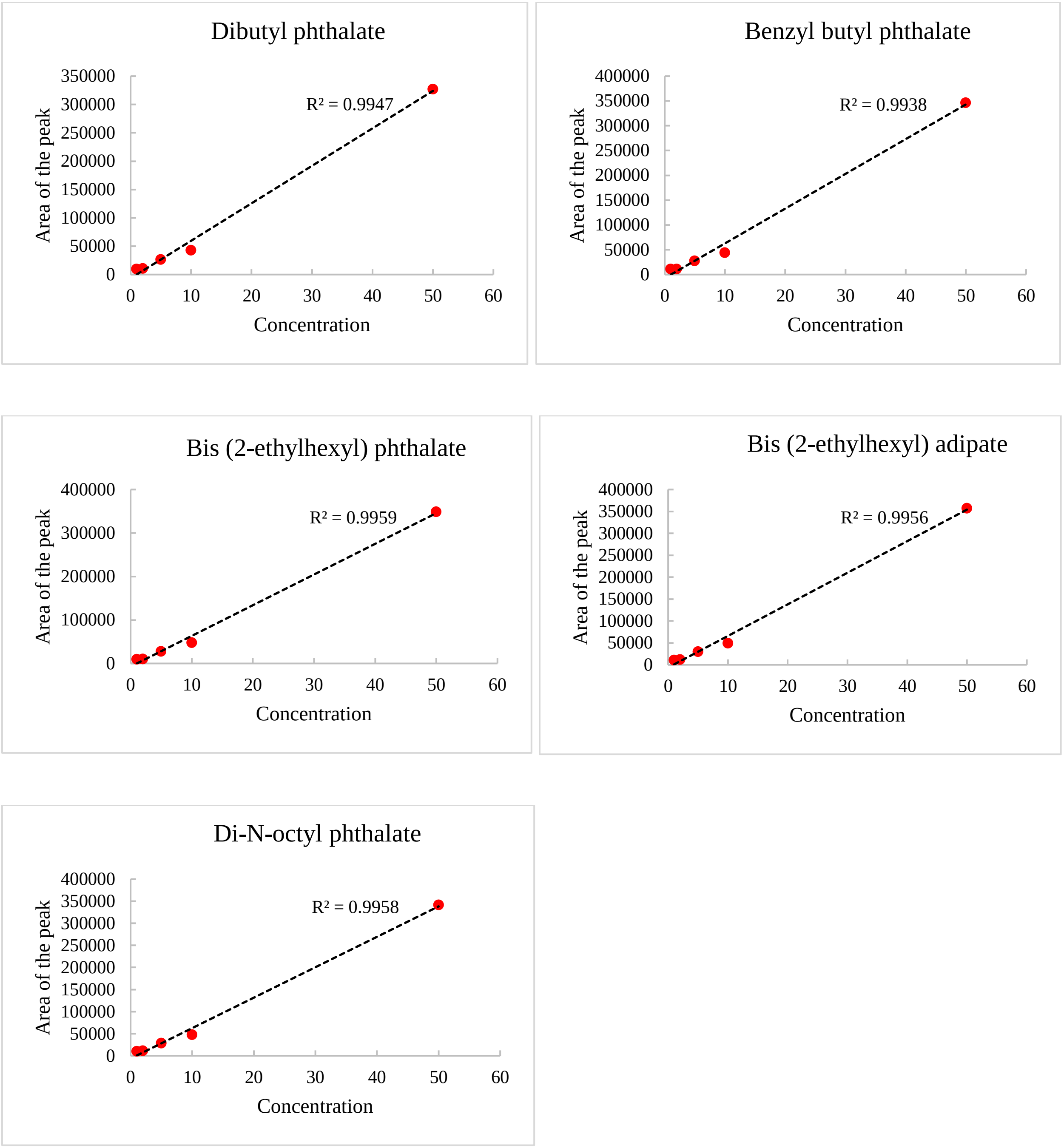


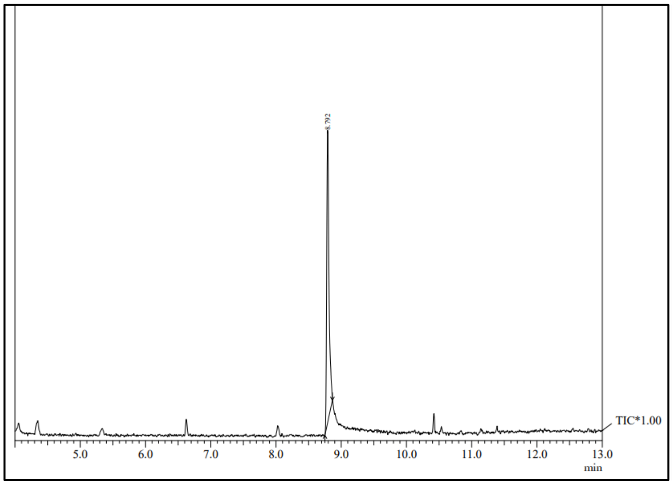
Fig. 2.4. Calibration curves for PAEs

LOD calculation

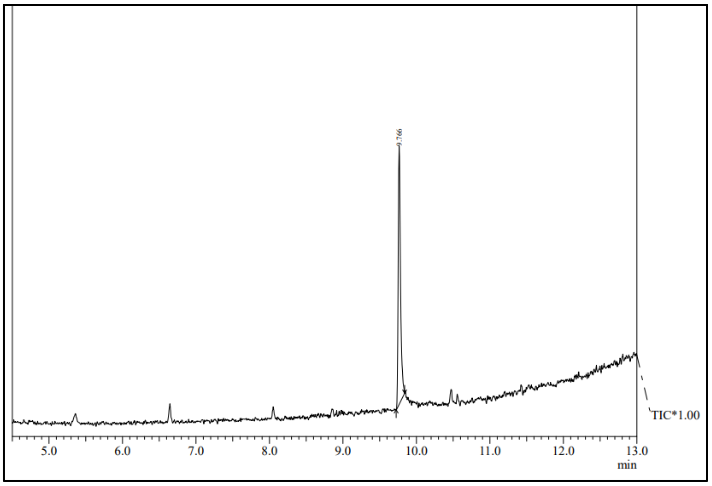
LOD for PAEs were calculated using equation 2.4.

PAEs s(Water)	**LOD (ng/L)**
Dimethyl Phthalate	1.31
Diethyl phthalate	1.12
Di-N-butyl phthalate	1.05
Benzyl butyl phthalate	1.07
Bis (2-ethylhexyl) phthalate	0.87
Bis (2-ethylhexyl) adipate	0.88
Di-N-octyl phthalate	0.90

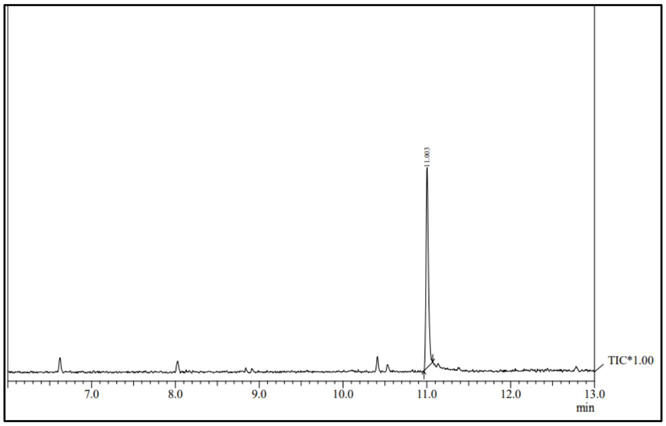
Table 2.4. LOD calculated for PAEs



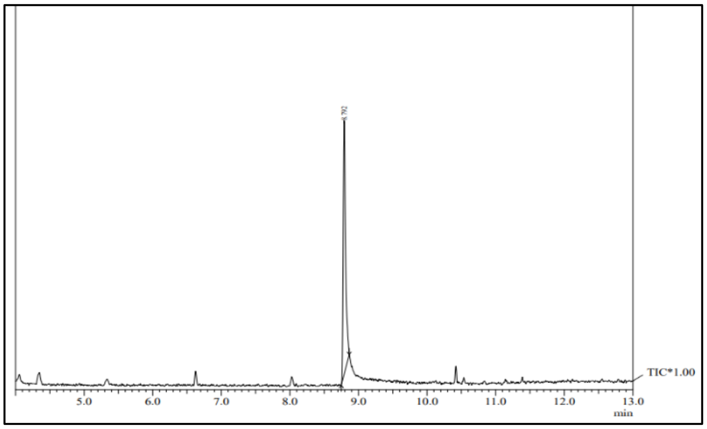
(a)



(b)



(c)



(d)

Fig. 2.5. Chromatogram for PCPs standard (a) Methyl paraben (b) Ethyl paraben (c) Benzophenone (d) Triclosan

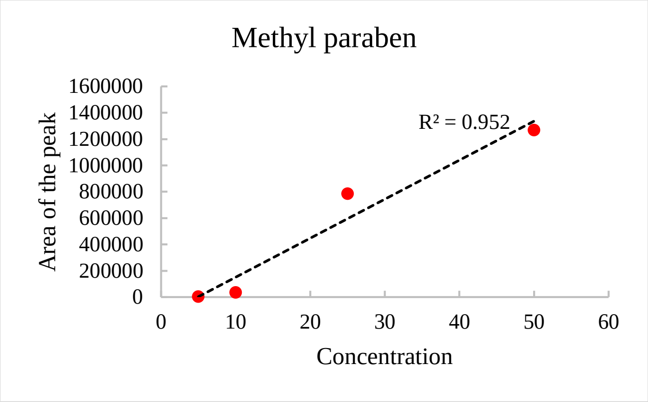
2.3.3 Personal Care Products (PPCPs)

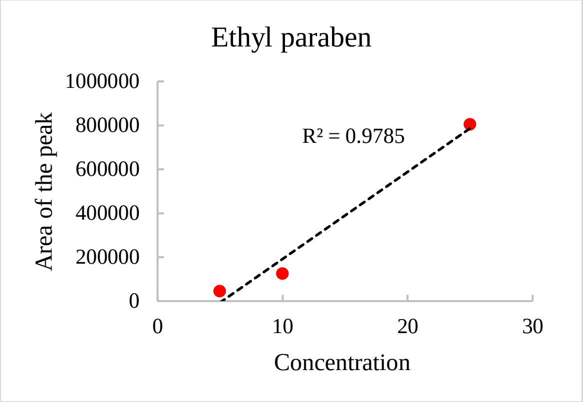
Retention time of the compounds for the PCPs standard are-:

Compounds	**Molecular weight**	**Retention time**	**Log K_{oc}**
Methyl paraben	152.15	8.792	1.94
Ethyl paraben	166.17	9.76	2.2
Benzophenone	182.217	11.010	2.64
Triclosan	16.034	16.034	3.8

Table 2.7. Standards with molecular weight (g/mol), retention time and octanol/water partition coefficients

Calibration Curves





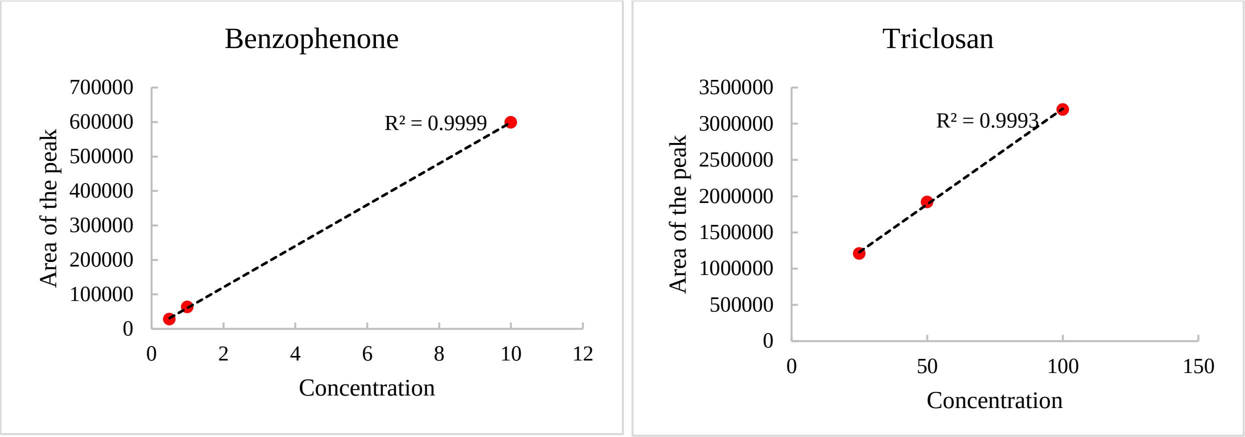


Fig. 2.6. Calibrations curves of PCPs

LOD calculation

LOD for PCPs were calculated using equation 2.4.

PCPs	**LOD (ng/L)**
Methyl paraben	0.172
Ethyl paraben	0.068
Benzophenone	0.02
Triclosan	0.091

Table 2.6. LOD calculated for PCPs

2.4 Statistical Analysis

Non-parametric multivariate statistical analysis was carried out to extract meaningful data information and interpretation. Nonparametric tests have various advantages over parametric tests specially when assumptions for the parametric tests are violated. In that case, the former proved to be statistically more powerful. The test allows lesser number of assumptions including non-applicability of normality and smaller sample sizes are acceptable. They are applicable for almost all data types, including nominal variables, interval variables, or data with outliers or imprecise data. In this study, the data was not normally distributed and due to low detection of some emerging contaminants, the data consisted of missing values and with outliers. Mainly two following tests were performed on CECs data in Ganga River basin:

- Kendall tau's correlation: It is a non-parametric measure of relationships between columns of ranked data This type of a correlation is alternative for parametric Pearson's correlation where Tau's correlation coefficient (**τ**) returns a value of -1 to 1 indicating a negative and positive perfect relationship, respectively. While a value of 0 show no relationship between variables. A significant relationship can be defined when the value of probability of significance (p) is less than 0.05 or 0.01. It is performed using IBM SPSS statistics 21.
- Kruskal-Wallis test: When assumption of normality is violated, the nonparametric Kruskal-Wallis (KW) test is frequently used for between-group comparisons as in case of its parametric equivalent statistics, one-way ANOVA. It is employed for comparison of two or more independent variables of equal or different sample sizes. It extends the Mann-Whitney U test to more than two groups. The null hypothesis of the Kruskal-Wallis test is that the mean ranks of the groups are the same. A significant result is when p value is below 0.05, in that case null hypothesis rejected showing at least one group stochastically dominates the other group. The test was performed using IBM SPSS statistics 21.

Chapter 3

Polyaromatic hydrocarbon (PAHs)

3.1 Physical and chemical properties

PAHs are ubiquitously present in the environment due to both natural and anthropogenic activities. Naturally they are released from forest fires, open burnings, natural seeping of petroleum or coal deposits and volcanic eruptions. Anthropogenic actions such as incomplete combustion of fossil fuels (such as wood, gasoline, petrol etc.) is the primary source. Important human -induced sources of PAHs include residential use of fuel, vehicular exhaust, coal-tar pitch and asphalt production, coal gasification and liquefying plants, carbon black, aluminum production, petroleum refineries and catalytic cracking in industries.

In this study, eleven PAHs were detected from fifteen analyzed PAHs which represent physical and chemical properties (TSCA[1], ICSC[2], OSHA[3] and HSDB[4]) as follows-:

(i) **Benzo (a) pyrene (BaP):** It is aromatic hydrocarbon with crystalline structure released during inefficient combustion of organic matter. It appears as colorless liquid and silver grey solid. It has pale yellow needle like crystals from benzene and alcohol and has faint aromatic odor. The boiling and melting point at STP (standard reference point of temperature and pressure) are 360°C and 179°C. It is very soluble in chloroform, soluble in benzene, toluene, xylene, and

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[1] Toxic Substances Control Act of 1976
[2] International Chemical Safety Cards
[3] Occupational Safety and Health Administration
[4] Hazardous Substances Data Bank

ether and slightly soluble in alcohol. Solubility for water is g/100ml at 20°C, density is 1.351 g/cm^3 and log K_{ow} = 6.13. The irradiation in indoor sunlight or results in photo-oxidation and release hazardous carbon oxides under fire conditions.

(ii) Benzo (a) anthracene (BaA): It is a crystalline aromatic hydrocarbon with four-fused benzene rings that is not produced commercially and released during incomplete combustion. The appearance of the chemical is leaflet or plate like with greenish-yellow fluorescence. These plates can be formed either from glacial acetic acid or alcohol. The boiling and melting are 435°C and 157.2°C at STP. The compound is soluble in most of the organic solvents such as ether, alcohol, acetone, benzene, slightly soluble inn acetic acid and insoluble in water. The solubility in water is 9.4x10^{-3} mg/L at 25 °C. Relative density is 1: 1.274 and log K_{ow}= 5.76. Just like benzo (a) pyrene under fine condition emits carbon oxides and is stable when stored.

(iii) Chrysene (Chy): It has four fused benzene rings and is naturally occurring in coal tar. It is white crystalline solid with strong blue fluorescence. The color can be turned yellow due to impurities. It is denser than water and have density of 1.27 g/cm^3. The boiling and melting point are 447.78°C and 253.89°C. It is soluble in benzene, slightly soluble in alcohol, ether, carbon bisulfide and glacial acetic acid, and insoluble in toluene and water (2.0x10^{-3} mg/L at 25 °C). The value for log K_{ow} is 5.73. It is stable under storage condition.

(iv) 5-methyl chrysene (MeC) It is a crystalline compound primarily released from gasoline exhaust and tobacco smoke. The structure consists of four fused benzene rings. It appears as purple needle like crystals that can be recrystallized from benzene and ethanol. The melting and boiling point are 118.3°C and 465.14°C. It is insoluble in water (0.062 mg/L at 27 °C) and soluble in acetone. It is lighter than chrysene and have density and log $K_{ow,}$ 1.10 g/cm^3 and 6.07 respectively.

(v) Benzo (b) fluoranthene (BbF): It is a colorless compound with five fused aromatic rings that comes from common sources of PAHs and amino acids and fatty acid pyrolysis. The ortho- and peri-fused polycyclic arene have benzene ring fused with acephenanthrylene ring. Colorless needles can be derived from recrystallization of toluene and glacial acetic acid. The melting and boiling point are estimated to be 162 to 165°C and 481°C at STP. There is no solubility in water (1.2-1.5x10^{-3} mg/L), slightly soluble in acetone while miscible with benzene. The log K_{ow} is 5.78 and is stable under storage condition and releases harmful carbon oxides just like others.

(vi) Benzo (j) fluoranthene (BjF): The compound has yellow crystallized appearance. The plates can be formed from alcohol while acetic acid gives needle like crystals. The organic compound boils at 480°C and melts at 166°C. It is soluble in hydrogen sulfide on heating, slightly soluble in ethanol and acetic acid and is not soluble in water (2.5x10^{-9} mg/L). Log K_{ow} = 6.11 and density= 1.286 g/cm^3.

(vii) Benzo (k) fluoranthene (BkF): It is another isotope of BbF with five fused rings (Fig 4.1(f)). The process of recrystallization from hexane and acetic acid produces yellow prism while, alcohol produces plate while acetic acid form needles. The boiling and melting point differs from its other isotopes (480°C and 217°C). Solubility in water is 8x10^{-4} mg/L at 25 °C. It is soluble in ethanol, benzene and acetic acid and insoluble in water. The log K_{ow} = 6.11. It inhibits photo-oxidation from fluorescent light or indoor sunlight when in organic solvents.

(viii) Indeno (1,2,3-cd) pyrene (IcdP): Structurally, it has six fused rings. The yellow crystals of the compound can be obtained from cyclohexane while bright yellow plates from petroleum ether. The melting varies from 163.6°C and 536.0°C. It is soluble in organic solvents and insoluble in water (solubility in water=1.9x10^{-4} mg/L at 25 °C). The estimated density and log K_{ow} are 1.1847 and 6.7. When decomposed, it emits acrid smoke and fumes similar to other PAHs.

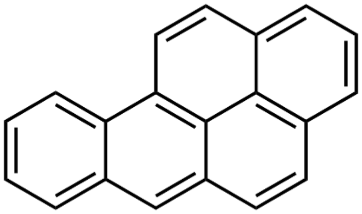
(ix) Benzo (ghi) perylene (BghiP): The compound has five fused aromatic rings with ortho- and peri-fused polycyclic arene. This white crystalline compound is insoluble in water and can be prepared from benzene as Yellow-green fluorescent leaflets. The melting and boiling points are 550°C and 278.0°C. It is soluble in 1,4-dioxane, dichloromethane, benzene, and acetone. The density is 1.3 g/cm³ and log K_{ow} = 6.63. It is stable both under storage and to photo-oxidation. The solubility of water is estimated to be $2.6x10^{-4}$ mg/L at 25 °C

(x) Dibenzo (a, e) pyrene (DaeP): The aromatic hydrocarbon has six fused rings and ortho- and peri-fused polycyclic arene just many of the PAHs. Pale yellow needles of this compound can be obtained from xylene. Its boiling point is roughly estimated to be 378.4°C and melting point is 233.5°C. It is insoluble in water with solubility=$0.6x10^{-4}$ mg/L at 25°C, slightly soluble in ethanol, acetone, benzene, acetic acid and soluble in toluene and concentrated sulfuric acid. The density and log Kow approximated to be 1.913 g/cm^3 and 7.28.

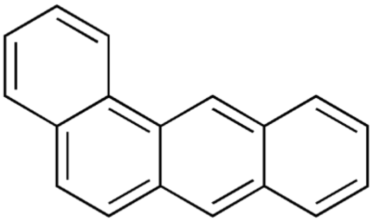
(xi) Dibenzo (a, i) pyrene (DaiP): The yellowish-reddish compound is formed from six fused rings that is anticipated to both mutagen and carcinogen. Benzene and ethanol forms yellow plates of the compound. The boiling and melting point 630.6°C and 162.4°C. It is insoluble in water like other PAHs ($3.62x10^{-3}$ mg/L at 25°C) and soluble in concentrated sulfuric acid and olive oil. The density is 1.28 g/cm^3 and log K_{ow} = 7.71.

(xii) Benzo (c) fluorene (BcF): It is an aromatic compound derived from fluorene with an extra benzene ring altogether with three fused aromatic rings. Plate like crystals are formed from ethanol. The boiling and melting points are 398°C and 125-127°C, respectively. It is insoluble in water and soluble in many organic solvents. The density of the compound is 1.185 g/cm^3. It is mutagenic and is capable of inducing ling tumors. On heating until decomposition results in unpleasant smoke and vapors similar to others.

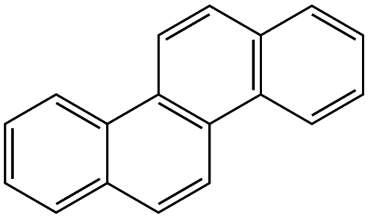
(xiii) Dibenz (a, h) anthracene (DahA): Originating from incomplete combustion of organic matter this compound is believed to be carcinogen similar to other discussed PAHs and also mutagen. It consists of five fused rings and ortho-fused polycyclic arene. It looks as white crystals or pale-yellow solid that can be recrystallized from acetic acid. It boils and melts at 524°C and 269.5°C respectively. The solubility in water $2.49\text{x}10^{-3}$ mg/L at 25 °C indicating it is not soluble in water. The density and log K_{ow} and 1.282 g/cm^3 and 6.5. Although stable under storage condition, undergoes photo-oxidation under sunlight in solution.



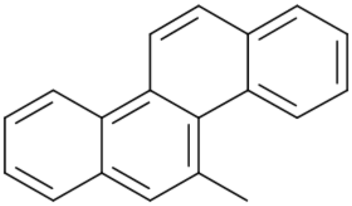
Benzo (a) pyrene



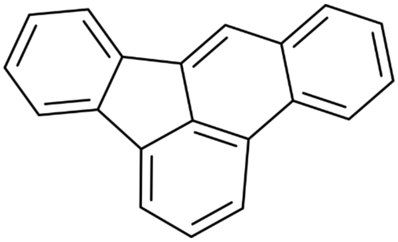
Benzo (a) anthracene



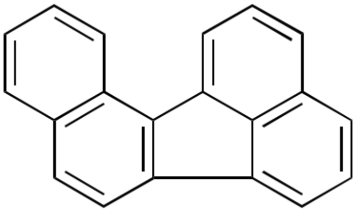
Chrysene



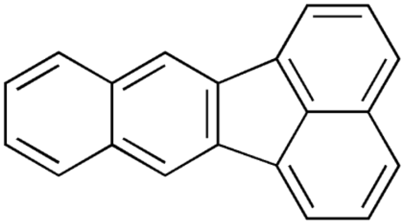
5-methyl chrysene



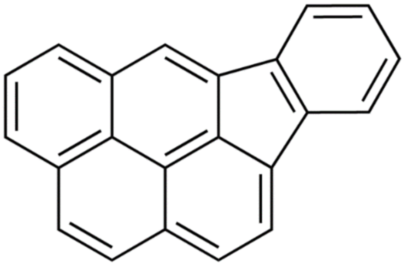
Benzo (b) fluoranthene



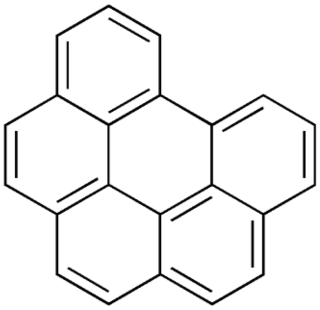
Benzo (j) fluoranthene



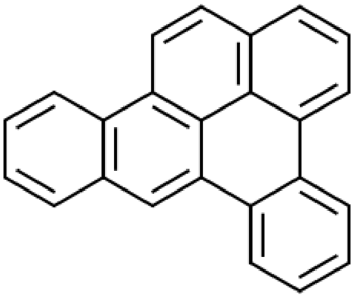
Benzo (k) fluoranthene



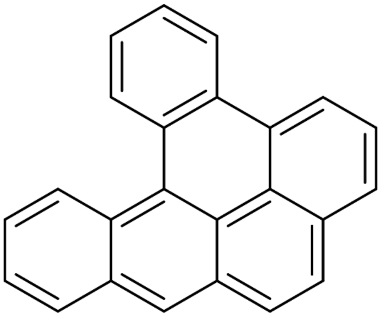
Indeno (1,2,3-cd) pyrene



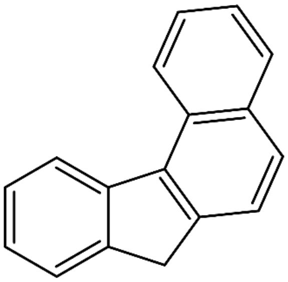
Benzo (ghi) perylene



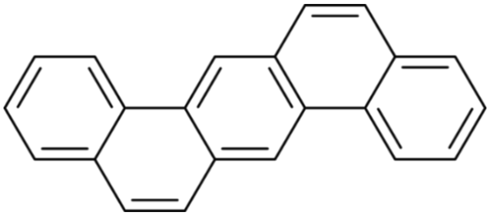
Dibenzo (a, e) pyrene



Dibenzo (a, i) pyrene



Benzo (c) fluorene



Dibenz (a, h) anthracene

2D chemical structures of PAHs

3.2 Literature Review

PAHs are ubiquitously present in environment across the globe. In the 1970s, the US EPA catalogued 16 PAHs as priority pollutants. These are volatile and semi-volatile compounds which are usually associated with local and regional PAHs sources. These can be remotely present which contribute to levels of these organic compound in the area via atmospheric processes and long-range transport (Rhea et al., 2005). The sum of the 15 PAH concentrations (∑15PAHs) ranged from 148 to 3079 ng/g with the median and average concentrations of 670 ng/g and 849 ± 646 ng/g, respectively in Brisbane River, Australia (Duodu et al., 2016). The highest concentration was observed for pyrene (Pyr) (527 ng/g) while two PAHs (acenaphthene (Ace) and fluorene (Flu)) were detected below detection limit. In Buffalo River Estuary, South Africa, the total PAHs concentration was higher in sediment 1107–22,310 ng/g than water (Adeniji et al., 2019). Individual PAHs levels in the water ranged from not detected (N.D) to 24900 ng/L and for sediment, N.D to 7792 ng/g, which was higher in comparison to Brisbane River sediment (Duodu et al., 2016). The most commonly detected PAHs in Colombian Cauca River were BbF, BkF, and Pyr in sediments; and Flu, acenaphthylene (Acy), and Anthracene (Ant) in water (Villa et al., 2015). The maximum PAHs for sediment (691 ng/g) were estimated to be higher than Brisbane River but lower than Buffalo River Estuary. In case of water samples, the total concentration was approximately half (12,888.2 ng/l) than those found in Buffalo River Estuary and also reported lower maximum concentration (1779 ng/l). However, the values were more or less similar to Ovia River, Southern Nigeria (2330- 25830 ng/L) (Tongo et al., 2017). In Taiwan, ∑PAHs reported from Ho-Jin River and Lover River sediments ranged from 160 to 1486 and 303 to 2161 ng/g, respectively (Tu et al., 2018). The higher-ring PAHs were found dominating the sediments in both rivers contributing 59-90% of the total PAHs. The maximum concentrations were identified for

Flu (357 ng/g) and Pyr (510.3 ng/g) in Ho-Jin River and Lover River, respectively which were low as compared to other studies. Zhao et al. (2021) observed higher PAHs level from more developed deltaic regions and megacities linked to economic activities. The study undertook source apportionment by performing principal component analysis-multiple linear regression (PCA–MLR) model. The model identified major contributions from coal and coke combustions besides vehicular emissions transported along the middle-lower Yangtze River. Recent studies also discovered PAHs in SPM (Dong et al., 2015; Liu et al., 2016; Zhang et al., 2017; Niu et al., 2018). Sun et al., 2017 studied PAHs partitioning in the sediment–water system and discovered unsteady the state of PAHs which tend to adsorb onto the sediment in Yinma River, China. The PAHs concentrations range (ND-402.1 ng/g) in sediment in Mahakam River of Indonesia were lower than the Buffalo River estuary while comparable to Brisbane River (Hadibarata, et al., 2019). Among these studies, highest total concentration (7370-167440 ng/g) were detected from Pearl River estuary, China (Niu et al., 2018). New analytical protocol for the determination of PAHs in sediments using microextraction was developed to identify even smaller concentration by Santos et al. (2018).

In India, Bharalu river in Guwahati, a tributary of Brahmaputra identified with $\sum_{16}$PAHs concentrations varying between 338 and 23,100 ng/g during post-monsoon and between 609 and 8620 ng/g during pre-monsoon in sediment (Hussain et al., 2015). The maximum concentration detected was 17420 ng/g for Phenanthrene (Phe). Compare to this study the seasonal total concentration for sixteen PAHs were lower in Cochin estuary (304 to 5874 in pre-monsoon and 194 to 10,691 ng/g in post-monsoon) (Ramzi et al, 2017). The study also discovered sediments to be moderately contaminated with low molecular weight PAHs fractions. One of the recent investigations also found out PAHs presence in drinking water in southern Jharkhand (Ambade et al., 2021). The USEPA's 16 priority pollutant PAHs total concentration was estimated to be 6.43–196.14 ng/L. The surface sediment of Mithi River, Mumbai observed total concentration for PAHs ranging from 1206 to 4735 ng/g which was lower compared to Bharalu river and Cochin estuary (Singare, 2015). High molecular weight PAHs contributed 90.83%, while low molecular PAHs supplying 9.17% to the total PAH concentrations which might pose inconspicuous ecological risks through food webs. The risk was calculated using toxic equivalent quantity (TEQ) and sediment quality guideline quotient (SQGQ). Goswami et al. (2016) explored aquatic system of southern India. The surface sediment collected from Adyar river, Cooum river, Ennore estuary, and Pulicat lake near Chennai city found total PAH concentration ranging from 13 to 31,425 ng/g, which was highest amongst the studies discussed in this review.

In the Ganga River Basin, PAHs were detected in Gomti River water in Lucknow. The total concentration varied from 4670-5342 ng/l and the most abundant hydrocarbon was Acy followed by Ace. At all sites concentrations were identified to be higher than the Bureau of Indian Standards (BIS, 1982) guideline value of 200 ng/l (Pandey et al., 2013). Malik et al. (2011) also discovered PAHs from water and sediment samples of Gomti. However, the maximum total concentration was higher in this study (84210 ng/l). The total concentrations of 16 PAHs (5.24–3,722.87 ng/g) in bed sediments were lower compared to rivers around world and in the country. In Yamuna, the most abundantly found compounds were fluoranthene (Fla), Chy, Flu and Pyr, and together accounted for more than 96% of the total 16 priority PAHs (Kumar et al., 2020). The total concentration ranged from 1576 to12,546 ng/g which was more or less comparable with similar studies conducted worldwide. However previous studies in the Delhi stretch of Yamuna River detected approximately twice this concentration (Agarwal et al, 2006). Miscellaneous pyrogenic activities such as combustion of fuels like biomass, petroleum and coal were identified as major sources of PAHs by exploiting composition profile, selected diagnostic molecular ratios, and Pearson’s moment correlation analysis. The sum of 16 PAHs were 3.9 and 65.9 ng/L in 2013 and 0.05–32.04 ng/L in 2014 (Sharma et al., 2018a). According to this study, Himalayan Reach had more pronounced seasonal influences due to marked forest fire or biomass burning especially for the period of dry pre-monsoon and possible outcomes of climate-modulated secondary source intensity (i.e., releases from melting glacier). The influence of seasons was not evident in the middle and lower Ganga basin where river water contamination is primarily affected by anthropogenic activities. Low molecular weight PAHs such as Pyr, Flu, Fla and Phe in two years and from higher reaches to lower (0.5 to 32 ng/L), concentration was found increasing as expected. In other study the lower segment of Ganga River known as Hooghly in West Bengal were discovered with $\sum_{16}$PAHs to be varying from ND to 32000 ng/Lin water and 48 and 1831 ng/g in bed sediment (Khuman et al., 2018). The maximum sum concentration for water was much more than what was reported by Sharma et al. (2018a) and river across the world. Dominance of Acy in Hooghly showed similarity with Gomti River (Malik et al., 2011) which was also identified to have moderate to heavy adverse effect. The concentrations of $\sum_{16}$PAHs in sediment followed the trend as suburban>rural>urban as identified by this study. Seventeen PAHs from Hooghly River along urban-industrial belt were investigated in surface sediment samples (Zanardi-Lamardo et al., 2019). The total concentration was observed in range of 129-825 ng/g which was lower than the other similar studies on Hooghly. In this study too, Flu was found at highest concentration (429.9 ng/g). Other recent studies on lower Ganges and Hooghly also identified PAHs as part of the persistent organic pollutants (Mitra et al., 2018; Duttagupta et al., 2020a and 2020b; Chakraborty et al., 2014). Duttangupta et al. (2020b) identified 16 PAHs from sediment and water in Western Bengal basin from Murshidabad to South 24 Parganas. The total concentration in these matrices varied from 1.15–23.13 ng/g and 20-6220 ng/L with low molecular weight PAHs (2–3 rings) predominant in surface water just like most of the studies. PAHs discovered in agricultural and rural regions were observed to be distinct from urban settings, implying land use to be a chief governing factor in relation to distribution and transport of the pollutants in Western Bengal Basin (Duttagupta et al., 2020b).

Location	Concentration range	∑PAH	Matrices	Reference
Hoor Al-Azim wetland, Iran	N.D-72	15.76–410.2	Sediment	Sheikh Fakhradini et al., 2019
	N.D-85	15.3–160.15	Water	
Brisbane River, Australia	B.D-527	148 to 3079	Sediment	Duodu et al., 2016
Buffalo River Estuary, South Africa	N.D to 24900	14910–206000	Water	Adeniji et al., 2019
	N.D to 7792	1107–22,310	Sediment	
Cauca River, Colombia	N.D-1901	52.1–12,888.2	Water	Sarria-Villa et al., 2016
	N.D–3739	212.3-1583	Sediment	
Huaihe River, China	27.87-560.2	79.94 to 421.07	Water	Liu et al., 2016
	2.42-342.32	10.87 to 201.42	SPM	
Mahakam River, Indonesia	N.D-402.1	54.7–2256.15	Sediment	Hadibarata, et al
Middle-lower Yangtze River, China		1.6-4463.9	Water	Zhao et al.,2021a
		2.4-4322.5	Sediment	
Pearl River estuary, China	12.70-160.15	25.99-522.26	Water	Niu et al., 2018
	2820-112320	7370-167440	SPM	
Paraguaçu River, Brazil	N.D-110	443.7-636.1	Sediment	Santos et al., 2018
Ovia river, Southern Nigeria	N.D-5330	2330- 25830	Water	Tongo et al., 2017
	0-155	5.25- 573.33	Sediment	
Ho-Jin River	1.6-357	183.8-1486	Water	Tu et al., 2018
Love River	0.3-188.4	303.3- 2160.6	Water	
Huai River, China		891-1951	Water	Zhang et al., 2017
		2054-5044	SPM	
		810-28228	Sediment	
Yellow River, China	38-468	101–803	Water	Dong et al., 2015
		98.1–329	SPM	

Yinma River, China	N.D-46.43 N.D-4245.24	147.03-315.87 914.17-5678.46	Water Sediment	Sun et al., 2017
India				
Bharalu River, Guwahati	BDL– 17,420	338-23,100	Sediment	Hussain et al., 2015
Cochin estuary, Kerela	N.D–8084	304- 14,149	Sediment	Ramzi et al., 2016
Southern Jharkhand	<LOD-8.84	6.43–196.14	Drinking Water	Ambade et al., 2021
Mithi River, Mumbai	5-1880	1206–4735	Sediment	Singare, 2015
Southern Rivers	<LOQ-8223	13-31,425	Sediment	Goswami et al., 2016
Brahmaputra River	N.D–29000 N.D-538	N.D-30000 2-798	Water Sediment	Khuman et al., 2018
Ganga River Basin				
Middle-lower basin	<MDL-20.05	0.05 to 65.9	Water	Sharma et al., 2018
Gomti river, Lucknow		467-5342 290.3- 25457	Water Sediment	Pandey et al., 2013
Gomti River	BDL–82670 BDL–2,726.4	60 to 84210 5.24–3,722.87		Malik et al., 2011
Hooghly River, West Bengal	N.D - 31000 N.D-600	N.D - 32000 54-1832	Water Sediment	Khuman et al., 2018
Hooghly River, West Bengal	<LOQ-429.9	129-825	Sediment	Lamardo et al., 2019
Hooghly estuary	<LOD-249.4	3.3-630	Sediment	Mitra et al., 2018
Western Bengal Ganga basin		20-6220 1.15–23.14	Water Sediment	Duttagupta et al., 2020b
Ganga and Brahmaputra River		BDL-31000	Water	Chakraborty et al., 2014
Yamuna River, Delhi	0.9-8391	1576-12546	Sediment	Kumar et al., 2020
Yamuna River, Delhi	N.D-4610	4,502–23,527	Sediment	Agarwal et al, 2006

BD: Below detection, LOD: Limit of detection, LOQ: Limit of quantification, BDL: Below detection limit, MDL: Method detection limit, N.D: Not detected

Table 3.1. Recent studies detecting PAHs in various environmental matrices across the world.

3.3 Results

3.3.1 Distribution of PAHs in water, bed sediment and SPM

River water

From PAHs analysis in river water, it was revealed that each location was identified with at least one of the PAHs in the basin. A total of nine PAHs were detected in water. The most frequently found was BbF (with detection frequency (df)=92%) followed by BaP (88%), MeC (68%) and BjF (64%). The lowest df (=3.8) was observed for IcdP, DahA and BghiP. The sum of the PAHs ranged 1.57 to 1115.46 ng/L with an average of 857.12 ng/g which was exceeding acceptable limits of BIS, 2012 (Table 3.2). While the average concentration varied from 1.1 to 920. 5 ng/L which (Table 3.2) followed the order as BbF> BkF> BjF> IcdP> BghiP> BaP> Daep> DahA> MeC. According to European economic community (1980), (Table 3.2) only BbF had mean value above standard limits. Most of the locations reported BbF value exceeding this standard value.

In the upper stretch of the basin, five PAHs were found namely MeC, BbF, BkF and BjF and IcdP with average ∑PAHs accounting for 652.04 ng/L (Table 3.3). Among them, BkF was detected in all the samples in the upper zone of the basin while the highest concentration was observed for BbF as 917.37 ng/L in Ganga downstream Haridwar (G1) (Fig. 3.1). In addition, G1 was also detected with other four mentioned PAHs summating to highest total PAHs concentration (=994.5 ng/L) recorded for this stretch followed by T3 (Tributary in Rishikesh-Haridwar) (Fig. 3.4). However, in the middle stretch, eight PAHs (Fig. 3.1) were discovered from river water including MeC, BbF, BkF, BjF, BaP, IcdP, BghiP and DahA with average sum to be higher than the upper stretch (776.3 ng/L). The maximum number of PAHs (seven) were found in Gomti (T13) followed by Ganga downstream Kanpur (G3) and Prayagraj (G5) with five PAHs (Fig. 3.1). BbF was most abundantly found PAH with highest detection frequency (=92%) followed by BaP (82%) in the middle stretch. According to ∑PAHs, G3 was detected with highest ∑PAH as 1115.5 ng/L followed by T13 and G4 (Fig. 3.4). Lowest number of PAHs were discovered from Chambal (TC) however, was observed with maximum concentration of BaP which was exceeding water quality guidelines (WQS) (Table 3.2) given by Canadian Council of Ministers of the Environment (1999 and 2001). In the lower stretch, six PAHs with average ∑PAHs equals to 960.41 ng/L was higher than the other two stretches (Table 3.3 and Fig. 3.4). Similar to middle basin, BbF was found with 100% df. The second most frequently detected compound was BaP followed by BjF (Table 3.3). While, DaeP was found with lowest df and was only discovered in Hooghly near Bansberia, West Bengal (G12). The site also observed maximum number of PAHs (total six) (Fig. 3.1). Ganga downstream Chhapra (G7) and tributary Mahananda showed highest concentration for BbF and comparatively high ∑PAHs (=1067 ng/L) (Fig. 3.1 and 3.4). Further downstream, Ganga (G10) also recorded maximum concentration of IcdP where four other PAHs were also found (Fig. 3.1). Tributaries such as Son (T8) and Mahananda (T12) were detected with more than three PAHs (Fig. 3.1).

PAHs	**River water (ng/L)**			**WQG[c]**	**Bed sediment (ng/g)**			**SPM (ng/g)**				**SQG[b]**	
	Min-Max.	**Mean±S.D**	**Df (n=25)**		**Min-Max.**	**Mean±S.D**	**Df (n=26)**	**Min-Max.**	**Mean±S.D**	**Df (n=7)**	**ISQG[c]**	**ERL**	**ERM**
BaP	0.9-16.2	2.2±3.1	93.2	15	N.D			N.D			31.9	430	1600
BaA	N.D			25	0.31-10.8	3.31±3.85	38	N.D			31.7	261	1600
Chy	N.D				0.22-27.5	13.29±8.2	62	1.37-8.35	3.41±2.34	85.7	57.1	384	2800
MeC	0.12-3.32	1.1±0.92	68		1.5-3.7	2.5±0.78	85.00	BDL	BDL	71.4			
BbF	716.7-1032.8	920.5-73.44	92	200[a]	1.4-2.7	2±0.45	31.00	1.94	1.94	14.3		320	1880
BjF	18.9-107.9	39.2±19.3	64		N.D			N.D					
BkF	25.9-93.8	41.9±22.8	28	200[a]	0.96-9.4	5.18±4.2	8.00	N.D				280	1620
IcdP	1.2-55.2	17.41±18.54	44	200 [a]	BDL	BDL	12.00	N.D					
BghiP	2.24	2.24	4	200 [a]	1.12-1.47	1.43±0.31	8.00	N.D				430	1600
DaeP	1.79	1.79	4		0.49-10.8	2.3±3.81	23.00	N.D					
DaiP	N.D				1.3-3.86	2.6±1.26	8.00	N.D					
BcF	N.D				2.4-191.2	36.25±57	81.00	6.1-24.9	11.04±5.9	100			
DahA	1.42	1.42	4		2.68	2.68	4	N.D			6.2	63.4	260
∑PAH	1.57-1115.5	857.12±311.6		100	0-218.64	41.8±60.3		7.71-35.2	14.24±8.77			4749	24940

n= number of samples, WQG: Water quality guidelines, SQG: Sediment quality guidelines, ISQG: Interim sediment quality guidelines, ERL: effects range low, ERM: effects range median, [a] British Columbia 1993; Jiao et al. 2012, [b] European economic community (1980), [c] Canadian Council of Ministers of the Environment (1999 and 2001)

Table 3.2. Descriptive statistics for PAHs in river water, bed sediment and SPM

	Water (ng/L)			Bed sediment (ng/g)		
	U.S (n=3)	**M.S (n=9)**	**L.S (n=13)**	**U.S (n=4)**	**M.S (n=9)**	**L.S (n=13)**
∑PAHs	652.0	776.3	960.4	16.84	89	10.6
BaP	1.8 (33.3)	3.4 (88.9)	1.5 (92.3)	N.D	N.D	N.D
BaA	N.D	N.D	N.D	0.31 (25)	5.04 (44.4)	1.1(38.5)
BbF	889(66.7)	920.1(77.8)	925.5(100)	N.D	2.3 (33.3)	1.8(38.5)
BcF	N.D	N.D	N.D	4.7(75)	84.1(88.9)	7.4(77)
BghiP	N.D	2.2(11.1)	N.D	N.D	1.1 (11.1)	1.74(7.8)
BjF	39.1 (33.3)	58.8(44.44)	32.1(84.6)	N.D	N.D	N.D
BkF	30.8 (100)	50.3(44.4)	N.D	9.4(75)	0.96(11.1)	N.D
Chy	N.D	N.D	N.D	12.7(75)	15.1(66.7)	10.4(53.8)
DaeP	N.D	N.D	N.D	N.D	0.7(11.1)	2.6(38.5)
DahA	N.D	1.4 (11.1)	N.D	2.7(75)	N.D	N.D
DaiP	N.D	N.D	1.8(7.7)	N.D	1.3(11.1)	3.9(15.4)
IcdP	21.3 (66.7)	14.9(55.6)	18.6(30.8)	N.D	0 (11.1)	1 (15.4)
MeC	2.3	0.8(66.7)	1.1(76.9)	2.9(75)	2.8(100)	1.9(76.9)

Table 3.3. Stretch-wise mean concentration of individual PAHs and ∑PAHs with detection frequency given in parentheses.

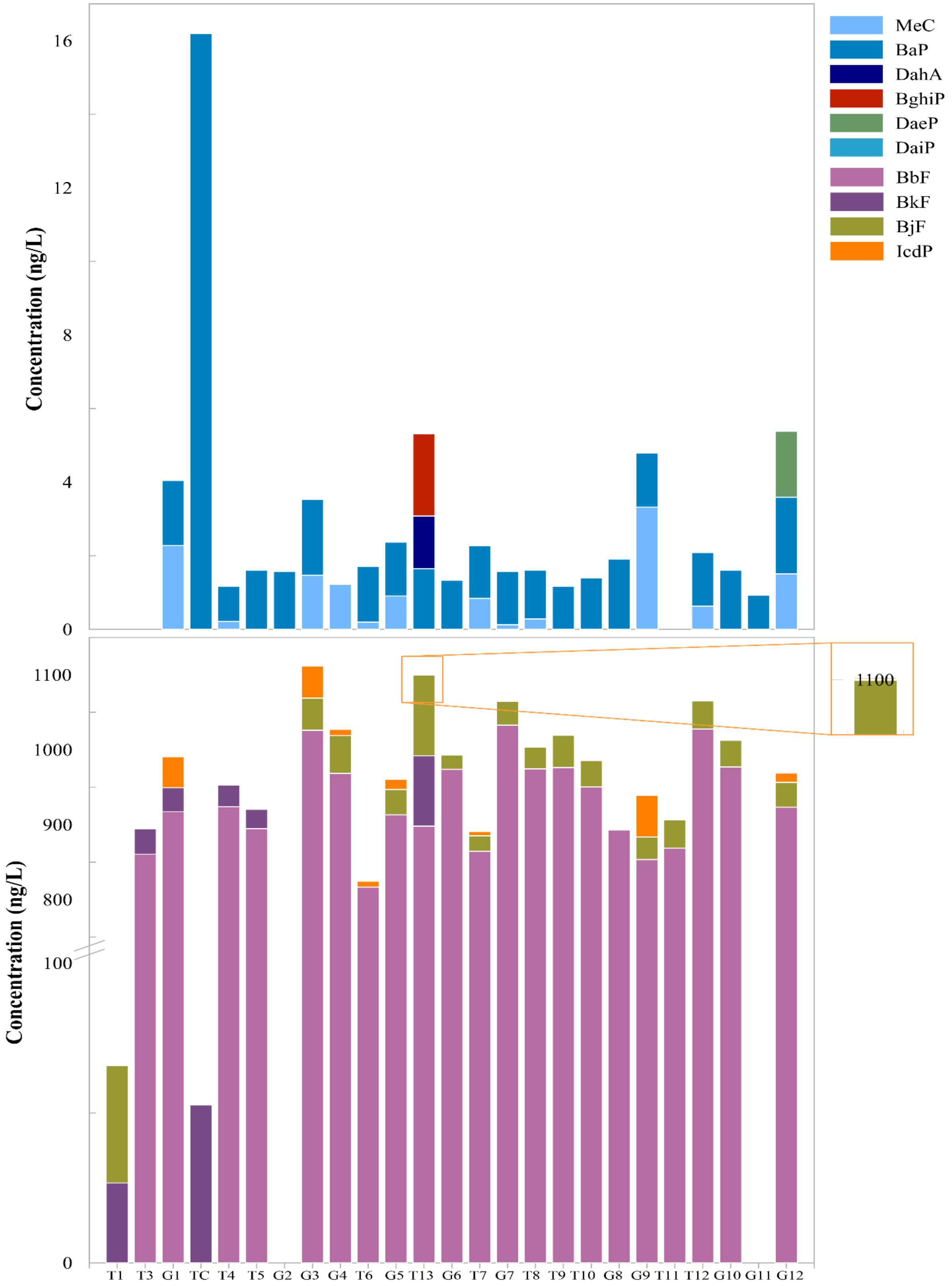


Fig. 3.1. PAHs distribution in river water (x axis indicate locations).

Bed sediment

In bed sediment, overall, eleven PAHs were detected. Their total sum varied from 0-218.64 ng/g. The highest df (=85%) was observed for MeC but found BDL at most of the location. While, BcF was detected with second highest df (=81%) and concentration (191.2 ng/g) followed by Chy (df= 62%, 27.5 ng/g) (Table 3.2). Other PAHs were found in less than 50% of the samples. The average concentration in the bed sediment ranged from 1.43-36.25 ng/g and observed the trend as follows: BcF> Chy> Bk> BaA> DahA> DaiP> MeC> DaeP> BbF > BghiP> IcdP. Based on US sediment quality guidelines (SQG), effect-range low (ERL) and effects range median (ERM) quantitively assess the adverse biological effects in sediment. The average concentration of PAHs and ∑PAHs were below both ERL and ERM values (Table 3.2).

In the upper stretch of the basin, six PAHs were reported and among them three PAHs such as BcF, Chy and MeC were detected more frequently than others with df above 75%. The average ∑PAHs was 16.84 ng/g. The maximum number (=5) of PAHs were detected at T2 (Fig. 3.2) with second highest concentration of Chy (24.28 ng/g). Other tributaries such as T1 (Song River) and T3 were found with three PAHs (Fig. 3.2). However, in Ganga River downstream Haridwar (G1) only two PAHs were detected with MeC being BDL. In the middle stretch, ten PAHs were discovered with approximately five times greater average ∑PAHs concentration (88.61 ng/g) than the upper stretch. Here, MeC was the most frequently found hydrocarbon followed by BcF and Chy with df given in Table 3.3. However, concentrations were BDL for MeC at most of the locations. According to the maximum concentration, PAHs such as BcF and Chy were highest at (Table 3.2) at T5 (Yamuna after Chambal confluence), in addition to highest ∑PAHs (=218.6 ng/g) recorded for the basin in bed sediment (Fig 3.2 and 3.4). Relatively higher ∑PAHs in bed sediment was also observed at G4 (upstream Prayagraj). Similar to river water, greater number of PAHs were detected from Gomti (six) and Prayagraj (five). The concentration for BcF was identified to be higher in this stretch. In the lower stretch, eight PAHs were identified with average ∑PAHs (=11 ng/g) comparable to upper stretch and much lower than the middle region. However as observed in middle stretch, most frequently found PAHs were MeC, BcF and Chy (df=77% and 54%, respectively), while other had df below 50%. With respect to sampling location, G12 in Bansberia was detected with maximum number of PAHs (Fig. 3.2) in this stretch alike water (section 3.3.1). Highest ∑PAHs observed for this stretch was 31.78 ng/g at G11 (Hooghly) which was much lower compared to maximum ∑PAHs measured from middle stretch. Other location in this stretch had relatively lower number of PAHs and ∑PAHs levels.

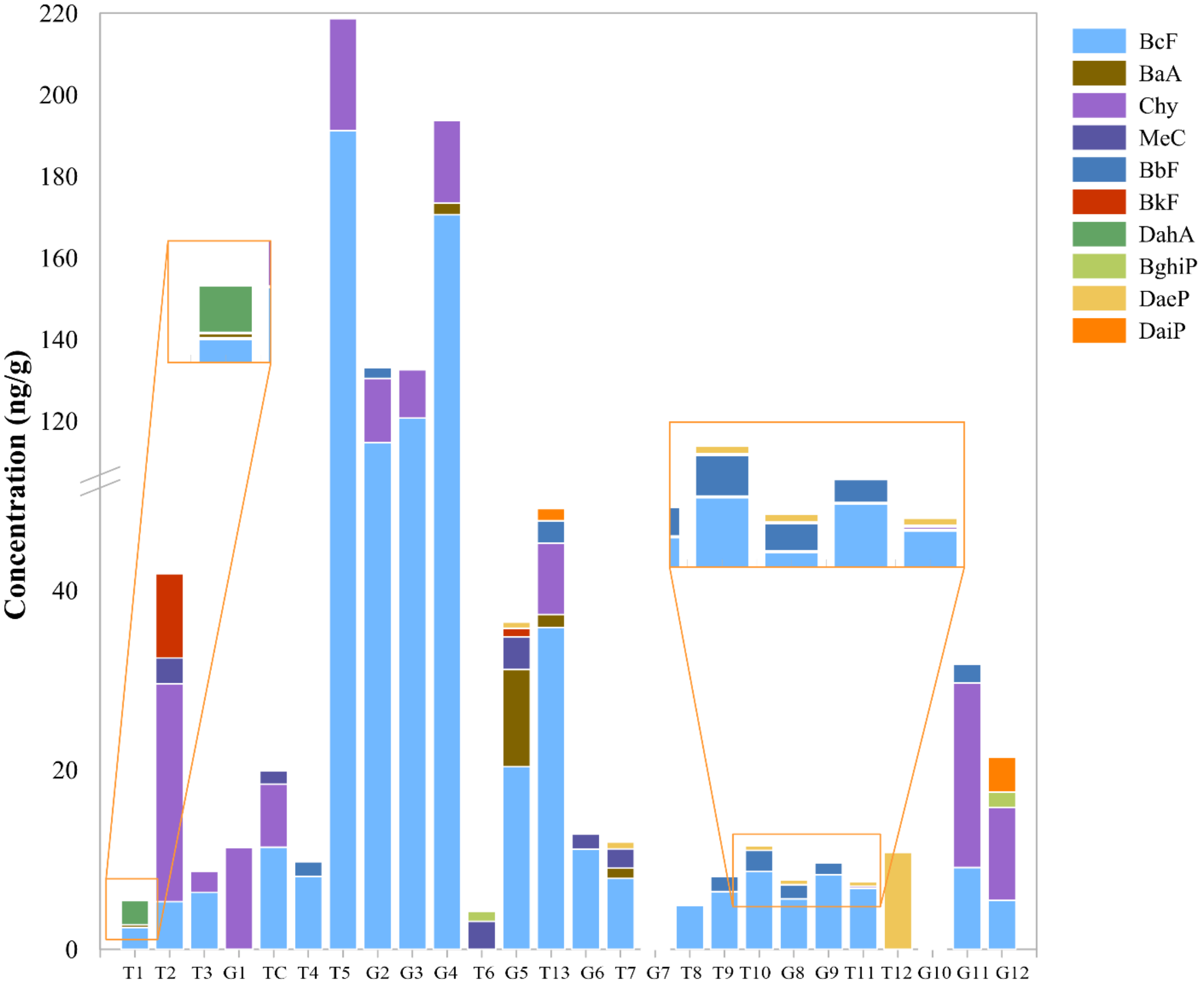


Fig. 3.2. PAHs distribution in bed sediment (x axis indicate locations).

SPM

Compared to river water and bed sediment, lower number of PAHs were detected in SPM (Fig. 3.3). Total four PAHs were detected in seven samples of SPM. The average concentration for each PAHs and ∑PAHs for each location ranged between 1.94 to 11 and 7.71-35.2 ng/g, respectively (Table 3.2). The trend followed by the average concentration was BcF>Chy>BbF>MeC. Similar to bed sediment, BcF was detected with higher df (=100%) and highest concentration followed by Chy (df=86%) in the basin. Further, MeC was detected BDL and BbF was only found in sample T4. T4 (Yamuna before Chambal confluence) also had maximum number of detected compounds and ∑PAHs (=35.2ng/g). The ∑PAHs for other locations were relatively low (7.7-13.6 ng/g).

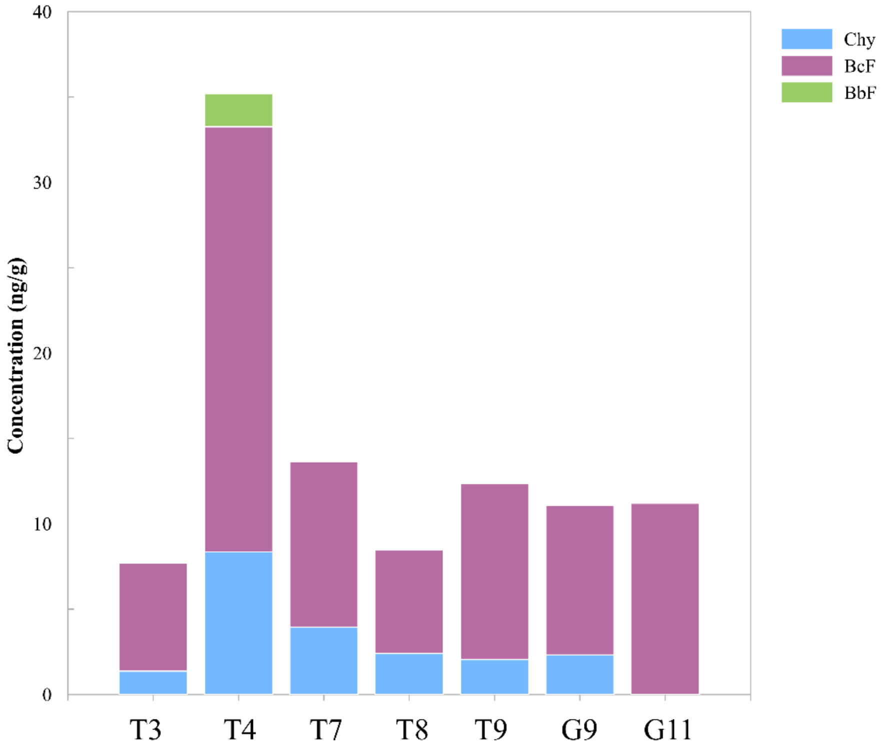


Fig. 3.3. PAHs distribution in SPM (x axis indicate locations).

3.3.2 Influence of tributaries

For identifying the effect of tributaries of the Ganga on concentration of emerging contaminants in the main channel, samples were collected before and after the confluence of the particular tributary. In river water, the concentrations of PAHs such as MeC and BbF were decreasing while BaP was increasing in Yamuna (T5) after the confluence Chambal (TC) (Fig. 3.1). However, in bed sediment, after the confluence, PAHs concentration were very high (except for BbF) in Yamuna compared to Chambal suggesting contribution from Chambal besides anthropogenic contamination. According to overall ∑PAHs, Chambal was slightly decreasing the concentration in river water while adding to the concentration in bed sediment (Fig. 3.4). This could be due to the settlement of the suspended particulate matter and contributing to bed sediment at T5 as Yamuna before confluence (T4) observed higher concentration in SPM. In Prayagraj, Ganga (G5) after meeting with Yamuna (T6) was detected with lower total PAHs concentration indicating dilution from Yamuna (Fig. 3.4) in both matrices. The concentration of MeC, BbF and BjF were decreasing in water while BcF, Chy and IcdP were found lowered in bed sediment. However, BaP and MeC were increased in Ganga River water and bed sediment, respectively. In case Ghaghara (T7), the addition of PAHs such as MeC, BjF and BaP increased the total concentration of PAHs in Ganga River water (G7) while there was overall decrease in concentration in bed sediment (Fig. 3.4). Similar to Ghaghara, Kosi and Mahananda (T11 and T12) enhanced total concentration of the PAHs in Ganga River water (Fig. 3.1 and 3.4). The results insinuated that the tributaries could be influencing the levels of PAHs in river water and bed sediment.

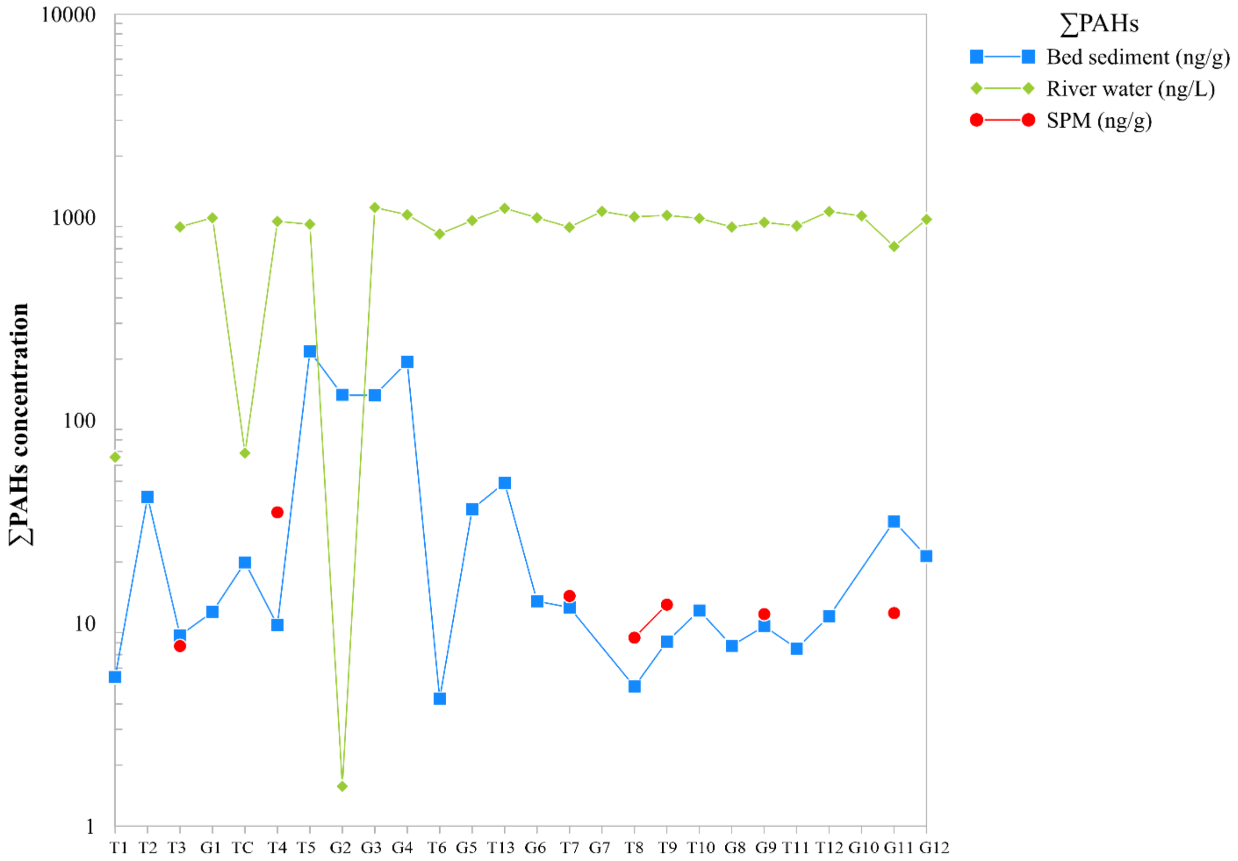


Fig. 3.4. Distribution of ∑PAHs in three environmental matrices along the Ganga River Basin.

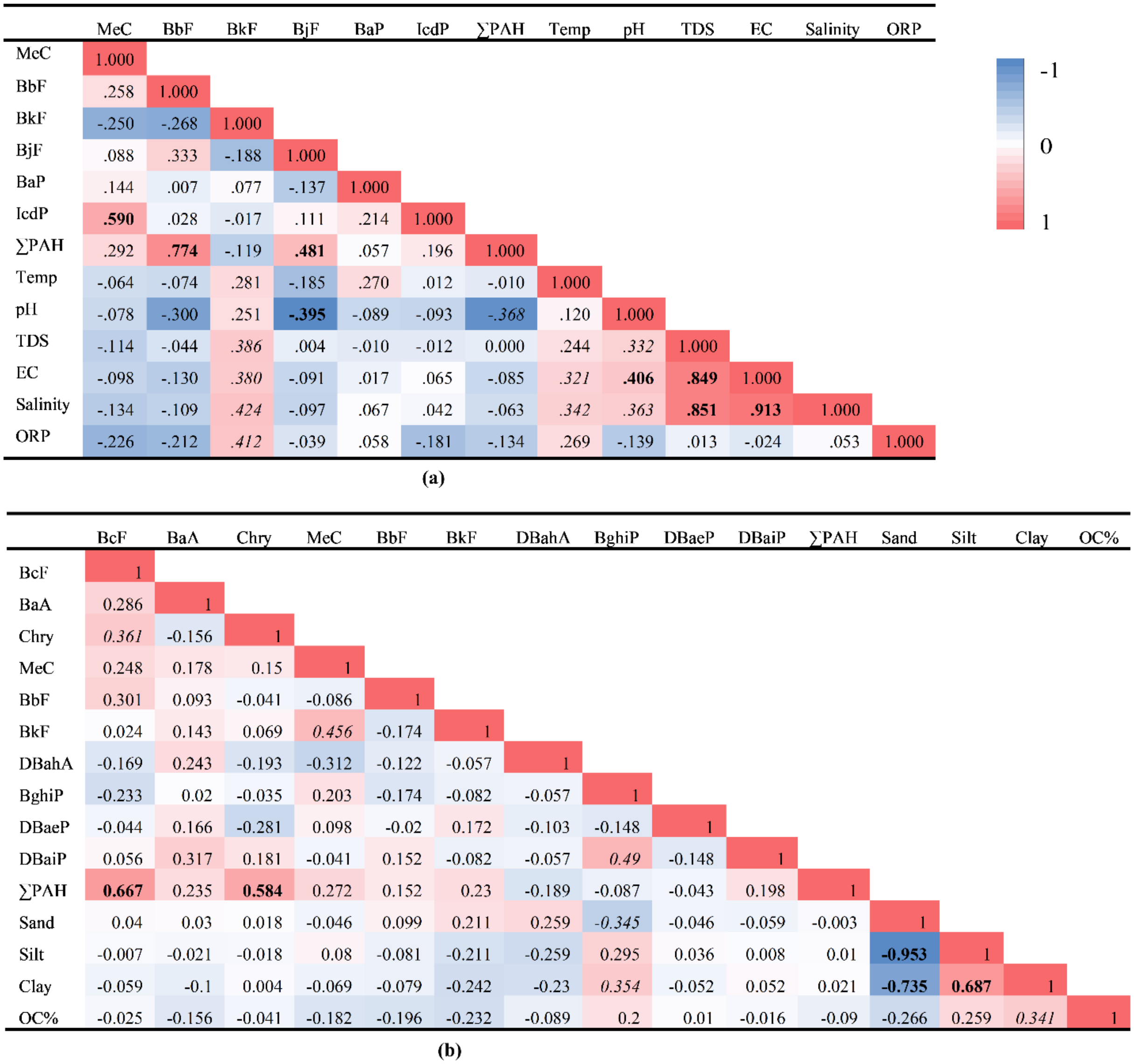
3.3.3 Statistical Analysis

The statistical analyses were performed to understand the distribution, influence of tributaries and effect of physicochemical parameters of water, grain size and organic carbon on distribution of PAHs in water and bed sediment.

Kendall tau's correlation

Kendall's tau correlation analysis (Fig. 3.5a) indicated BbF showing a low significant negative correlation with pH (p=0.05) suggesting a decrease in pH could result in degradation of the compound. It was observed that in general acidic soil had greater photo-degradation rates (Pawar, 2012). While BkF was positively correlated with EC, TDS, salinity and ORP (p=0.05) indicating major control of physicochemical factors on degradation and occurrence in water bodies (Hussain et al., 2016). BbF and BjF were positively correlated with ∑PAHs ($p=0.01$) representing their contribution and significantly raising the total concentration of PAHs. Common sources and/or behavior of IcdP and MeC ($\tau=0.59$, $p=0.01$), and BjF and BbF were suggested from their positive correlation with each other. Further, source identification requires calculating ratios between high molecular weight and low molecular weight PAHs (Tobiszewski and Namiesnik, 2012).

In bed sediment (Fig. 3.5b), only BghiP showed a significant positive correlation with clay and negative with sand indicating its accumulation in finer fraction of the grain size (Kuppusamy et al., 2017). BcF and Chy were representative of the total concentration of PAHs in bed sediment, i.e., their concentrations were significantly affecting the overall levels of the PAHs.



	MeC	BbF	BkF	BjF	BaP	IcdP	∑PAH	Temp	pH	TDS	EC	Salinity	ORP
MeC	1.000												
BbF	.258	1.000											
BkF	-.250	-.268	1.000										
BjF	.088	.333	-.188	1.000									
BaP	.144	.007	.077	-.137	1.000								
IcdP	**.590**	.028	-.017	.111	.214	1.000							
∑PAH	.292	**.774**	-.119	**.481**	.057	.196	1.000						
Temp	-.064	-.074	.281	-.185	.270	.012	-.010	1.000					
pH	-.078	-.300	.251	**-.395**	-.089	-.093	*-.368*	.120	1.000				
TDS	-.114	-.044	*.386*	.004	-.010	-.012	0.000	.244	*.332*	1.000			
EC	-.098	-.130	*.380*	-.091	.017	.065	-.085	*.321*	**.406**	**.849**	1.000		
Salinity	-.134	-.109	*.424*	-.097	.067	.042	-.063	*.342*	*.363*	**.851**	**.913**	1.000	
ORP	-.226	-.212	*.412*	-.039	.058	-.181	-.134	.269	-.139	.013	-.024	.053	1.000

(a)

	BcF	BaA	Chry	MeC	BbF	BkF	DBahA	BghiP	DBaeP	DBaiP	∑PAH	Sand	Silt	Clay	OC%
BcF	1														
BaA	0.286	1													
Chry	*0.361*	-0.156	1												
MeC	0.248	0.178	0.15	1											
BbF	0.301	0.093	-0.041	-0.086	1										
BkF	0.024	0.143	0.069	*0.456*	-0.174	1									
DBahA	-0.169	0.243	-0.193	-0.312	-0.122	-0.057	1								
BghiP	-0.233	0.02	-0.035	0.203	-0.174	-0.082	-0.057	1							
DBaeP	-0.044	0.166	-0.281	0.098	-0.02	0.172	-0.103	-0.148	1						
DBaiP	0.056	0.317	0.181	-0.041	0.152	-0.082	-0.057	*0.49*	-0.148	1					
∑PAH	**0.667**	0.235	**0.584**	0.272	0.152	0.23	-0.189	-0.087	-0.043	0.198	1				
Sand	0.04	0.03	0.018	-0.046	0.099	0.211	0.259	*-0.345*	-0.046	-0.059	-0.003	1			
Silt	-0.007	-0.021	-0.018	0.08	-0.081	-0.211	-0.259	0.295	0.036	0.008	0.01	**-0.953**	1		
Clay	-0.059	-0.1	0.004	-0.069	-0.079	-0.242	-0.23	*0.354*	-0.052	0.052	0.021	**-0.735**	**0.687**	1	
OC%	-0.025	-0.156	-0.041	-0.182	-0.196	-0.232	-0.089	0.2	0.01	-0.016	-0.09	-0.266	0.259	*0.341*	1

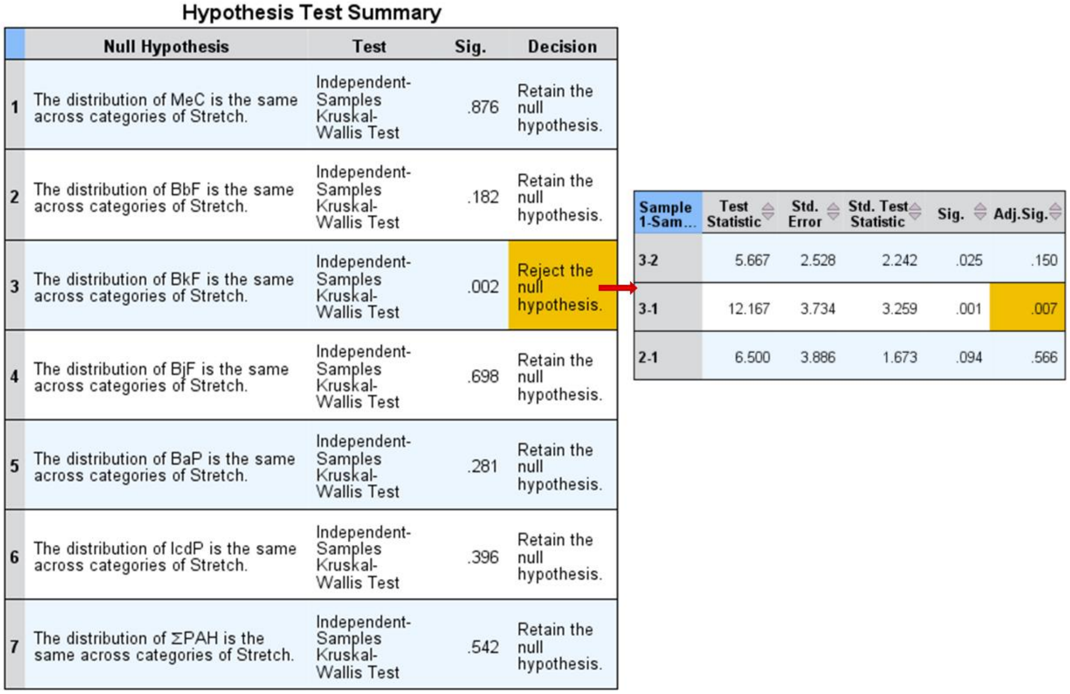
(b)

Fig. 3.5. Kendall's Tau correlation analysis for PAHs in (a) river water (b) bed sediment.

Kruskal-Wallis test

The non-parametric equivalent ANOVA called Kruskal-Wallis was employed to recognize the significant difference between the concentrations of different PAHs in three stretches. A fixed factor as "stretch" with three groups were considered, i.e., upper, middle, and lower designated by 1, 2 and 3, respectively. Fig. 3.6a showed only BkF with p value below 0.5 rejecting the null hypothesis. From pair wise comparisons, BkF in river water was showing significant spatial variations with upper indicating higher levels of BkF than the lower region (Fig. 3.6a). On the other hand, in bed sediment (Fig. 3.6b), the middle stretch showed significantly higher BcF than other two stretches. Further, sum of PAHs (∑PAHs) was also found to be substantially higher in the middle region (Fig. 3.6b). Positive relationship between BcF and ∑PAHs was also shown by the correlation analysis (section 3.3.3). This could be due to the fact that most of the sampling sites were located near major urban centers conversely to lower and upper stretch where samples were mainly collected from sub-urbans and rural area. Additionally, due to arrival of the monsoon in lower basin could have resulted in release of PAHs bound to bed sediment by disturbing the matrix from high flow condition (Abdel-Shafy and Mansour, 2016; Fan et al., 2008) could have resulted in lower levels of PAHs in bed sediment. The results of the Kruskal-Wallis were consistent with the distribution of the PAHs in respective matrices.

Kruskal-Wallis test was also performed to identify the significant effect of tributaries (Fig. 3a-d). Two positions were regarded as Ganga and tributaries mentioned as numbers 1 and 2, respectively. From the analysis no significant differences were found between the PAHs levels of Ganga and its tributaries in water and bed sediment. However, lower p values for MeC and IcdP were observed indicating higher concentration in Ganga water (Fig. 3.6c) suggesting major contributions of these compounds from anthropogenic sources along the Ganga River and not tributaries. The latter could be diluting the concentrations as discussed in section 3.3.2. However, BkF (p value close to 0.05) was higher in tributaries indicating contribution to the Ganga (Fig. 3.6c and Fig. 3.4).

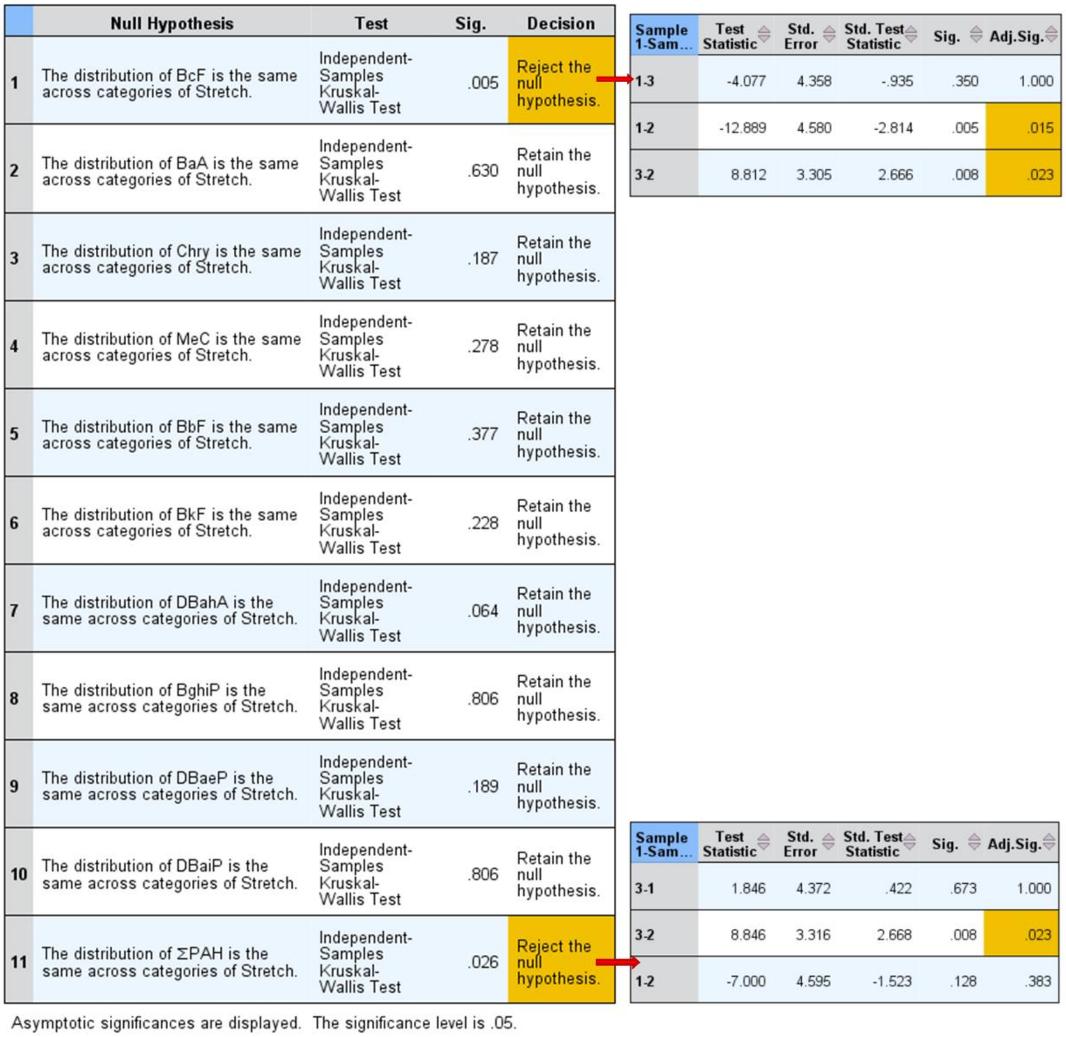


Hypothesis Test Summary

	Null Hypothesis	Test	Sig.	Decision
1	The distribution of MeC is the same across categories of Stretch.	Independent-Samples Kruskal-Wallis Test	.876	Retain the null hypothesis.
2	The distribution of BbF is the same across categories of Stretch.	Independent-Samples Kruskal-Wallis Test	.182	Retain the null hypothesis.
3	The distribution of BkF is the same across categories of Stretch.	Independent-Samples Kruskal-Wallis Test	.002	Reject the null hypothesis.
4	The distribution of BjF is the same across categories of Stretch.	Independent-Samples Kruskal-Wallis Test	.698	Retain the null hypothesis.
5	The distribution of BaP is the same across categories of Stretch.	Independent-Samples Kruskal-Wallis Test	.281	Retain the null hypothesis.
6	The distribution of IcdP is the same across categories of Stretch.	Independent-Samples Kruskal-Wallis Test	.396	Retain the null hypothesis.
7	The distribution of ΣPAH is the same across categories of Stretch.	Independent-Samples Kruskal-Wallis Test	.542	Retain the null hypothesis.

Sample 1-Sam...	Test Statistic	Std. Error	Std. Test Statistic	Sig.	Adj.Sig.
3-2	5.667	2.528	2.242	.025	.150
3-1	12.167	3.734	3.259	.001	.007
2-1	6.500	3.886	1.673	.094	.566

(a)



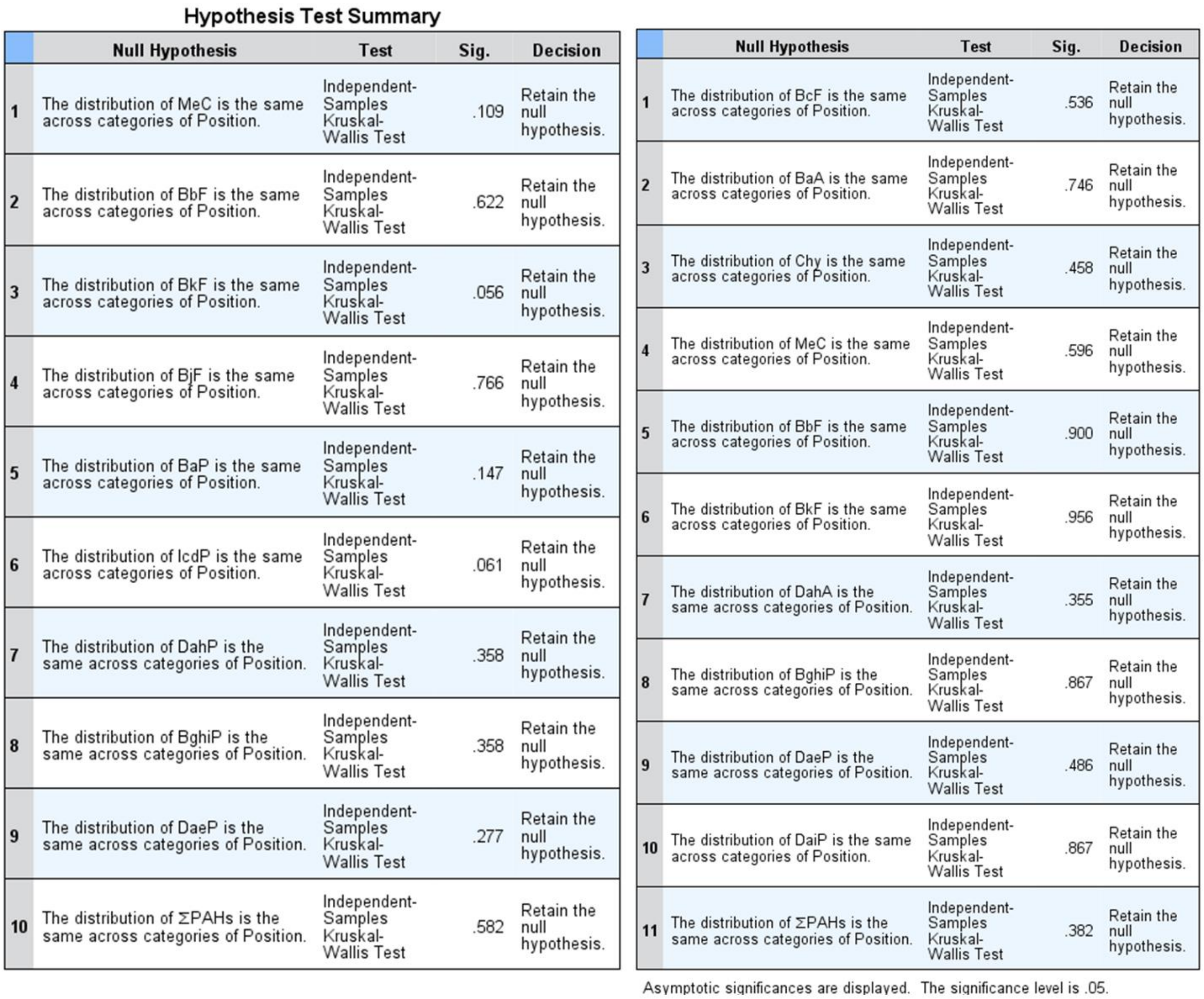
	Null Hypothesis	Test	Sig.	Decision
1	The distribution of BcF is the same across categories of Stretch.	Independent-Samples Kruskal-Wallis Test	.005	Reject the null hypothesis.
2	The distribution of BaA is the same across categories of Stretch.	Independent-Samples Kruskal-Wallis Test	.630	Retain the null hypothesis.
3	The distribution of Chry is the same across categories of Stretch.	Independent-Samples Kruskal-Wallis Test	.187	Retain the null hypothesis.
4	The distribution of MeC is the same across categories of Stretch.	Independent-Samples Kruskal-Wallis Test	.278	Retain the null hypothesis.
5	The distribution of BbF is the same across categories of Stretch.	Independent-Samples Kruskal-Wallis Test	.377	Retain the null hypothesis.
6	The distribution of BkF is the same across categories of Stretch.	Independent-Samples Kruskal-Wallis Test	.228	Retain the null hypothesis.
7	The distribution of DBahA is the same across categories of Stretch.	Independent-Samples Kruskal-Wallis Test	.064	Retain the null hypothesis.
8	The distribution of BghiP is the same across categories of Stretch.	Independent-Samples Kruskal-Wallis Test	.806	Retain the null hypothesis.
9	The distribution of DBaeP is the same across categories of Stretch.	Independent-Samples Kruskal-Wallis Test	.189	Retain the null hypothesis.
10	The distribution of DBaiP is the same across categories of Stretch.	Independent-Samples Kruskal-Wallis Test	.806	Retain the null hypothesis.
11	The distribution of ΣPAH is the same across categories of Stretch.	Independent-Samples Kruskal-Wallis Test	.026	Reject the null hypothesis.

Sample 1-Sam...	Test Statistic	Std. Error	Std. Test Statistic	Sig.	Adj.Sig.
1-3	-4.077	4.358	-.935	.350	1.000
1-2	-12.889	4.580	-2.814	.005	.015
3-2	8.812	3.305	2.666	.008	.023

Sample 1-Sam...	Test Statistic	Std. Error	Std. Test Statistic	Sig.	Adj.Sig.
3-1	1.846	4.372	.422	.673	1.000
3-2	8.846	3.316	2.668	.008	.023
1-2	-7.000	4.595	-1.523	.128	.383

Asymptotic significances are displayed. The significance level is .05.

(b)



Hypothesis Test Summary

	Null Hypothesis	Test	Sig.	Decision
1	The distribution of MeC is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.109	Retain the null hypothesis.
2	The distribution of BbF is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.622	Retain the null hypothesis.
3	The distribution of BkF is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.056	Retain the null hypothesis.
4	The distribution of BjF is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.766	Retain the null hypothesis.
5	The distribution of BaP is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.147	Retain the null hypothesis.
6	The distribution of IcdP is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.061	Retain the null hypothesis.
7	The distribution of DahP is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.358	Retain the null hypothesis.
8	The distribution of BghiP is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.358	Retain the null hypothesis.
9	The distribution of DaeP is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.277	Retain the null hypothesis.
10	The distribution of ΣPAHs is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.582	Retain the null hypothesis.

(c)

	Null Hypothesis	Test	Sig.	Decision
1	The distribution of BcF is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.536	Retain the null hypothesis.
2	The distribution of BaA is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.746	Retain the null hypothesis.
3	The distribution of Chy is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.458	Retain the null hypothesis.
4	The distribution of MeC is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.596	Retain the null hypothesis.
5	The distribution of BbF is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.900	Retain the null hypothesis.
6	The distribution of BkF is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.956	Retain the null hypothesis.
7	The distribution of DahA is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.355	Retain the null hypothesis.
8	The distribution of BghiP is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.867	Retain the null hypothesis.
9	The distribution of DaeP is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.486	Retain the null hypothesis.
10	The distribution of DaiP is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.867	Retain the null hypothesis.
11	The distribution of ΣPAHs is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.382	Retain the null hypothesis.

Asymptotic significances are displayed. The significance level is .05.

(d)

Fig. 3.6. Kruskal-Wallis test for PAHs in (a and c) river water and (b and d) bed sediment.

3.3.4 Risk assessment

In order to assess the potential ecological risk of PAHs on aquatic organisms in Ganga River basin, risk quotient (RQ) was measured (Kalf et al. 1997; Yan et al. 2016). The risk posed by PAHs in river water, bed sediment and SPM were characterized by calculating the RQ using following formula-:

$$\boldsymbol{RQ = \frac{C_{PAHs}}{C_{QV}}} \tag{3.1}$$

Where,

C_{PAHs}=Concentration of PAHs in the medium

C_{QV}=Corresponding quality values of the PAHs in the medium

In this study, the negligible concentration (NCs) and the maximum permissible concentrations (MPCs) of PAHs in water, sediment and SPM reported by Kalf et al. (1997) were applied as the quality values. Therefore, RQ_{NCs} and RQ_{MPCs} were calculated as follows-:

$$\boldsymbol{RQ_{NCs} = \frac{C_{PAHs}}{C_{QV(NCs)}}} \tag{3.2}$$

$$\boldsymbol{RQ_{MPCs} = \frac{C_{PAHs}}{C_{QV(MPCs)}}} \tag{3.3}$$

where $C_{QV(NCs)}$ and $C_{QV(MPCs)}$ depicts quality values of the NCs and MPCs of PAHs species in the medium, respectively. The QV was available for only 10 individual PAHs for which risk could be assessed. Evaluation of ecosystem risk for other PAHs, the toxic equivalency factors (TEFs) for individual PAHs (Nisbet and LaGoy 1992) were used to determine the NCs and MPCs (Table 3.4). TEFs value represents the toxic equivalency factors of 16 individual PAHs (Table 3.4), and various mentioned PAHs with identical TEFs reflects similar toxicity to each other (Cao et al., 2010). However, for DaiP and BcF the TEF is estimated to be 10 and 20 in recent studies for which NCs and MPCs have not been evaluated (Richter-Brockmann and Achten, 2018).

PAHs	**TEFs**	**Water (ng L^{-1})**		**Sediment (ng g^{-1})**	
		NCs	**MPCs**	**NCs**	**MPCs**
BghiP	0.01	3	300	26	2,600
BaA	0.1	0.1	10	3.6	360
Chy	0.01	3.4	340	107	10,700
BbF	0.1	0.1	10	3.6	360

BkF	0.1	0.4	40	24	2,400
BaP	1	0.5	50	27	2,700
DahA	1	0.5	50	27	2,700
IcdP	0.1	0.4	40	59	5,900
BghiP	0.01	0.3	30	75	7,500
MeC	1	0.5	50	27	2,700
BjF	0.1	0.1	10	3.6	360
DaeP	1	0.5	50	27	2,700

Table 3.4. NCs and MPCs values for water and sediment (Nisbet and LaGoy 1992; Kalf et al., 1997; Cao et al., 2010)

To estimate RQ further investigations for these particular PAHs are required. Further, according Cao et al., (2010), $RQ_{\sum PAHs}$, $RQ_{\sum PAHs(NCs)}$ and $RQ_{\sum PAHs(MPCs)}$ were measured as follows:

$$\boldsymbol{RQ_{\sum PAHs} = \sum_{i=1}^{n} RQ_i} \qquad (\boldsymbol{RQ_i \geq 1}) \tag{3.4}$$

$$\boldsymbol{RQ_{\sum PAHs(NCs)} = \sum_{i=1}^{n} RQ_{i(NCs)}} \qquad (\boldsymbol{RQ_{i(NCs)} \geq 1}) \tag{3.5}$$

$$\boldsymbol{RQ_{\sum PAHs(MPCs)} = \sum_{i=1}^{n} RQ_{i(MPCs)}} \qquad (\boldsymbol{RQ_{i(MPCs)} \geq 1}) \tag{3.6}$$

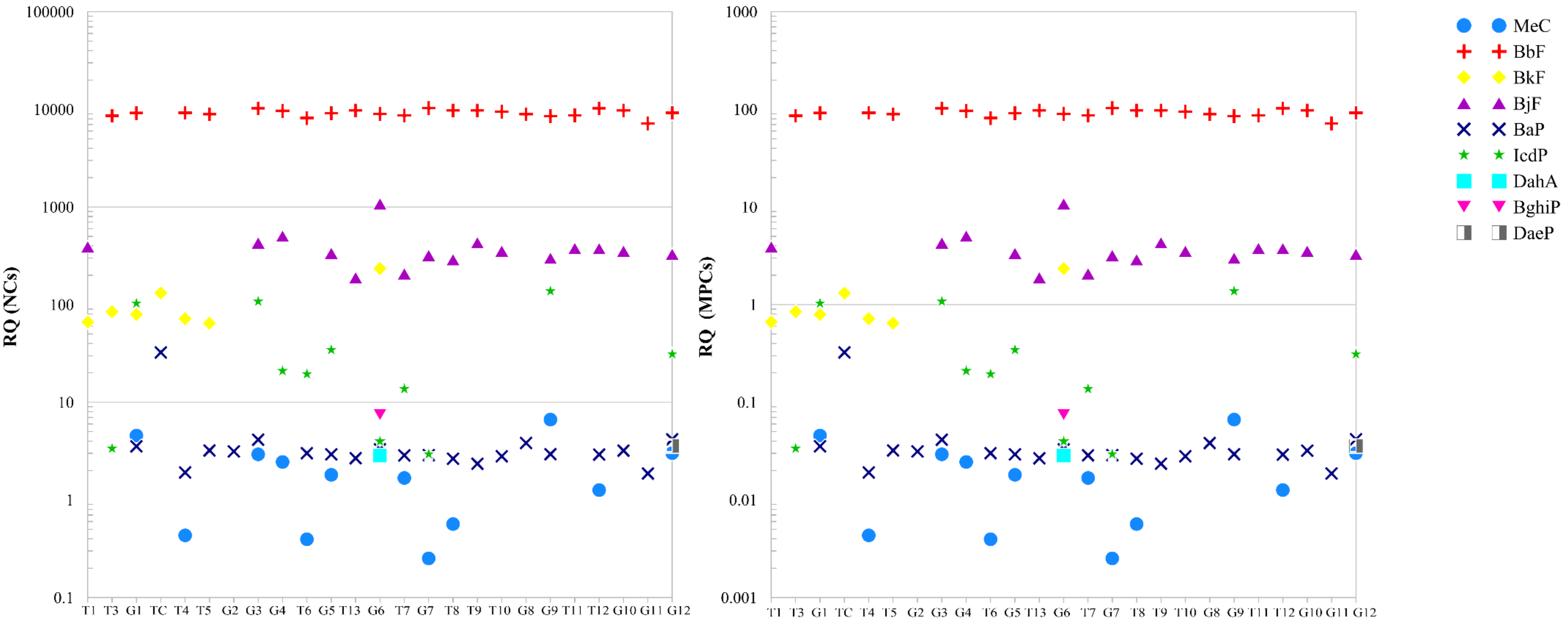
For an individual PAHs, $RQ_{(NC)}<1$ indicate negligible concern, $RQ_{(NC)}>1$ but $RQ_{(MPC)}<1$ indicate medium contamination while $RQ_{(MPC)}>1$ suggest severe contamination and remedial actions must be taken.

Individual PAHs			∑**PAHs**		
	RQ$_{(NCs)}$	**RQ$_{(MPCs)}$**		**RQ$_{\sum PAHs(NCs)}$**	**RQ$_{\sum PAHs(MPCs)}$**
Risk-free	0		Risk-free	=0	
			Low-risk	≧1; <800	=0
Moderate-risk	≧1	<1	Moderate-risk$_1$	≧800	=0
			Moderate-risk$_2$	<800	≧1
High-risk		≧1	High-risk	≧800	≧1

Table 3.5. Risk characterization based on RQ value for individual PAHs and ∑PAHs (Cao et al., 2010)

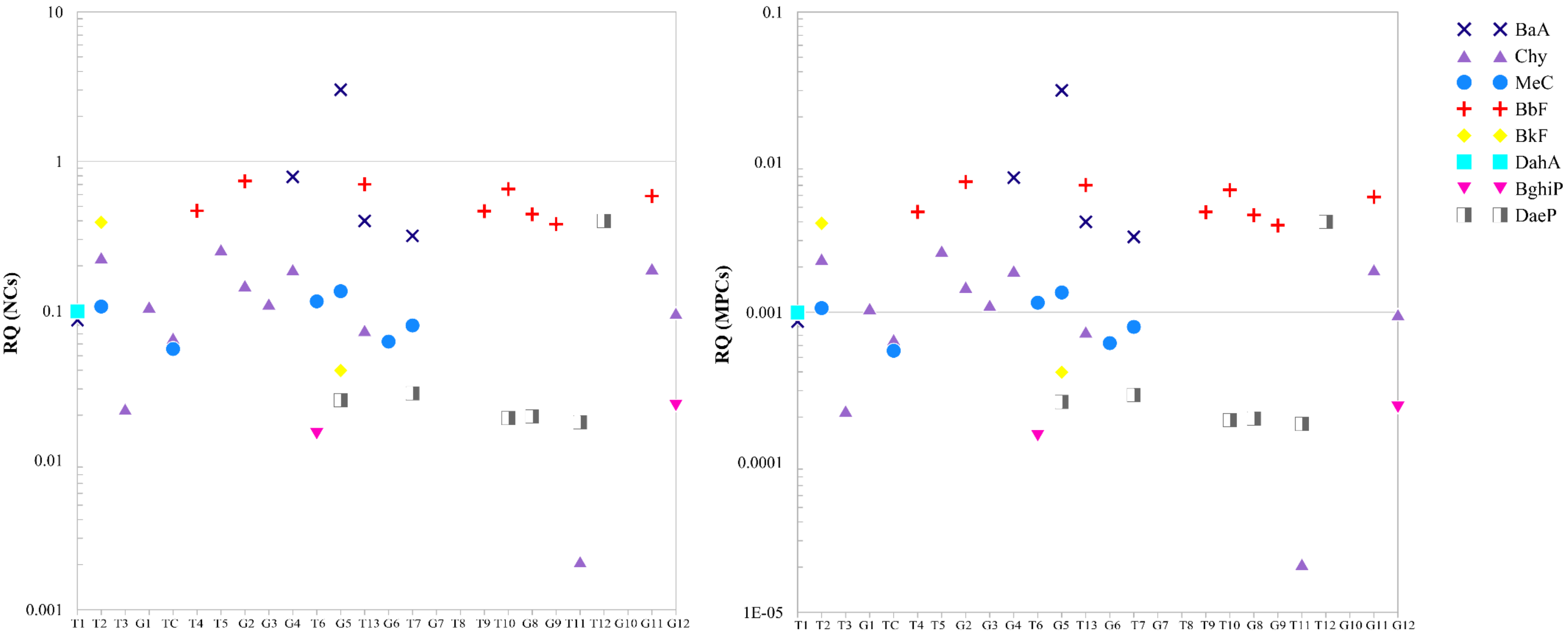
In river water, BbF was showing high risk (RQ$_{(NC)}$= 7167.1- 10328.3; RQ$_{(MPC)}$=71.7-103.3 ng/L) at most of the locations except at T1, TC and G2 (Fig. 3.7a and b). In case of other PAHs, high risk was measured for IcdP and BkF for 12% and 8% of the samples. While moderate risk was shown for 84% of the samples from BaP, 32% from IcdP, 20% from BkF and 4% from DahA, BghiP and DaeP (Fig. 3.7a and b). According to RQ$_{\sum PAHs(NCs)}$ and RQ$_{\sum PAHs(MPCs)}$ 4% sample showing low risk, 8% showing moderate risk$_1$ and 88% showing high risk mainly due to BbF (Fig. 3.7f). This was also suggested by its higher concentration in water exceeding background limits in section 3.3.1.

In bed sediment, BaA showed moderate risk at G5 (RQ$_{(NC)}$=3.6) in Prayagraj (Fig. 3.7c and d), while all other PAHs showed negligible risk. RQ$_{\sum PAHs(NCs)}$ and RQ$_{\sum PAHs(MPCs)}$ was not calculated for sediments as due to absence of RQ value of BcF and DaeP. The summation of RQ would be underestimated in this case. Risk assessment in SPM also showed no significant risk to ecology as all values of RQ$_{(NC)}$ were below 1 (Fig. 3.7e). Similarly, the concentrations were also lower than the SQG as mentioned in section 3.3.1 indicating negligible negative effects.


RQ (NCs)
100000
10000
1000
100
10
1
0.1
RQ (MPCs)
1000
100
10
1
0.1
0.01
0.001
T1 T3 G1 TC T4 T5 G2 G3 G4 T6 G5 T13 G6 T7 G7 T8 T9 T10 G8 G9 T11 T12 G10 G11 G12
MeC
BbF
BkF
BjF
BaP
IcdP
DahA
BghiP
DaeP

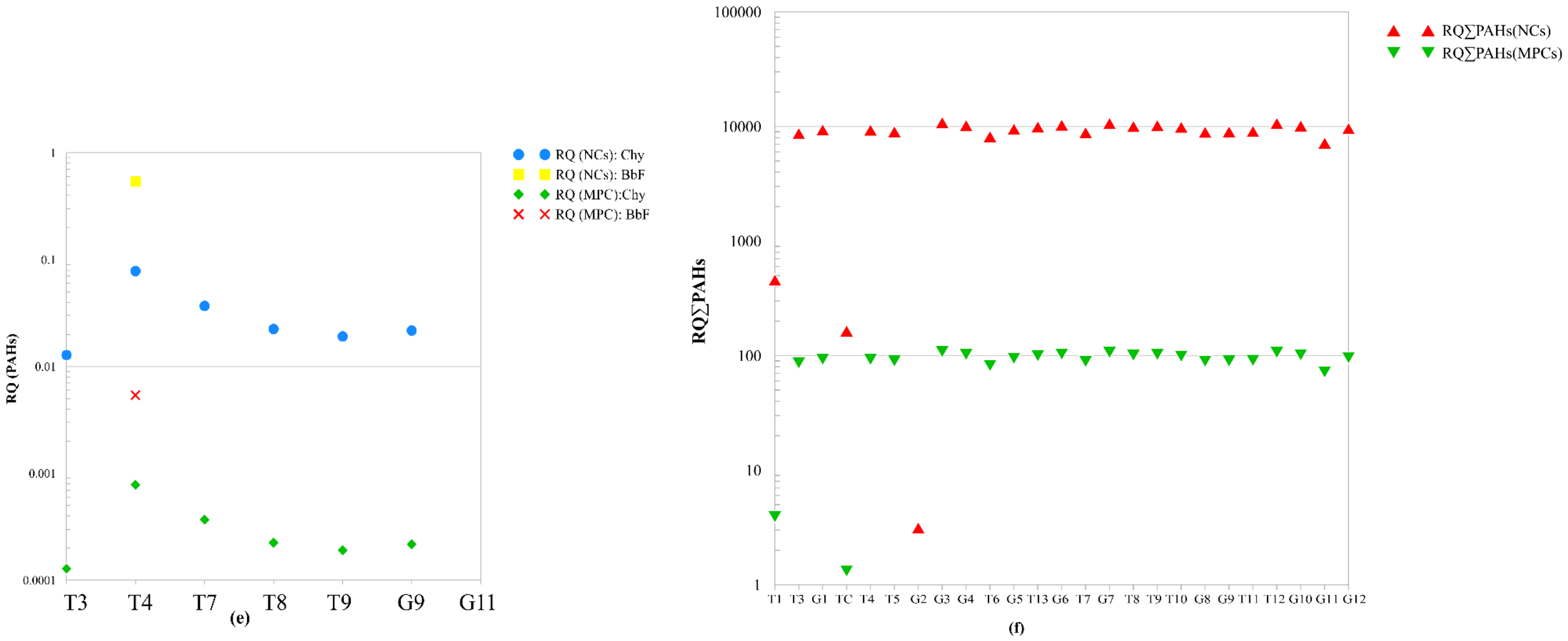
(a)

(b)


RQ (NCs)
10
1
0.1
0.01
0.001
RQ (MPCs)
0.1
0.01
0.001
0.0001
1E-05
T1 T2 T3 G1 TC T4 T5 G2 G3 G4 T6 G5 T13 G6 T7 G7 T8 T9 T10 G8 G9 T11 T12 G10 G11 G12
BaA
Chy
MeC
BbF
BkF
DahA
BghiP
DaeP

(c)

(d)



(e)

(f)

Fig.4.7. Location wise calculated values of (a) RQ_{NCs} and (b) RQ_{MPCs} in river water, (c) RQ_{NCs} and (d) RQ_{MPCs} in bed sediment, (e) RQ_{NCs} and RQ_{MPCs} in SPM, (f) $RQ_{\sum PAHs(NCs)}$ and $RQ_{\sum PAHs(MPCs)}$ in water

3.4 Discussion

From the above results, the lower stretch showed maximum average ∑PAHs followed by middle and upper stretch but the difference was found non-significant indicating less spatial variation in total concentration of the PAHs in river water which might be due to its ubiquitous presence in the environment (Abdel-Shafy and Mansour, 2016). Otherwise, higher ∑PAHs in lower stretch could be due to regions receiving high rates of precipitation resulting in “washout” of contaminants from the atmosphere (Scott et al., 2012) into the water bodies. One or the PAHs are being constantly released due to combustion activities (Hussain et al., 2020). In upper stretch, the possible sources at G1 could be PAHs released from thermal power plants, municipal and industrial wastewater discharge from Haridwar (Sun et al., 2017). Similar anthropogenic activities from Rishikesh contributed to the PAHs at T1 in river water. Other possible sources responsible for contamination by PAHs could be combustion of fossil fuels in vehicles at T3, which was identified as a tourist spot. In the middle stretch, Gomti was reported to be contaminated by PAHs in previous studies (Malik et al., 2004; Malik, 2011). The sources such as biomass burning in the rural and agricultural areas and untreated domestic wastewater discharge could be responsible for the PAHs pollution of river water. Other tributaries such as Chambal was also detected with maximum concentration of BaP which may be due to high wood and charcoal burning in rural areas and smoke from burning farm plants (Klauser et al., 2015; Hellén et al., 2017). Ganga downstream Kanpur (G3) which was found with highest total PAHs concentration indicated influences from urbanization and industrialization. Similarly, concentrations near Prayagraj (G4 and G5) were also comparatively high due presence of vast variety of industries such as brick klins, iron and steel industries, chemical industries, thermal generation of electricity and religious pyre burning along with municipal wastewater dumped into the river (Gaga, 2004). In lower stretch too, river water in urban centers was contaminated with PAHs from the city sewage including wastewater from industries and households from Bansberia and Kalyani established on either side of the river. Apart from contribution from tributaries such as Ghaghara and, Kosi and Mahananda in G7 and, G10, respectively, could also be contaminated from anthropogenic sources such thermal power station and domestic effluents from Chhapra and other nearby small towns located at the bank of the river. However, tributaries such as Son (T8) and Mahananda (T12) indicated contamination from rural discharge and biomass burning.

In bed sediment, on contrary, the total concentration of PAHs was found significantly higher in middle stretch than lower stretch showing spatial variation. This was mainly due to direct discharge from urban influences and densely packed residential areas in the middle stretch as no significant correlation was found between finer fraction of grain size, OC% (silt+clay%) and PAHs (except for BghiP) which could result in geochemical accumulation of the PAHs in bed sediment. The urban centers are generally influenced by the atmospheric deposition, storm and sanitary sewer effluents as well as roadway runoff which tend to have greater concentration than the runoff from rural areas (Abdel-Shafy and Mansour, 2016). Relatedly, water showed evidences of urban contamination as higher number of PAHs were discovered from middle stretch similar to bed sediment. Lesser total concentration in lower basin could also be due to the disturbance in the sediment due high river flow during monsoon in lower section of the basin (Fan et al., 2008). Among three stretches, in upper stretch, T2 showing higher ∑PAHs could be due to small scale industries and wastewater discharge from the towns located on right side of the river. Both bed sediment and SPM similar to water, showed presence of BcF, Chy and MeC at T3 suggesting their accumulation in these matrices due to tourism. Likewise, G5 was also found to have relatively higher concentration in bed sediment as river water. However, rural areas such as G4, T5 and T4 with highest $\sum$PAHs in bed sediment and SPM, respectively could be due to crop burning in agricultural fields and use of wood as fuel in rural areas (Usmani et al., 2020; Lee and Vu, 2010; Villalobos et al., 2015). Also, long distance transportation of PAHs could have also resulted in higher concentration (Aubin and Farrant, 2000). In the lower stretch, G11 was ferry point with many vehicles crossing river using these big ferries on daily basis leading to PAHs contamination from vehicles. PAHs found at this location (Chy, MeC) have environmental anthropogenic sources such as combustion of gasoline and diesel (Wang et al., 2015).

Among three stretches, only BcF showed significant spatial variations in bed sediment which is a major lung deoxyribonucleic acid (DNA) adductor (Weyand et al., 2004) and is a component of coal tar, cigarette smoke and smog. Larger spatial variation in most of the PAHs (except BbF) concentration in water and bed sediment (Fig. 3.1, 3.2 and 3.4) could be explained by the different types of sources represented by urban, suburban and rural areas contributing to PAHs along the basin. Similar studies also reported high pollution levels in surface river water and bed sediment because of the abundance of contamination sources, higher population with enormous consumption formations, and industrialized district (Zhang et al., 2004; Zhao et al., 2010). The low spatial variability of BbF in river water could be due to its higher persistence in the environment which enabled the species to travel long distance resulting in contamination of areas with fewer sources (Aubin and Farrant, 2000; Liu et al., 2017). However, BbF non detection from Song River (T1), Chambal (TC) and Ganga upstream Kanpur has resulted in lower total PAHs and risk assessment ($RQ_{\sum PAHs(NCs)}$ and $RQ_{\sum PAHs(MPCs)}$) at these locations (Fig. 3.4 and Fig. 3.7f). All of the sites are marked as rural areas indicating no prominent nearby source for BbF.

With respect to number of PAHs, seven common PAHs were detected from both water and bed sediment (Fig. 3.1 and 4.2). Generally low molecular weight PAHs are found in water inversely to high molecular weight which are mostly deposited in sediment (Abdel-Shafy and Mansour, 2016). Although regarding study, in river water BbF, BjF and BaP were found with higher df (Table 3.2) than in bed sediment and SPM. This could be due to the concentration levels of PAHs in the water and sediment can influence the activity of the sediment–water exchange and equilibrium status between these matrices (Cui et al., 2016). Similarly, bed sediment was acting as a sink for PAHs with fewer rings such as BcF, Chy and BaA due to differences in PAH concentrations in adjacent environmental media affecting net flux trends (Wang et al., 2011). This achieved by affecting PAH migration, transfer, and diffusion. Similar trend as also observed by Fakhradini et al. (2019) with high molecular PAHs having greater fugacity fraction (ff) greater than 0.5 indicating release of these PAHs from sediment to water. Similarly, SPM with lesser number of PAHs point towards their release into the water from the former.

3.5 Conclusion

In the present study, the spatial distribution showed variation depending upon the different sources of the PAHs along the Ganga basin in three matrices especially in bed sediment where the ∑PAHs difference were found significant. Higher concentration and number of PAHs were detected in urban areas in both water and bed sediment. Based on the concentrations of different PAHs in three matrices, absorption and desorption process were playing a major role to reach the equilibrium between the water, sediment and particulate phase. This resulted in release of high molecular weight PAHs species from sediment to water. For instance, BbF which showed persisting nature and thus less variations in sum of PAHs in water body. No significant tributaries influence was found in water and bed sediment. Lower p values observed for MeC could indicate its dilution in Ganga River from tributaries. From the risk assessment, BbF was found to be causing high risk to the ecosystem and its elevated value also resulted in higher observed $RQ_{\sum PAHs(NC)}$ and

$RQ_{\sum PAHs(MPC)}$ for most of the site putting them at high risk. In bed sediment only BaA showed moderate ecological risk. There was no general agreement with respect to the control of grain size on PAHs distribution. Thus, it can be inferred that both distribution and concentration of PAHs were dominantly influenced by direct entries rather than particle size or total organic carbon (TOC) content in bed sediment. From the study the concentrations of BcF and DaiP was measured but due to lack to toxicity data, risk assessment couldn’t be evaluated. Further steps should be taken to identify the levels of these compounds in natural environment and in aquatic animal tissues with extensive toxicological studies which would facilitate the administrative authorities to set guideline values. While definite measures should be taken to control the release of BbF which was shown to cause high risk to the ecosystem. This could be done by reliable source identification using stable carbon isotopic signatures and taking preventative measure at point sources to control the release of harmful PAHs.

Chapter 4

Phthalate esters (PAEs)

4.1 Physical and chemical properties

Phthalates are esters of phthalic acid which are primarily employed to soften the polyvinyl chloride (Fan et al., 2011). They find a wide variety of use in many products belonging to categories like personal care products, manufacturing of plastics, coatings and paints and adhesives (Saeidnia, 2014). These are released into the environment and generally undergo biodegradation, photodegradation, and anaerobic degradation (Rudel and Perovich, 2009). Main routes for exposure to living beings are by ingestion of food and water in contact with plastic, medical treatments, dermal contact from using phthalates containing cosmetics. In the present study seven PAEs were investigated whose physical and chemical properties (TSCA, ICSC, OSHA and HSDB) are described as below-:

(i) Dimethyl phthalate (DMP): DMP is diester and methyl ester which is used in the manufacturing of plastics, insect repellents, safety glass, and lacquer coatings. The compound as clear oily liquid with subtle aromatic order. The flash point is 142.9ºC that boils and melts at 283.7°C and 0°C, respectively. DMP is insoluble in water with water solubility of 4,000 mg/L at 25 °C. It is found miscible with alcohol, ether, chloroform, benzene and slightly soluble in carbon tetrachloride. DMP sink in water as it is denser than water and has density 1.189 at room temperature. The log K_{ow} is 1.60. On decomposition releases toxic gases and can release CO due to burning.

(ii) Diethyl phthalate (DEP): It is the diethyl ester of benzene-1,2-dicarboxylic acid an is teratogenic agent and neurotoxin. It is applied during plastic manufacturing to make it soft plastic products such as toothbrushes, automobile parts, tools, toys, and food packaging. It also found use in cosmetic products (such as perfumes), insecticides and pharmaceuticals (aspirin) and easily released from these products. It is also a colorless oily liquid with no particular smell and tastes bitter. It has a flash point of 162.8 ºC. The boiling and melting point stands at 297.8 ºC and -2.8 at NTP, respectively. Insoluble in water with solubility= 1,080 mg/L at 25 °C and soluble in acetone, benzene, carbon tetrachloride (CCl_4), ethanol and ethyl ether. The density is greater than water (1.12 at 25 °C) and log K_{ow} = 2.47. It is stable in light and decompose to emit acrid smoke and irritating fumes.

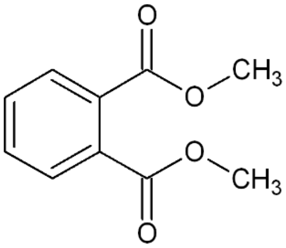
(iii) Di-n-octyl phthalate (DnOP): It is the straight chain diester and isomer of di(2-ethylhexyl) phthalate (DEHP). It is a synthetic organic compound used to keep plastics more flexible for medical tubing and blood storage bags, adhesives, wire and cables, floor tile. It also found use in cosmetics and pesticides. It is a clear oily liquid and has mild order. The lowest temperature at which the vapors of the liquid ignite at (i.e., flash point) is 221.1 ºC. The compound boils and melts at 220 °C and -25 °C. It is insoluble in water and has solubility= 0.022 mg/L at 25 °C. The compound floats on water as it is lighter than water with density= 0.978 at 20 °C and log K_{ow}= 8.10. Stable under recommended storage condition and give smoke and harmful fumes on decomposition.

(iv) Bis(2-ethylhexyl) phthalate (BEHP): It is a phthalate ester that is the bis(2-ethylhexyl) ester of benzene-1,2-dicarboxylic acid which primarily used as plasticizer. The compound is anticipated to be carcinogenic and enters the body by ingestion, inhalation and dermal contact. It appears as colorless to pale yellow liquid without any significant order and pellet like crystals. The melting and boiling point of the compound is -50 °C and 383.9°C at NTP, respectively. The flash point stand at 207.22°C. It is soluble in blood and fluids containing lipoproteins, slightly soluble in carbon tetrachloride and miscible with mineral oil and hexane. There is no solubility (=2.7×10^{-1} mg/L at 25°C) in water. It is less dense than water and have density and Log K_{ow} 0.98 and 7.6, respectively. The compound is stable and decompose to emit acrid smoke.

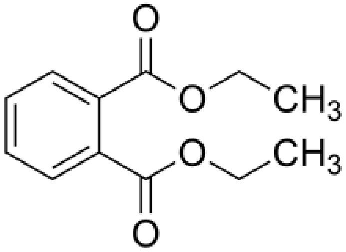
(v) Bis(2-ethylhexyl) adipate (BEHA): It is an ester of adipic acid and 2-ethylhexanol and is used as a plasticizer in manufacturing of polymers, hydraulic fluid, and a component of aircraft lubricants. It is potential carcinogen. The compound is a colorless to straw-colored liquid with a mild aromatic odor. The flash point for the vapors is 196.1°C. The boiling and melting points are 417.2°C and -67.8°C, respectively. The organic compound is soluble in most of the organic solvents such as ethanol, ethyl ether, acetone, acetic acid, insoluble to slightly soluble in glycerine & glycols and insoluble in water (0.78 mg/l at 22 °C). Being lighter it floats on water (density=0.922 at 25 °C) with Log K_{ow} = >6.11. It has half-life of 2.7 days.

(vi) Dibutyl phthalate (DBP): The condensation process between carboxy groups of phthalic acid and two molecules of butanol lead to formation of this diester. It is ubiquitous and find use as plasticizer, solvent for oil-soluble dyes, textile fiber lubricant, antifoam agent, insecticides and other organics, fragrance fixative, insect repellent. It is known less toxic than its other substitutes and like others is colorless oily liquid with subtle aromatic order. Taste is strong and bitter. The boiling and melting points are 340°C and -35°C. The vapors ignite at 157.2 °C. It is very soluble with acetone and benzene, soluble in carbon tetrachloride and is miscible with ethanol, ethyl ether and benzene. The compound is more soluble in perspiration than in water and increases with pH. The solubility in water is 11.2 mg/L at 20 °C, denser than water with density as 1.05 and log K_{ow} is 4.50. It shows excellent stability under light.

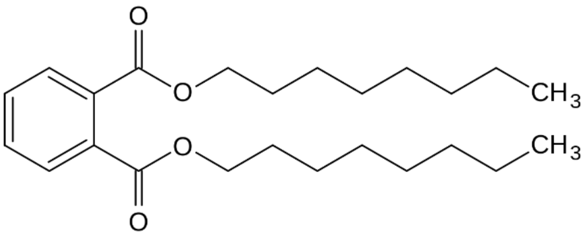
(vii) Benzyl butyl phthalate (BBP): Benzyl butyl phthalate (BBP) is a phthalate, an ester of phthalic acid, benzyl alcohol, and n-butanol and is a potential toxicant. It is exploited as a plasticizer for PVC-made flooring items, adhesives, other plastics, like ethyl cellulose, automobiles coatings which easily penetrates soil and contaminate groundwater and waterways like other phthalates. Also, similar to other species this is also clear oily liquid with mild smell and tastes bitter. The flash, boiling and melting points are 198.9°C, 370°C and -35°C at NTP, respectively. Solubility in water is very poor (2.69 mg/L at 25 °C) but soluble in most organic solvent, is denser than water (density=1.12) and have log K_{ow}= 4.73. Stable under storage condition.



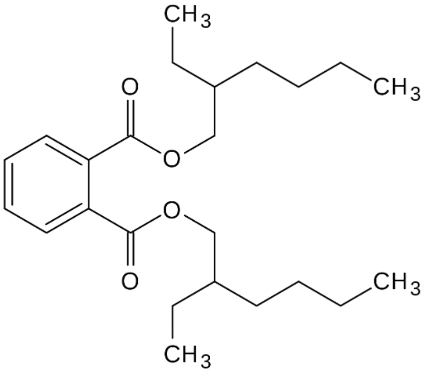
Dimethyl phthalate



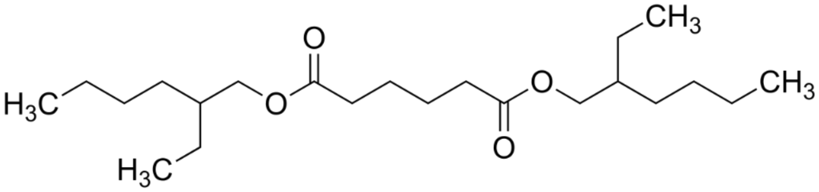
Diethyl phthalate



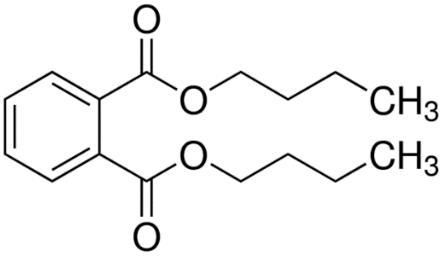
Di-n-octyl phthalate



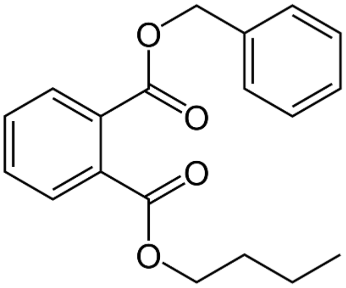
Bis(2-ethylhexyl) phthalate



Bis(2-ethylhexyl) adipate



Dibutyl phthalate



Benzyl butyl phthalate

2D chemical structures of PAEs

4.2 Literature Review

Like PAHs, PAEs are ubiquitously present cross the world in river ecosystem. They have been detected in the environment since decades. Still many recent studies have been undertaken to identify these ECs in natural ecosystem and understand their fate in the environment. In Asia, Jiulong River, Southeast China found sediment and river water to be contaminated with six phthalates with cumulative concentrations as 3480–17700 ng/L in water and 46–1650 ng/g in sediment (Li et al., 2017). From the outcomes of the potential ecological risk assessment revealed that diisobutyl phthalate (DIBP) and DEHP was posing a higher risk due to their comparatively higher levels, while DBP (di-n-butyl phthalate) and diisononyl phthalate (DINP) posed a medium risk to the aquatic system. Out of twenty-one PAEs most frequently found in Haihe River, Northern China were DEHP, DBP, and DIBP (Liu et al., 2020). The Σ_{21}PAEs in the surface sediment ranged from 45.9 to 1474.1 ng/g and 1.79 to 262.8*10^4 ng/L in the pore water. Similar to Jiulong River, Pearl River estuary, greater ecological risks were shown to be posed by DEHP to the studied aquatic environments based on risk quotients (RQs) (Li et al., 2016 and 2017). Zhang et al., (2020) showed temporal variations according to seasons in Yangtze River estuary with highest concentration in winter (2630–22900 ng/L). This study also reported DEHP to be the most abundantly present phthalate and having maximum total concentration more than other locations in China except for Haihe River. In Yellow River, twenty-two congener phthalates were investigated with total concentration ranging from N.D- 6039.9 ng/L in water during rainy season (Zhao et al., 2020) while in Taiwan, seven PAEs were reported from sediment of Tamsui River with total concentration ranged from N.D-23570 ng/g (Lee et al., 2020). Similar to other studies (Lui et al., 2020; Weizhen et al., 2020; Li et al., 2016), the spatial-temporal distribution trends were attributed to urbanization, industrial discharge and effluents from wastewater treatment plants. Further, Muhammad et al., (2016) determined the existence and pollution level of phthalates in the Sembrong River sediments, Malaysia with DBP, and DEHP found at the highest concentration in sediment. One of the few studies by Chen et al., (2019) discovered PAEs from SPM in addition to water and sediment. The sum of PAEs reported were high in SPM (1970-34100 ng/g). With respect to Europe, Rhone River water was identified with eight phthalates with highest concentration as 406.8 ng/L associated with most abundant species as DEHP (Paluselli et al., 2018). The total concentration was ranging from 182.2-615.5 ng/L. In more recent study on Rhone River, phthalates esters (PAE) were the most abundant class among other classes of plasticizers with DEHP again being the most frequent (Schmidt et al., 2020). In North America, two recent studies reported PAEs from river system (Ortiz-Colón et al., 2016; Borges Ramirez et al., 2019). Two urban rivers namely Río Piedras and La Plata in Puerto Rico were investigated for presence of phthalates. Only one, DBP, was found in concentrations ranging from 3-8x10^3 ng/L (Ortiz-Colón et al., 2016). In other study, urban channel of the Ria in Mexico reported seven PAE from sediments which indicated diversity in their distribution based on the season and site. Most frequently discovered being (DEHP) and di-n-octyl phthalate (DnOP) reported with highest concentrations (6973 and 2801 ng/g). From the recently reviewed studies it can be said that DEHP is the most commonly found PAE (Borges Ramirez et al., 2019).

In India, studies reported phthalates in rivers like Gomti, Kaveri and different sections of the Ganga (Srivastava et al., 2010; Selvaraj et al., 2015; Chakraborty et al. 2019; Ghosh et al., 2020; Mukhopadhyay and Chakraborty, 2021). The research has been also carried out on drinking water of South Delhi (Das et al., 2014). In Kaveri, two PAE (DEP and DMP) were detected in 100% water samples and DEP in 94% of the sediment samples (Selvaraj et al., 2015). The total PAEs ranged from 313 to 1,640 ng/l in water while 2 to 1,438 ng/g in sediments with DEHP having the highest concentration (822 ng/L and 1400 ng/g, respectively). Similarly, Gomti river also reported DEHP as the most commonly found PAE with highest concentration (324.72 ng/g). The total concentration however was 1,869.46 ng/g (Srivastava et al., 2010). Roy and Kalita (2011) reported DBP and BBP below the detection limit in the Bahruli River in Assam, India. Das et al. (2014) examined fifteen phthalates from bottled and drinking water sampled from Okhla, India, and the Jawaharlal Nehru University (JNU) campus, New Delhi. The total concentration from Okhla (3804 ng/L) was higher than JNU (390 ng/L) and also Kaveri River water (1640 ng/L). Similar to previous studies DEHP was the most dominant phthalate species. The phthalate concentration was found to increase with an increase in shelf life (Selvaraj et al., 2016).

Three stretches of Ganga were monitored for presence of PAEs (Chakraborty et al. 2021). Among these plasticizers, DEHP showed the highest average mass flow which was estimated to be 164 kg/year. Along the entire stretch, ∑plasticizer was found to be highly variable: upper mean (800 – 3300 ng/L), middle (850–7630 ng/L), and lower (430–1480 ng/L) with total concentration summing up to 430-7630 ng/L. In another study, the middle zone of Ganga water was sampled at nine different points of Prayagraj and Varanasi, Uttar Pradesh and tested for presence of diverse groups of emerging contaminants including seven PAEs (Rendedula et al., 2021). The sum of all the phthalates was estimated to be 0.9-7.58 ng/L with DBP (7.72 ng/L) contributing most to the total concentration. In lower stretch of the Ganga, the river water from Bhagirathi-Hooghly part situated in urban centers such as Kalyani and Kolkata, West Bengal was identified with DEHP (Ghosh et al., 2020). Mukhopadhyay and Chakraborty (2021) also found seven phthalate plasticizers in surface and storm-water of lower Ganga. The concentrations varied between 92.62-770 ng/L and 120.9-781.5 ng/L, respectively. Using site-specific principal component analysis, likely point sources for plasticizers were recognized as unregulated dumping of plastic waste by industries and tourist activities. While riverine sediment from this stretch was examined by Chakraborty et al., (2019) and discovered DEHP to be most commonly occurring phthalate in the sediment samples. $\sum_7$PAEs ranged between 2–422 ng/g with a mean concentration of 145ng/g. Approximately 95% of $\sum_7$PAEs was consisted of DEHP (47%), DEHA (34%) and DBP (14%) consistent with the finding of other investigations in India (Srivastava et al., 2010). PAEs concentrations in river Ganga, UP ranged from 1.49 to 8.67 ng/L with DBP detected as most frequently PAEs than DMP, DEP and DnOP (Rendedula et al., 2020). Possible risk due to DEHP and DnOP were identified by aquatic health risk assessment with RQs calculated as 43 and 5.6, respectively. Further, from sediment risk evaluation, again DEHP was reported to be phthalate of concern in Kaveri River while values in Gomti were under described environmental risk limits for DBP (700 ng/g) and DEHP (1000 ng/g) (Selvaraj et al., 2015; Srivastava et al., 2010). Ecotoxicological risk assessment using predicted no effect concentrations (PNEC) showed DEHP and DnBP with low PNEC values risking organisms like protists, mollusks and fishes in Ganga (Chakraborty et al., 2021; Mukhopadhyay and Chakraborty,2021). Chakraborty et al., (2019) found all seven PAEs to pose very high risk to algae, crustaceans and fishes. From the research on these chemical compounds in India, DEHP was the most abundantly found PAE which in accordance with world’s distribution.

Location	Matrices	DMP	DEP	DnOP	BBP	DBP	BEHP	BEHA	∑PAEs	Reference
Haihe River, China	Sediment	N.D-1.82	0.18-4.7	0.12-16.1	N.D-13.3	9.01-229.8	23.4-1146.1		35.8-1242.2	Liu et al., 2020
Jiulong River, Southeast China	Sediment	N.D-4(64)	N.D-6 (82)			3-230 (100)	7-1280 (100)		37-1650	Li et al., 2017
Pearl River estuary, China	Water	N.D-3390 (57.5-100)	N.D-950 (85.7-100)	N.D-4300 (0-100)	N.D-5320 (0-100)	42-2500 (100)	150-12100 (100)		500-20700	Li et al., 2016
	Sediment	N.D-1750 (25.9-100)	N.D-180 (14.3-65.2)	N.D-310 (28.6-100)	N.D-160 (42.8-78.3)	150-14800 (100)	470-12100 (100)		880-13600	
Rhone River, France	Water	5.7 (0.9)	30.5 (5)	N.D	5.4 (0.9)	40.5 (6.6)	406.8 (66.1)		615.1	Paluselli et al., 2018
Rhone River, France	Water	0.8-2.4	6.9-42.1	N.D-0.9	N.D-0.6	7.3-107.7	69.6-414.4		97-540.8	Schmidt et al., 2020
Ria River, Mexico	Sediment			2801 (100)			6970 (100)		21702	Borges Ramirez et al., 2019
Sembrong River, Malaysia	Sediment	10-40	240-1000	10-320	40-1000	210-1563	2070-7500			Muhammad et al., 2016
Tamsui River,Taiwan	Sediment	N.D-<50	N.D-80	ND-<50	<50-430	<50-411	N.D-23570			Lee et al., 2020
La Plata River, Puerto Ric	Water					3000-8000				Ortiz-Colón et al., 2016
Yangtze River Delta, Chin	Water	10-1550	10-2650	30-1220		330-12580	960-10210		2650-39310	Chen et al., 2019

	SPM	N.D-65	N.D-2790	180-2510		51-3250	420-19350	1970-34100	
	Sediment	ND-80	ND-18	210-8560		120-5870	250-13270	930-34700	
Yangtze River estuary, China	Water	530-55690	250-63020	0.22-4097*10^3	25800-48900	183-13938*10^3 (97.3)	0-5041*10^3 (86.9)	588-22901	Zhang et al., 2020
	Sediment	0-83500	0-326*10^3		169-13798*10^3	3.32-171*10^3 (24.4)	488-24112*10^3 (48.7)	1650-48301	
Yellow River, China	Water	47.9-1027.6 (100)	39.5~884.5 (100)	N.D-13.3 (33.3-58.3)	N.D-5.99 (8.3-33.3)	45.6-2030.1 (100)	36.3-2002.9 (100)	N.D-6039.9	Zhao et al., 2020
	Sediment	23-216.5 (100)	15.8-752.9 (100)	0.9-38 (100)	0.6-37.9 (66.7-100)	61.2-1386.7 (100)	520.8-5537.9(100)	N.D-9897.6	
India									
Kaveri River Basin	Water	ND-94 (92)	36-520 (100)	ND-85 (67)	5.4-145 (92)	ND-372 (67)	ND-822 (92)	313-1,640	Selvaraj et al., 2015
	Sediment	ND-3.71	ND-185.2	ND-8.54	ND-7.8	ND-664	ND-1,400	2-1,438	

		(13)	(94)	(66)	(31)	(88)	(88)			
Ganga River	Water	30-50	40-2140	N.D-50	N.D-130	N.D-2270 (>85)	110-6300 (>85)	N.D-190	430-7630	
Gomti River	Sediment	BDL-49.2 (66.7)	BDL-35.17 (80)	BDL-53.27 (36.7)		BDL-34.29 (76.7)	BDL-324.7 (93.3)		0-364.1	Srivastava et al., 2010
JNU, Delhi	Tap water	3	7	13	N.D	N.D	146		390	Das et al., 2014
Okhala, Delhi	Bottled water	380	198	248	633	317	257		3804	
Lower stretch of River Ganga	Water	N.D-41	18.3-56.4	N.D-81.2	N.D-32.5	25.8-117.9	26.45-599.7	ND-27.7	92.6-770	Mukhopadhyay and Chakraborty, 2021
Ganga, UP	Water	N.D-5.12	BQL-2.9	BQL		1.9-7.7			1.5–8.7	Rendedula et al., 2020
Lower stretch of River Ganga	Sediment	N.D-5	N.D-6	0.1-0.4	1.8-2	N.D-55	N.D-300	N.D-96	2–422	Chakraborty et al., 2019

Table 4.1. Recent studies detecting PAEs concentration (d.f) in various environmental matrices across the world.

4.3 Results

4.3.1 Distribution of PAEs in water, bed sediment and SPM

River water

In river water, six PAEs were detected with most frequent being DEP (df=100%) followed by DMP (52%)>DnOP (32%)>BEHA (28%)>BBP (20%)>BEHP (8%). All water samples were detected with at least one phthalate species (Fig. 4.1). The mean concentration and total sum of PAEs (∑PAEs) varied from 11.1-26.1 and 17.7-83.98 ng/L, respectively (Table 4.2). The trend followed by the mean concentration was BEHP>DEP>DnOP>DMP>BBP>BEHA. According to the WQG, none of the PAEs were found exceeding the guideline concentration (Table 4.2).

With respect to upper stretch, three phthalates were detected, out of which two of them (DMP and DEP) occurred at all locations with average ∑PAEs to be 58.3 ng/L (Table 4.3). T1 (Song River) recorded highest ∑PAEs (=84 ng/L) and concentrations of DMP and DNOP (Table 4.2 and Fig. 4.1 and 4.4) in the basin. Similarly, T3 also detected all three phthalates from river water. In the middle stretch, only DEP was found with 100% df with stretch's highest concentration (=21.04 ng/L) observed in Ganga at Kanpur (G3). Other PAEs found in this stretch were DMP, DEP, DnOP, BEHP and BEHA. Only BEHA among them had df above 50% (i.e., 53%). Compared to upper stretch, average ∑PAEs (=41.8 ng/L) was less. In Prayagraj, Yamuna (T6) had the highest ∑PAEs (=69.9 ng/L) and BEHP concentration (=38.11 ng/L). Total sum of PAEs was also slightly high in Gomti (T13) and Yamuna (T5) (Fig. 4.4). In lower basin, minimum average ∑PAEs was detected, 35.3 ng/L. The maximum number of PAEs (=5) were detected from tributary Gandak (T10, Fig. 4.1) which also observed highest ∑PAEs (=64.11 ng/L) for this stretch followed by G8 downstream Patna with ∑PAEs=50 ng/L. While highest concentration of BBP (Table 4.2) was found in Kosi (T11) with third highest ∑PAEs level (46.4 ng/L).

	River water (ng/L)				Bed Sediment (ng/g)			SPM (ng/g)			SCB[c]
	Min.-Max.	Mean±S.D	D.F (n=25)	WQG	Min-Max.	Mean±S.D	D.F (n=26)	Min.-Max.	Mean±S.D	D.F (n=7)	
DMP	9.7-18.4	14.6±3.4	52		2.2-25.4	9.14±6.4	46.15	71.82	71.82	12.5	
DEP	14.7-25.9	19.5±2.4	100		0-816.98	243.4±315.4	38.46		ND		603
DnOP	10.8-45.99	17.7±11.2	32		6.6-63.2	26.8±19.99	80.77	5.4-29.4	15.6±8.9	75	
BBP	11.3-13.4	12.2±0.8	20		1.3-15.6	6.2±4.4	23.08		ND		10,900
BEHP	14.03-38.1	26.1±12.04	8	6000[a], 8000[b]	3.3	3.3	3.85		ND		180
BEHA	BDL -12.7	11.1±1.04	28	4*10^{5}[a]	4.5-29.03	17.5±9.1	76.92	BDL	39.27	85.7	
∑PAEs	17.7-83.98	40.4±15.7			0-868.34	144.2±258.1		0-136.8	25.6±42.9		

[a] Maximum Contaminant Level (MCL) by US EPA, 2018

[b] Guideline value by WHO, 2017

[c] Screening bencmark values by US EPA, 2006

Table 4.2. Descriptive statistics for PAEs in river water, bed sediment and SPM

	Water (µg/L)			Bed sediment (mg/kg)		
	U.S (n=3)	M.S (n=9)	L.S (n=13)	U.S (n=4)	M.S (n=9)	L.S (n=13)
∑PAEs	58.3	41.8	35.3	49.3	375.6	21.4
DMP	17.9(100)	16.4(44)	11.7(46)	7.9(100)	11.8(22)	7.3(46.2)
DEP	20.8(100)	18.3(100)	20.1(100)	15.9(100)	326.8(67)	N.D
DnOP	29.4(67)	19(22)	11.1(31)	23.6(100)	35.7(78)	18.3(76.9)
BBP	N.D	N.D	12.2(38)	4.6(25)	2.3(22)	8.7(23.1)
BEHP	N.D	26.1(22)	N.D	3.3(25)	N.D	N.D
BEHA	N.D	11.2(56)	10.9(15)	BDL(75)	16.6(78)	4.5(84.6)

Table 4.3. Stretch-wise mean concentration of individual PAEs and ∑PAEs with detection frequency given in parentheses.

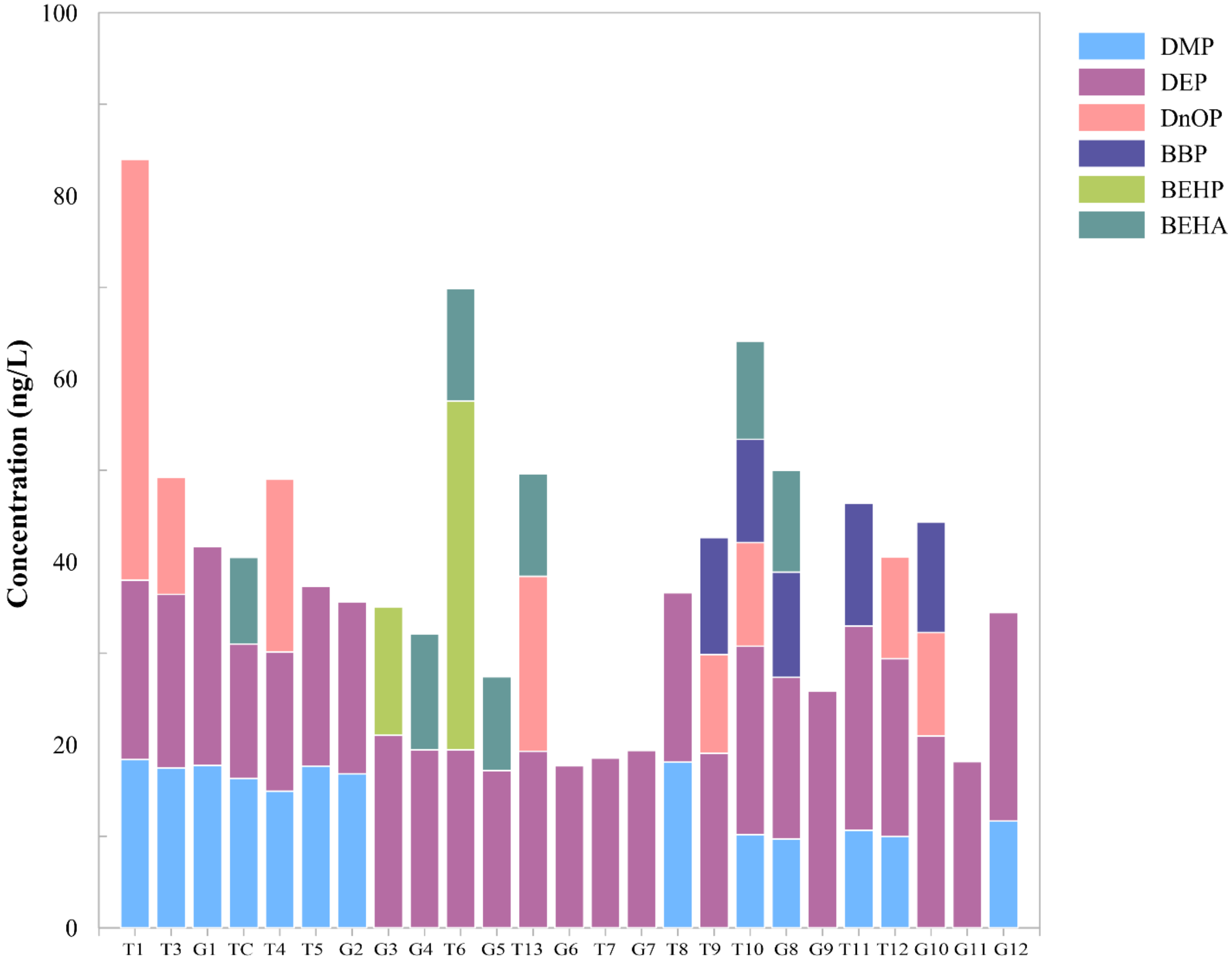


Fig. 4.1. PAEs distribution in river water (x axis indicate locations).

Bed sediment

In bed sediments, total six PAEs were detected (Fig. 4.2) with highest df=81% for DnOP followed by BEHA (77%)>DMP (46%)>DEP (38%)>BBP (23%)>BEHP (4%). According to mean concentration which varied from 6.2 to 243.4 ng/g (Table 4.2), the series can be described as DEP>DnOP>BEHA>DMP>BBP>BEHP. The total sum of the PAE ranged between 0- 868.39 ng/g in bed sediment. The average concentrations of all phthalate species were below screening benchmark values given by US EPA, 2006.

In upper stretch, six PAE species were detected with their mean ∑PAEs as 49.3 ng/g (Table 4.3). BEHA was found below detection limit. Maximum number of phthalates (=5) were detected at T2. Except BEHA, concentrations of all phthalates were found elevated at this site and also observed highest ∑PAEs (=92 ng/g) for the respective stretch (Fig. 4.4). In the middle stretch, average sum of PAEs was much higher than the upper basin, 375.6 ng/ g. Except BEHP all other phthalates were present and amongst them most frequently found were DnOP and BEHA (Table 4.2 and Fig. 4.2). However, similar to water BEHA remained BDL or N.D at most of the locations. Further, DEP was also found in more than half of the samples (df= 67%) (Table 4.3). Very high concentrations of DEP and comparatively higher of DnOP were found at T5 (Yamuna after confluence with Chambal), G2 (upstream Kanpur), G3 (downstream Kanpur) and G4 (upstream Prayagraj) (492.9-817 and 46.97-63.2 ng/g) (Fig. 4.2) elevating total sum of PAEs concentrations (highest observed at T5, Fig. 4.4). Also, at T5 and G4 concentration were exceeding SCB (Table 4.2). Further, downstream Kanpur, Ganga (G3) observed maximum number of phthalates (DEP, DnOP, BBP, and BEHA). In lower stretch, four phthalates were detected namely DMP, DnOP, BBP and BEHA with lowest mean ∑PAEs (=21.45 ng/g), similar to water. Relatively higher total phthalate concentrations were discovered in Gandak (T10, 38.6 ng/g) and Hooghly in West Bengal (G11, 53.8 ng/g) (Fig. 4.4). Gandak also found highest concentration for BBP (Fig. 4.2).

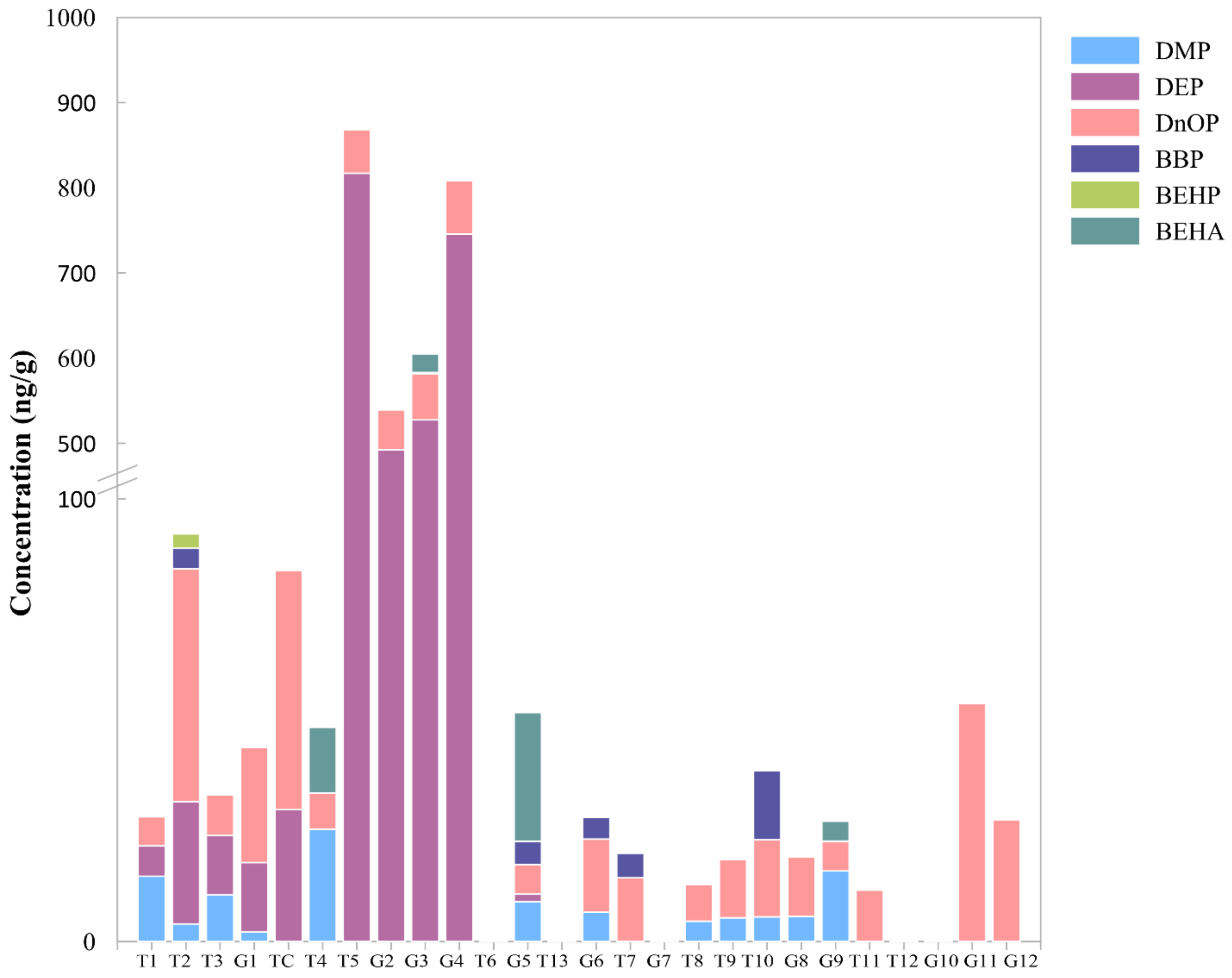


Fig. 4.2. PAEs distribution in bed sediment (x axis indicate locations).

SPM

In this environmental matrix, only three phthalates were detected (Fig. 4.3) with most frequently found PAE as DnOP followed by BEHA and DMP (Table 4.2). The mean concentration in SPM varied from 15.6-71.8 ng/g which followed the order as DMP>BEHA>DnOP. T4 was detected with all three phthalates and displayed highest total phthalate concentration (136.8 ng/g) like bed sediment. Other locations were detected with relatively lower ∑PAEs (Fig. 4.4).

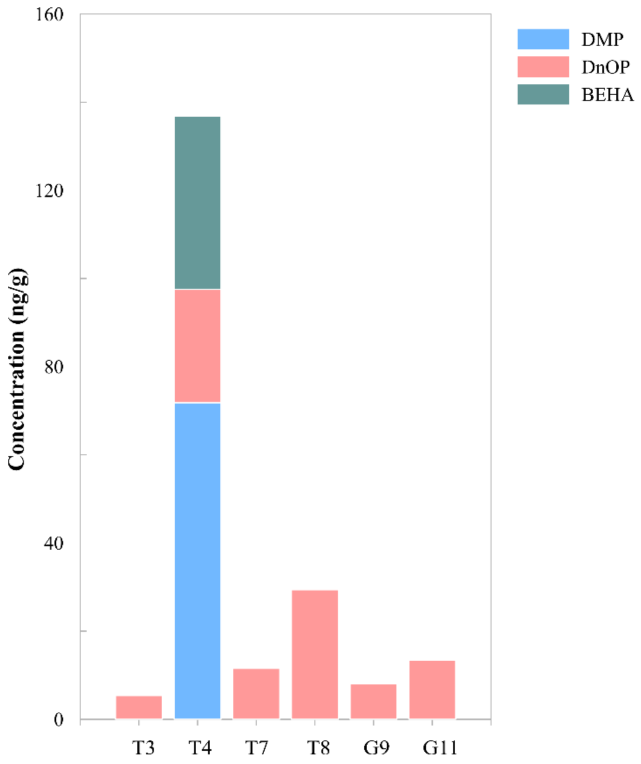


Fig. 4.3. PAEs distribution in SPM (x axis indicate locations)

4.3.2 Influence of tributaries

In river water, there was slight decrease in the total PAEs concentration (Fig. 4.4) with noticeable lowering of DnOP to level where it was not detected in the river water of Yamuna (T5). However, in bed sediment there was a drastic increase in the total concentration of PAEs (Fig. 4.4) mainly due to addition of DnOP from Chambal with little contribution of DEP (which was majorly coming from other contaminant sources as concentrations were much higher in Yamuna (T5)). Other reason for no detection of DnOP in river water at T5 could be due to phase transition from dissolved form in water to adsorbed form in bed sediment. This might also be the reason for higher DnOP in Yamuna in bed sediment after confluence besides addition from Chambal. Further downstream basin, Ganga (G5) after confluence with Yamuna was found to have slightly lower ∑PAE, DEP and BEA due to dilution from Yamuna. Similarly, in bed sediment there was a decrease in overall total concentration but the change was major compare to water. This was because of non-detection of the phthalates in Yamuna River due to high flow condition during monsoon resulting in desorption from bed sediment while diluting the concentration in water as in case of PAHs (Abdel-Shafy and Mansour, 2016; Fan et al., 2008). This further decreased the concentration in Ganga after confluence. Ghaghara did not show significant influence on concentration of PAEs in Ganga River water. However, Kosi (T11) and Mahananda (T12) increased ∑PAEs in river water of Ganga by increasing concentration of BBP and DnOP, respectively, similar to PAHs. Before confluence both of the PAEs were not detected from the Ganga. On contrary, the PAEs concentrations were below detection limit in Ganga (G10) bed sediment after confluence of Mahananda due to dilution.

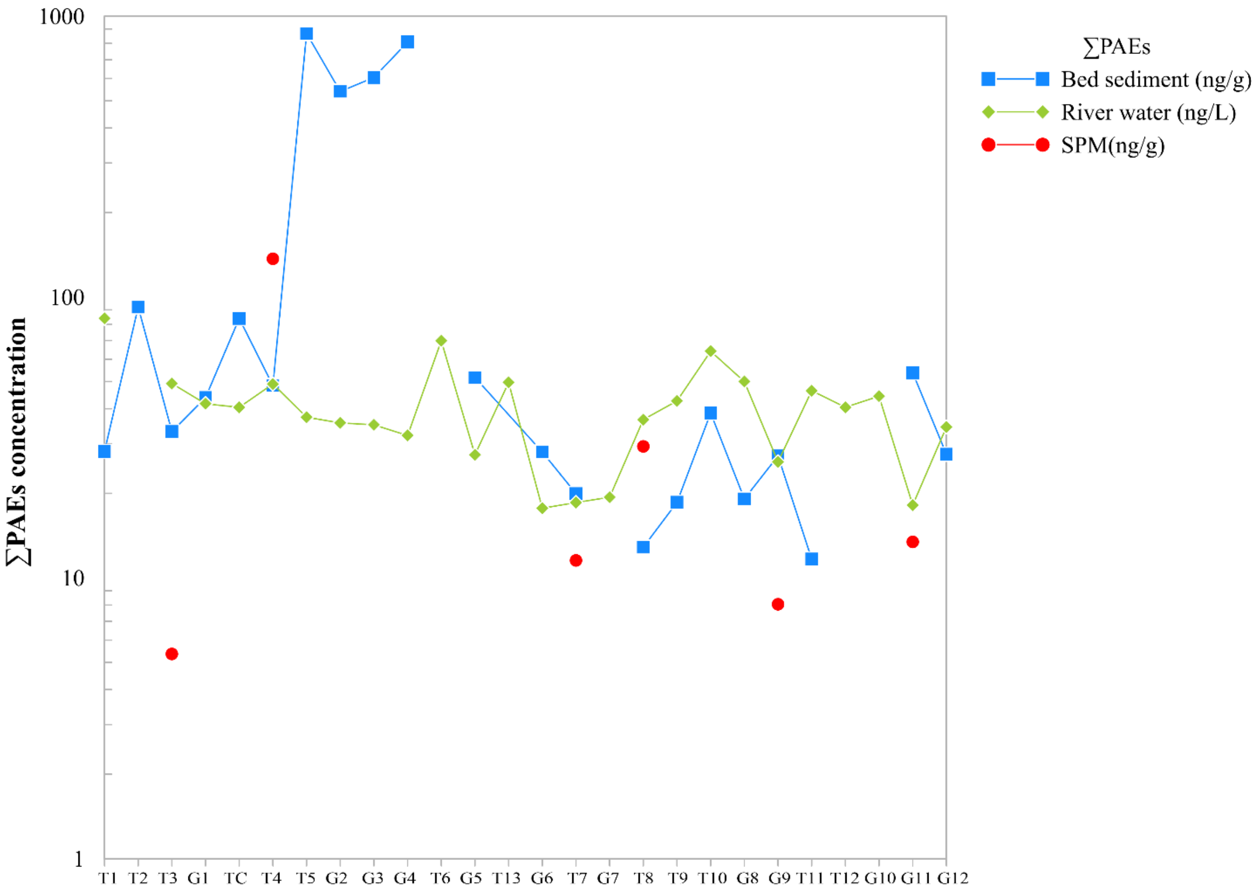


Fig. 4.4. Distribution of ∑PAHs in three environmental matrices along the Ganga River Basin

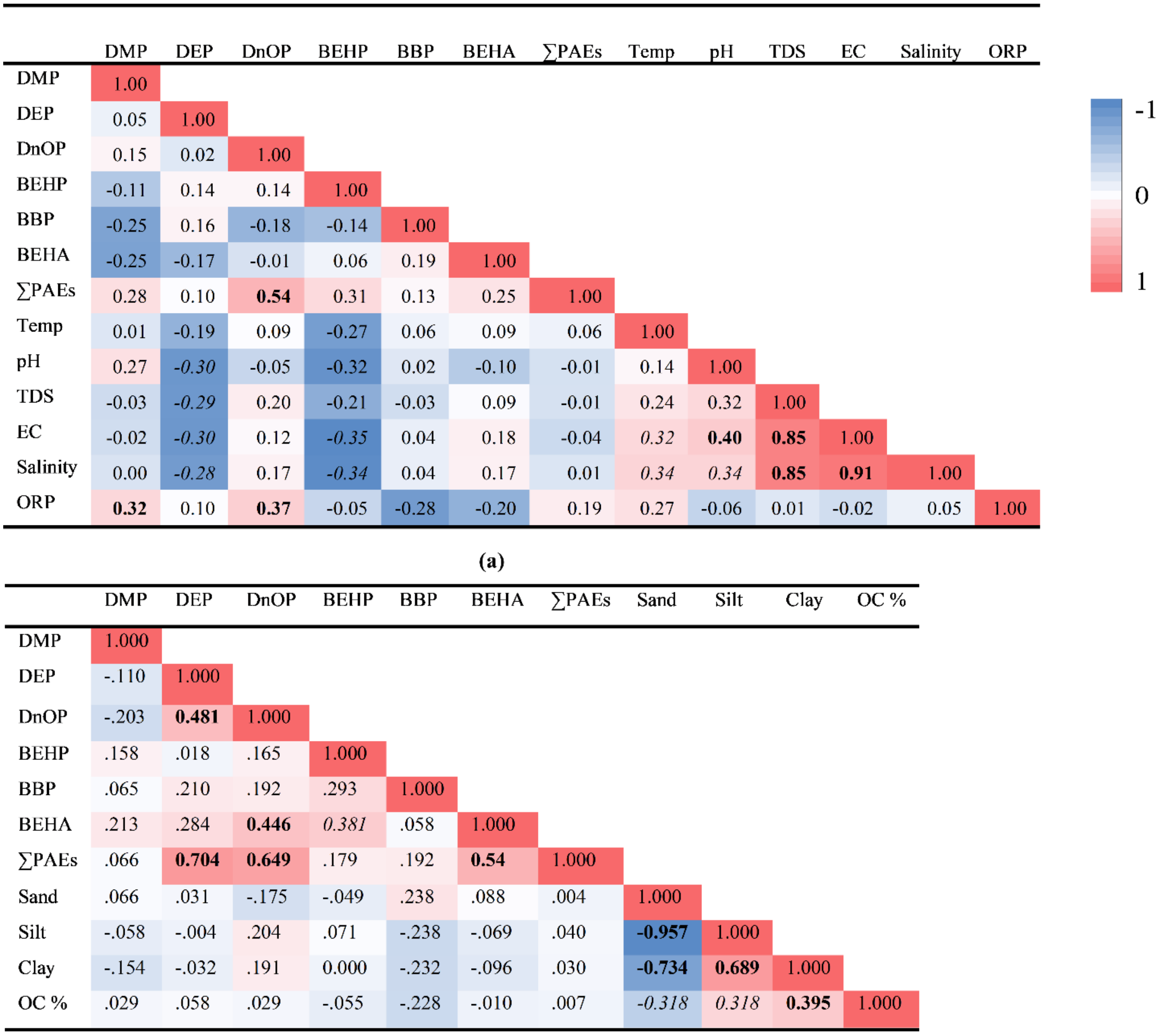
4.3.3 Statistical Analysis

The statistical analyses were performed to understand the distribution, influence of tributaries and effect of physicochemical parameters of water, grain size and organic carbon on distribution of PAE in water and bed sediment.

Correlation

From the Kendall tau's correlation analysis performed for river water (Fig. 4.5a), DMP and DnOP showed a low positive correlation with ORP (p=0.05) suggesting it's control over distribution of these phthalates. The latter was also found to be significantly correlated with ∑PAEs (p=0.01) indicating DnOP was representative of ∑PAEs concentration and can act as potential marker pollutant for detecting phthalate esters in water samples (Kingsley and Witthayawirasak, 2020). Other significant correlations (p=0.05) shown were negative by DEP and BEHP with water quality parameters suggesting influence of latter on their concentrations in water (Huang et al., 2008; Weizhen et al., 2020) (Fig. 4.5a). The negative correlation with salinity suggested that increase in salinity could have reduced the level of PAEs by decreasing their solubility which resulted in the adsorption onto sediment phase. While increase in pH could cause the aqueous hydrolysis of DEP thus removing the species from the water phase. The higher electrical conductivity (EC) with increased electron accepting species might be facilitating the degradation of the ester under anerobic conditions thus decreasing their levels in river water. (Prasad, 2021).

In case of bed sediment, there was no significant correlation with grain size and organic carbon percentage indicating that these parameters were not controlling the behavior of the sediment associated PAEs in the study. The distribution of PAEs were supposed to be mainly derived directly from the local anthropogenic sources linked to urban and rural areas (Weizhen et al., 2020). However, BEHA showed moderate and low significant correlation with DnOP and BEHP pointing towards similar source (Fig. 4.5b). Three of them belong to high molecular weight PAEs which are mainly used as plasticizer in a wide variety of products (Chen et al., 2019; Chen et al., 2013; Net et al., 2015). DEP, DnOP and DEHA showed significant positive correlation with ∑PAEs (p=0.01) indicating these PAEs were majorly contributing to total concentration. Strong correlations of DEP and DnOP suggested that these PAEs can be used as pollution markers in bed sediment (Kingsley and Witthayawirasak, 2020), however, due to DEP lower log K_{ow} and higher solubility (Section 4.1) it is more prone to biodegradation (Prasad, 2021). So, DnOP just like water could serve as potential pollution tracer in bed sediment too due to its hydrophobic nature with low water solubility and high log K_{ow} values, increasing the tendency to get adsorb onto sediment particles resisting biodegradation (Li et al., 2016; Peterson and Freeman, 1982; Gao et al., 2016; Weizhen et al., 2020).



	DMP	DEP	DnOP	BEHP	BBP	BEHA	∑PAEs	Temp	pH	TDS	EC	Salinity	ORP
DMP	1.00												
DEP	0.05	1.00											
DnOP	0.15	0.02	1.00										
BEHP	-0.11	0.14	0.14	1.00									
BBP	-0.25	0.16	-0.18	-0.14	1.00								
BEHA	-0.25	-0.17	-0.01	0.06	0.19	1.00							
∑PAEs	0.28	0.10	**0.54**	0.31	0.13	0.25	1.00						
Temp	0.01	-0.19	0.09	-0.27	0.06	0.09	0.06	1.00					
pH	0.27	*-0.30*	-0.05	-0.32	0.02	-0.10	-0.01	0.14	1.00				
TDS	-0.03	*-0.29*	0.20	-0.21	-0.03	0.09	-0.01	0.24	0.32	1.00			
EC	-0.02	*-0.30*	0.12	*-0.35*	0.04	0.18	-0.04	*0.32*	**0.40**	**0.85**	1.00		
Salinity	0.00	*-0.28*	0.17	*-0.34*	0.04	0.17	0.01	*0.34*	*0.34*	**0.85**	**0.91**	1.00	
ORP	**0.32**	0.10	**0.37**	-0.05	-0.28	-0.20	0.19	0.27	-0.06	0.01	-0.02	0.05	1.00

(a)

	DMP	DEP	DnOP	BEHP	BBP	BEHA	∑PAEs	Sand	Silt	Clay	OC %
DMP	1.000										
DEP	-.110	1.000									
DnOP	-.203	**0.481**	1.000								
BEHP	.158	.018	.165	1.000							
BBP	.065	.210	.192	.293	1.000						
BEHA	.213	.284	**0.446**	*0.381*	.058	1.000					
∑PAEs	.066	**0.704**	**0.649**	.179	.192	**0.54**	1.000				
Sand	.066	.031	-.175	-.049	.238	.088	.004	1.000			
Silt	-.058	-.004	.204	.071	-.238	-.069	.040	**-0.957**	1.000		
Clay	-.154	-.032	.191	0.000	-.232	-.096	.030	**-0.734**	**0.689**	1.000	
OC %	.029	.058	.029	-.055	-.228	-.010	.007	*-0.318*	*0.318*	**0.395**	1.000

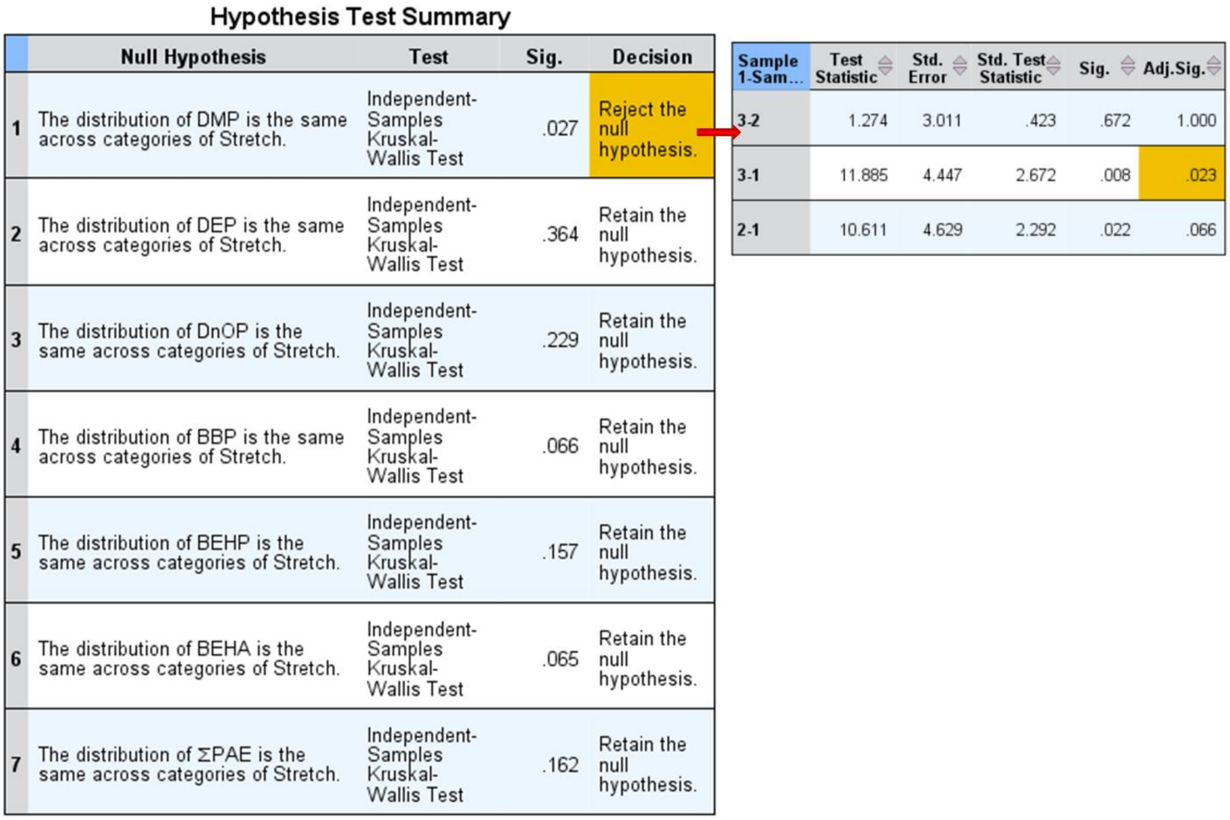
(b)

Fig. 4.5. Kendall’s Tau correlation analysis for PAEs in (a) river water (b) bed sediment.

Kruskal-Wallis test

The non-parametric equivalent ANOVA called Kruskal-Wallis was employed to recognize the significant difference between the concentrations of different PAHs in three stretches. A fixed factor as “stretch” with three groups were considered, i.e., upper, middle, and lower designated by 1, 2 and 3, respectively. Fig. 4.6a, showed only DMP was rejecting the null hypothesis with p=0.27, i.e, lower than the 0.05. This reveled that DMP was showing significant spatial variation between stretch 1 and 3, with upper basin showing higher values than lower. No other significant differences were obtained. However, BEHA and BEHP showed lower p values showing noticeable higher mean rank for middle and lower stretches, respectively. On the other hand, in bed sediment, significant variations were observed for DEP and ∑PAEs among stretches (Fig. 4.6b). DEP was significantly higher in middle and upper stretch than the lower stretch while ∑PAEs was higher in middle stretch than lower basin. Only low molecular weight PAEs were showing significant differences. This could be due to lower number of carbon atoms in DEP and DMP making them more prone to biodegradation in natural environment (Chen et al., 2017; Prasad, 2021) causing variability in PAEs concentration (Weizhen et al., 2020).

Kruskal-Wallis test was also performed to identify the significant effect of tributaries (Fig. 4.6a-d). Two positions were regarded as Ganga and tributaries mentioned as numbers 1 and 2, respectively. The analysis showed significant differences between tributaries and Ganga for DnOP and total PAEs concentrations (Fig. 4.6c). The mean rank was observed higher for tributaries indicating they were significantly contributing to DnOP and total PAEs concentrations in Ganga River water. Also, in bed sediment lower p values were identified for DnOP and ∑PAEs. These findings were also consistent with the discussion in section 4.3.2.

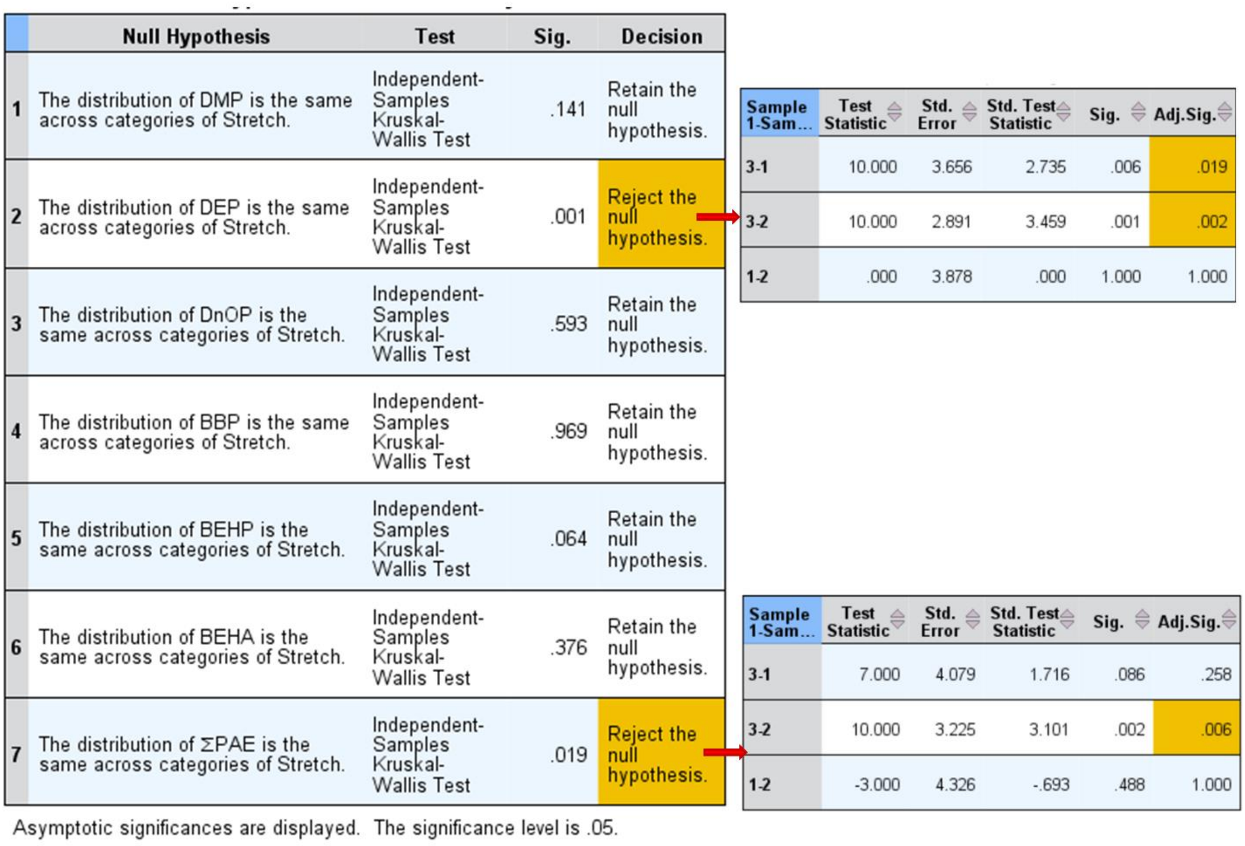


Hypothesis Test Summary

	Null Hypothesis	Test	Sig.	Decision
1	The distribution of DMP is the same across categories of Stretch.	Independent-Samples Kruskal-Wallis Test	.027	Reject the null hypothesis.
2	The distribution of DEP is the same across categories of Stretch.	Independent-Samples Kruskal-Wallis Test	.364	Retain the null hypothesis.
3	The distribution of DnOP is the same across categories of Stretch.	Independent-Samples Kruskal-Wallis Test	.229	Retain the null hypothesis.
4	The distribution of BBP is the same across categories of Stretch.	Independent-Samples Kruskal-Wallis Test	.066	Retain the null hypothesis.
5	The distribution of BEHP is the same across categories of Stretch.	Independent-Samples Kruskal-Wallis Test	.157	Retain the null hypothesis.
6	The distribution of BEHA is the same across categories of Stretch.	Independent-Samples Kruskal-Wallis Test	.065	Retain the null hypothesis.
7	The distribution of ΣPAE is the same across categories of Stretch.	Independent-Samples Kruskal-Wallis Test	.162	Retain the null hypothesis.

Sample 1-Sam...	Test Statistic	Std. Error	Std. Test Statistic	Sig.	Adj.Sig.
3-2	1.274	3.011	.423	.672	1.000
3-1	11.885	4.447	2.672	.008	.023
2-1	10.611	4.629	2.292	.022	.066

(a)



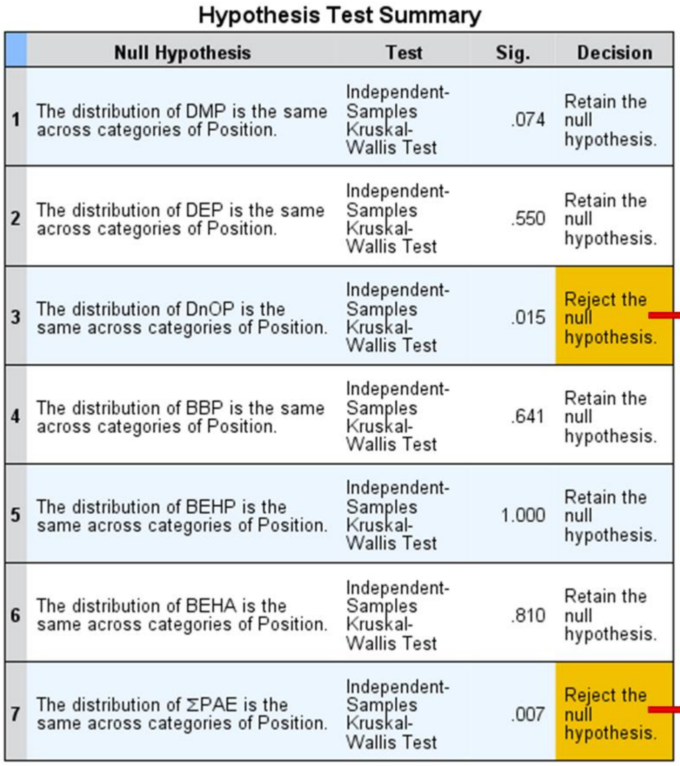
	Null Hypothesis	Test	Sig.	Decision
1	The distribution of DMP is the same across categories of Stretch.	Independent-Samples Kruskal-Wallis Test	.141	Retain the null hypothesis.
2	The distribution of DEP is the same across categories of Stretch.	Independent-Samples Kruskal-Wallis Test	.001	Reject the null hypothesis.
3	The distribution of DnOP is the same across categories of Stretch.	Independent-Samples Kruskal-Wallis Test	.593	Retain the null hypothesis.
4	The distribution of BBP is the same across categories of Stretch.	Independent-Samples Kruskal-Wallis Test	.969	Retain the null hypothesis.
5	The distribution of BEHP is the same across categories of Stretch.	Independent-Samples Kruskal-Wallis Test	.064	Retain the null hypothesis.
6	The distribution of BEHA is the same across categories of Stretch.	Independent-Samples Kruskal-Wallis Test	.376	Retain the null hypothesis.
7	The distribution of ΣPAE is the same across categories of Stretch.	Independent-Samples Kruskal-Wallis Test	.019	Reject the null hypothesis.

Asymptotic significances are displayed. The significance level is .05.

Sample 1-Sam...	Test Statistic	Std. Error	Std. Test Statistic	Sig.	Adj.Sig.
3-1	10.000	3.656	2.735	.006	.019
3-2	10.000	2.891	3.459	.001	.002
1-2	.000	3.878	.000	1.000	1.000

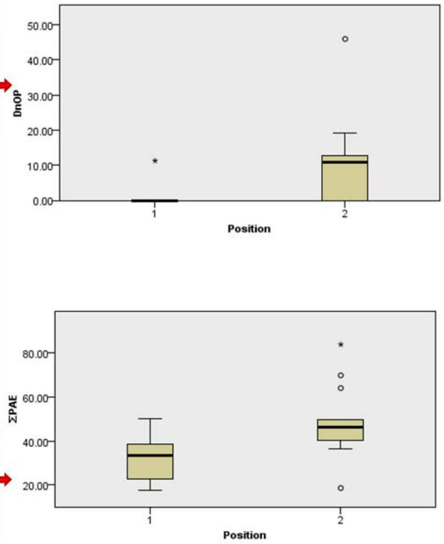
Sample 1-Sam...	Test Statistic	Std. Error	Std. Test Statistic	Sig.	Adj.Sig.
3-1	7.000	4.079	1.716	.086	.258
3-2	10.000	3.225	3.101	.002	.006
1-2	-3.000	4.326	-.693	.488	1.000

(b)



Hypothesis Test Summary

	Null Hypothesis	Test	Sig.	Decision
1	The distribution of DMP is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.074	Retain the null hypothesis.
2	The distribution of DEP is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.550	Retain the null hypothesis.
3	The distribution of DnOP is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.015	Reject the null hypothesis.
4	The distribution of BBP is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.641	Retain the null hypothesis.
5	The distribution of BEHP is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	1.000	Retain the null hypothesis.
6	The distribution of BEHA is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.810	Retain the null hypothesis.
7	The distribution of ΣPAE is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.007	Reject the null hypothesis.



(c)

	Null Hypothesis	Test	Sig.	Decision
1	The distribution of DMP is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.716	Retain the null hypothesis.
2	The distribution of DEP is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.703	Retain the null hypothesis.
3	The distribution of DnOP is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.314	Retain the null hypothesis.
4	The distribution of BBP is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.972	Retain the null hypothesis.
5	The distribution of BEHP is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.355	Retain the null hypothesis.
6	The distribution of BEHA is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.496	Retain the null hypothesis.
7	The distribution of ΣPAE is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.380	Retain the null hypothesis.

Asymptotic significances are displayed. The significance level is .05.

(d)

Fig. 4.6. Kruskal-Wallis test for PAEs in (a and c) river water and (b and d) bed sediment.

4.3.4 Risk assessment

PAEs are identifies as endocrine disrupting chemicals that cause functional damage to endocrine organs of the living organisms (Kudlak et al., 2015). The US EPA have considered these PAEs (DMP, DEP, DBP, BBP, DEHP, and DnOP) in the priority list (Keith and Telliard, 1979) and also classified DEHP and BBP as probable (group 2B) and possible human carcinogen, respectively (US EPA, 2012). It is important to assess their ecological risk. For this purpose, RQ was derived using the following equation-:

$$\boldsymbol{RQ = \frac{MEC}{PNEC}} \qquad \textbf{(4.1)}$$

where, MEC stands for measured environmental concentration and PNEC is the predicted no effect concentrations. The PNECs were obtained from division of the lowest relevant acute effect concentration short-term (LC50, EC50) or the lowest No Observed-Effect Concentration (NOEC) in chronic toxicity by an assessment factor (AF) (Gros et al., 2010). Due to absence of toxicity data equivalent to the studied PAEs in sediment, ecological risk associated with contaminants in sediment is identified by predicting pore water concentration by using following formula (Zhao et al., 2010)

$$\boldsymbol{C_{porewater}\left(\frac{ng}{L}\right) = \frac{1000 \times C_s\left(\frac{ng}{g}\right)}{K_{OC}} \times \%\ total\ organic\ carbon} \qquad \textbf{(4.2)}$$

where, Cs is the concentration detected in sediment and K_{oc} is the organic carbon partitioning coefficient. The values of PNEC were used for three groups of organisms and are taken from previous literature (Li et al., 2016, Table 4.4). The organisms include algae (*Pseudokirchneriella subcapitata*), crustacean (*Daphnia magna*) and fish (*Lepomis macrochirus, Danio rerio (Zebra Danio) or* Channel Catfish). However, DEHA values were calculated using toxicity values from Environment Canada,

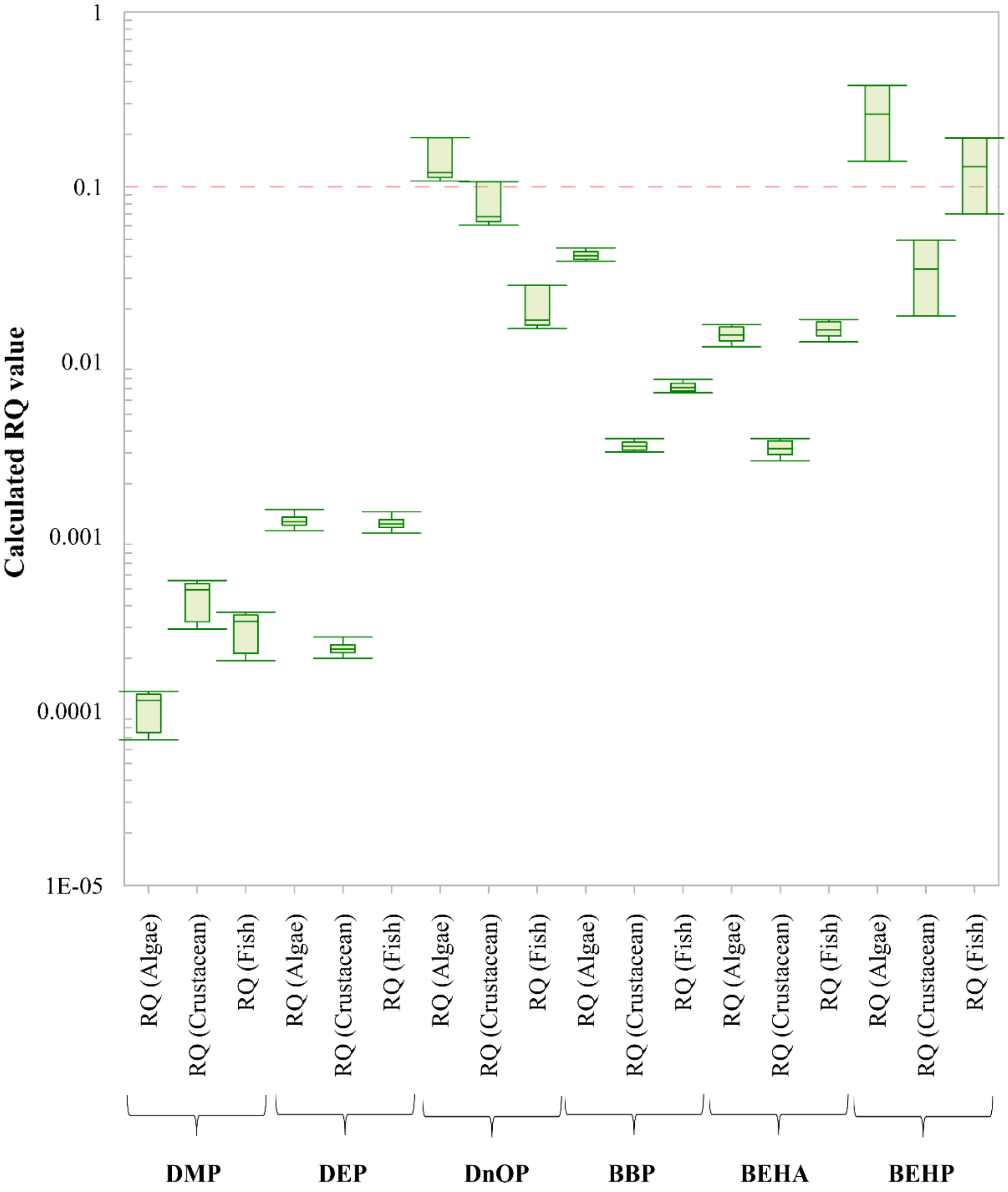
2011. Based on the RQ value, RQ< 0.1 is considered as “low risk”; RQ ranging from 0.1 to 1 as “medium risk”; and RQ> 1 as “high risk”.

	Species group	**Species scientific name**	**Toxicity data (μg/L)**	**Assessment factor**	**PNEC$_{water(\mu g/L)}$**	**References**
DMP	Algae	*Pseudokirchneriella subcapitata*	EC_{50} =142000	1000	142	Adams et al., 1995
	Crustaceans	*Daphnia magna*	EC_{50}=33000	1000	33	
	Fish	*Lepotnis macrochirus*	E EC_{50} = 50000	1000	50	
DEP	Algae	*Pseudokirchneriella subcapitata*	EC_{50} =16000	1000	16	
	Crustaceans	*Daphnia magna*	EC_{50}= 86000	1000	86	
	Fish	*Lepotnis macrochints*	NOEC= 1650	100	17.	
DBP	Algae	*Pseudokirchneriella subcapitata*	EC_{50} =400	1000	0.4	
	Crustaceans	*Daphnia magna*	EC_{50}=3000	1000	3	
	Fish	*Danio rerio (Zebm Danio)*	NOEC= 100	100	1	Ortiz-Zarragoitia et al. 2006
BBP	Algae	*Pseudokirchneriella subcapitata*	NOEC = 30	100	0.3	Rhodes et al., 1995
	Crustaceans	*Daphnia magna*	EC_{50} =3700	1000	4.	Gledhill et al., 1980
	Fish	*Lepomis macrochirus*	EC_{50} =1700	1000	2.	Adams et al., 1995
DEHP	Algae	*Pseudokirchneriella subcapitata*	EC_{50} =100	1000	0.1	
	Crustaceans	*Daphnia magna*	EC_{50} =77	1000	0.77	
	Fish	*Lepomis macrochirus*	EC_{50} =200	1000	0.2	
DnOP	Algae	*Pseudokirchneriella subcapitata*	EC_{50} =100	1000	0.1	

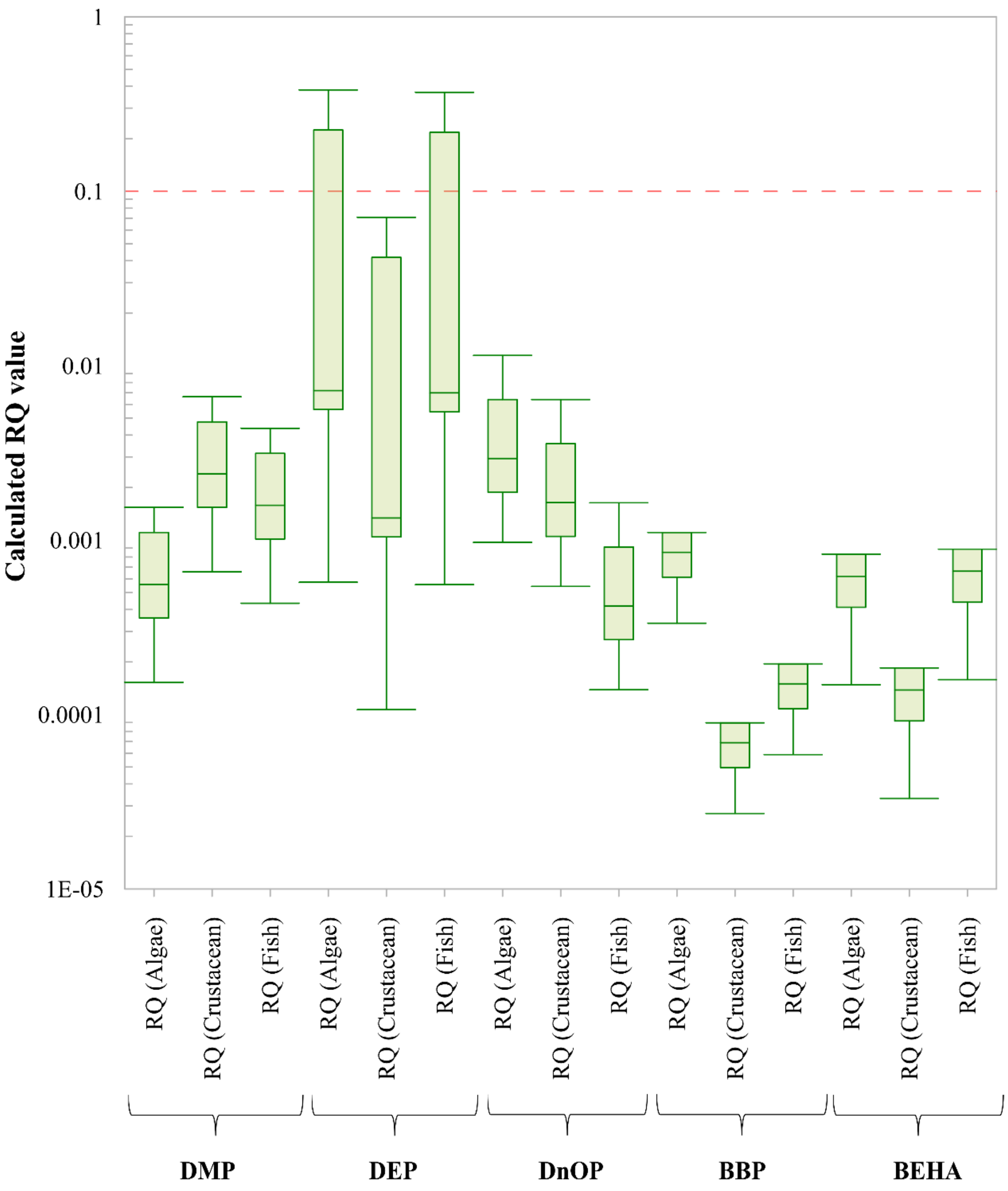
	Crustaceans	*Molluscs Haliotis diversicolor*	NOEC= 17.9	100	0.179	Liu et al., 2009
	Fish	*Channel Catfish*	EC$_{50}$ =700	1000	0.7	He et al., 2013
DEHA	Algae	*Pseudokirchneriella subcapitata*	EC$_{50}$ =780	1000	0.78	
	Crustaceans	*Daphnia magna*	MATC=35	10	3.5	
	Fish	*Lepomis macrochirus*	LC$_{50}$ =730	1000	0.73	

Table 4.4. The toxicity values of PAEs for the aquatic organisms (Li et al., 2016)

Based on calculated RQ value, DnOP posed moderated risk to algae and crustacean species namely *Pseudokirchneriella subcapitata* and *Daphnia magna*, respectively. While DEHP was posing moderate risk to algae (RQ= 0.38-0.14) and fish species, *Lepomis macrochirus* (RQ=0.19) in river water, as shown in the box whiskers plot (Fig. 4.7a). From the box plot, the median and lower extreme value for DnOP and DEHP in case of algae lie above 0.1 indicating DnOP and DEHP posing risk to algae at all locations from where they were detected. The RQ value for DnOP varied from 0.11 to 0.46 for algae while 0.11 to 0.26 for crustacean in 32% and 12% of the sampling location, respectively. All other values were below 0.1 signifying low risk. In bed sediment, algae and crustacean species were at moderated risk from DEP (RQ=0.19-0.38 and 0.18-0.37, respectively). Fig. 4.7b showed upper extreme limit for DEP to lie above 0.1. The locations showing moderate risk also showed very high concentration of DEP as mentioned in section 4.3.1. No other PAE concentration recorded RQ above 0.1. Risk assessment for SPM could not be calculated due to lack of organic carbon data for SPM.


Calculated RQ value
1
0.1
0.01
0.001
0.0001
1E-05
RQ (Algae)
RQ (Crustacean)
RQ (Fish)
RQ (Algae)
RQ (Crustacean)
RQ (Fish)
RQ (Algae)
RQ (Crustacean)
RQ (Fish)
RQ (Algae)
RQ (Crustacean)
RQ (Fish)
RQ (Algae)
RQ (Crustacean)
RQ (Fish)
RQ (Algae)
RQ (Crustacean)
RQ (Fish)
DMP
DEP
DnOP
BBP
BEHA
BEHP

(a)



(b)

Fig. 4.7. Box whiskers plot showing RQ calculated for PAEs for different groups of organisms in (a) river water and (b) bed sediment.

4.4 Discussion

The results regarding river water indicated that the highest and lowest total PAE concentration in upper and lower stretch could be due to the fact that sampling was done before the monsoon arrival in upper basin while in lower basin monsoon had been already arrived by the time of sampling. However, in middle basin, monsoon had just started in Uttar Pradesh. Despite the higher pollution load from densely populated cities and suburban areas downstream, there could be dilution of the overall PAEs concentration in lower basin from increased river flow with huge volume of water brought by the tributaries downstream (Pandey and Singh, 2017). The most ubiquitous phthalate was DMP which found use in a wide variety of cosmetic products, household and personal care products showed signification variations between upper and lower stretches possibly due to monsoonal dilution effect as no correlation were found between water quality parameters influencing its distribution (Fig 4.5a and 4.6a) (Lyche, 2017). However, higher mean value of BEHA and BEHP in middle and lower regions indicated that anthropogenic contamination of these PAEs surpassed the dilution (Weizhen et al., 2020). With respect to elevated concentration at certain locations, possible sources were identified. Industrial effluents from manufacturing of tyres, plastic, disposable cups, rubber industries, plastic molding, and city municipal wastewater discharge from Rishikesh on right bank of the river were thought to be the likely sources for PAEs at T1. While tourist activities disposing plastic waste might be influencing levels at T3 in upper basin (Chakraborty et al., 2021). Ganga (G3) and Yamuna located in major cities like Kanpur and Prayagraj (T6) received wide range of point sources from industrial effluents from tanneries, paper and pulp units, textile, pigments and paints, plastic manufacturing, household garbage discharging PAEs (Khwaja et al., 2001; Suthar et al., 2009; Zota et al., 2014). While non-point sources such as road runoff, aeolian deposition from vehicular traffic, domestic effluents and storm water discharge also releases a variety of PAEs (Ahamad et al., 2021; Weizhen et al., 2020) from these urban centers in middle basin. Rural areas with intensive agriculture and primitive infrastructure at T13 and T4 could have received inputs from agricultural runoff, untreated domestic sewage and huge piles of garbage near river banks (Weizhen et al., 2020; Srivastava et al., 2010; Liu et al., 2020). In lower basin, urban influences could be seen from Patna (in Ganga (G8) and Gandak (T10)) which is highly populated area leading to huge amounts of effluents from small scale agro-based industries, plastic and PVC manufacturing and household activities discharged into the water bodies (Singh et al., 2018). While T11 (Kosi), received inputs from sub-urban areas with be small scale industries and untreated sewage form multiple small towns located near banks. Further, Kosi was also seemed to affecting the concentration in Ganga (G10) (Section 4.3.2).

In bed sediment, ∑PAEs was significantly higher in middle stretch than lower stretch, similar to the PAHs distribution (refer to section 3.4) which was due to the higher urban influences with more population, residential areas, industries and roadside drains (Weizhen et al., 2020; Liu et al., 2020). The monsoon also effected the levels of PAEs in sediment just like in water by disturbing surface deposits resulting in reduced PAE contamination in the lower basin (Fan et al., 2020). Similar to PAHs, no significant correlation between PAEs and geochemical parameters (Table 4.4b) indicated direct contamination from the sources. In upper basin, alike water T2 was found with highest level of total PAEs concentration. Highest level of DEP and DnOP was found in middle stretch at T5, G2, G3 and G4 which were also detected with relatively higher levels of BcF (114.6-191.9 ng/g) suggesting pollution from local inputs such as rural and agricultural discharge at T5, G4; suburban and agricultural discharge from G2 and city discharge at G3 from Kanpur (He et al., 2015; Chakraborty et al., 2019; Sharma et al., 2019). The higher concentration of DnOP could also be derived from Chambal (TC) in Yamuna after confluence (T5) as suggested in section 4.3.2. Locations such as in Yamuna (T5), Chambal (TC) and Ganga (G2), fishing activities were also prominent which resulted in release of high molecular weight PAEs (Chakraborty et al., 2021). Regular bathing and washing activities locally in rural and suburban areas and surface run-off from openly burnt plastic waste could contribute to PAEs such as DEP and DMP from application of soaps and detergents (Khalid and Abdollah, 2021; Chakraborty et al., 2019). Concentrations at other locations in Ganga in lower basin were relatively low compared to upper and middle stretch. In lower basin, similar to water T10 was recorded with relatively higher ∑PAEs and Ganga (G11) with highest stretch wise total concentration which only represents DnOP probably coming from nearby Purbasthali water treatment and leaching from vehicle tyres and paints that usually occupied the region for ferry transport. In SPM, lower number of PAEs were discovered as also seen in case of PAHs due dissociation of phthalates associated with suspended particles as result of high river flow during monsoon especially downstream Kanpur. Evidences of influence of monsoon in other environmental matrices have been discussed earlier in this section.

In water bodies, most abundantly found PAHs with df above 50% were DMP and DEP (Table 4.2) which are low molecular weight PAEs with 3-6 carbon atoms in the backbone of their structure and are more water soluble than other PAEs due to lower log K_{ow} (Lee et al., 2019; Liu et al., 2020). These compounds are also more susceptible to degradation in environment causing larger spatial variations in river water than bed sediment together with monsoon and urban influences (Prasad et al., 2021; Chakraborty et al. 2021). Selvaraj et al., (2015) also detected DEP with 100% df in water samples in Kaveri River. While in case of bed sediment and SPM high molecular weight PAEs with 7-13 backbone carbons such as DnOP and BEHA were more frequently found with df above 70% (Table 4.2). Other PAEs were found in less than half of the samples. This is because longer alkyl and/or branch structure PAEs manage to adsorb strongly to the suspended particulate matter and sediment due to their hydrophobic property and higher log K_{ow} resulting in lower water solubility in aquatic environment (Chen et al., 2017; Liu et al., 2020).

4.5 Conclusion

Based on this study on PAEs in different environmental matrices, PAEs showed spatial variations which were found significant for DMP and DEP in water and bed sediment due to their higher degradation in natural environment, monsoonal dilution of river water and disturbances in sediment during high flow conditions. In river water, physicochemical parameters were showing some control over the distribution of DEP, DnOP and BEP by facilitating their degradation and/or adsorption on to sediment phase. Further in bed sediment, ∑PAEs were significantly higher in the middle than the lower basin due to variety of human activities and larger population releasing PAEs from urban> suburban and rural areas while in lower basin arrival of monsoon resulted in reduced levels of phthalates. With respect to tributaries, Kruskal-Wallis test for DnOP and ∑PAE was significant showing addition of phthalates to river water. Depending upon the differences in water solubility and log K_{ow}, low molecular weight PAEs such DEP and DMP were abundant in water while bed sediment and SPM were mostly enriched with high molecular weight species including DnOP and BEHA. Further, DnOP could also act a tracer for pollution in both water and bed sediment due it’s persistence in environment. Positive correlation of high molecular weight PAEs also suggested similar source from their application mainly as a plasticizer in variety of products. Further from the risk assessment, only DnOP and DEP were posing moderate threat to algae and crustacean in water and bed sediment respectively. Due to absence of toxicological studies in sediment, there is lack of data to ensure accurate assessment of risk posed to the flora and fauna of the Ganga River basin. Further research should be taken in this context to fill the knowledge gap to better understand the behavior and hazardous effect on the organisms of the soil ecosystem. Proper management of plastic waste and segregation of recyclable waste from other kinds could help in lowering the release of harmful plasticizer, such as DnOP in this study, from dumping and landfill sites nearby the water bodies. Uncontrolled disposal of waste by locals and especially tourists should be kept in check.

Chapter 5

Personal Care Products (PCPs)

5.1 Physical and chemical properties

PCPs is broad category which includes wide a variety product with different chemical properties. Over the centuries, due to their increase use in modern day life has led to release into the environment risking flora and fauna. New synthetic compounds used for personal care are still being added which needs investigation about their occurrence and health effects. Personal care compounds are commonly transmitted to the aqueous environment through wastewater treatment plants. Many of these compound cause endocrine disruptions aquatic organisms (Peinado et al., 2020). In this study, PCPs from diverse classes were analyzed which chemical and physical properties as described below (TSCA, ICSC, OSHA and HSDB)-:

(i) Benzophenone (BP): Benzophenone is a formaldehyde with both hydrogen atoms substituted by phenyl groups and appears as white solid with a flowery odor. It is used as UV filter in sunscreen, a food additive and in auto products. Orthorhombic prisms are obtained from alcohol (alpha) and monoclinic prisms (beta). The boiling and melting points are 305.89°C and 47.8°C. The flash point is estimated to be greater than 132.2°C. It is insoluble (0.137 mg/mL at 25 °C) in water and glycerol, soluble in benzene and methanol and very soluble in acetone, ethanol, acetic acid, carbon disulfide. The relative density of the compound is (water =

1): 1.1 with log K_{ow}= 3.18. It decomposes at temperature >320 °C and emits acrid and irritating fumes on heating.

(ii) Parabens: Two parabens methyl and ethyl parabens (MP and EP, respectively) have been analyzed. Methyl paraben is a 4-hydroxybenzoate ester derived from the condensation between carboxy group of 4-hydroxybenzoic acid and methanol. It is the most frequently used antimicrobial preservative in a number of products belonging to cosmetics, food industries and is a neuroprotective and an antifungal agent. It is also found in various fruits, especially in blueberries. Methylparaben is used in allergenic testing. It has small colorless crystals obtained from dilute alcohol with no significant odor and has slight burning taste. The boiling and melting points are 270.5°C and 131.0 °C, respectively. It is slightly soluble in water ($2.50x10^3$ mg/L at 25 °C), soluble in trifluoroacetic acid, and very soluble in ethanol, ether, acetone. The log K_{ow} is 1.96 and are stable against hydrolysis during autoclaving & resist saponification.

Ethylparaben obtained employing condensation of the carboxy group of 4-hydroxybenzoic acid with ethanol and found similar uses and appearance as methyl paraben. The compound boil and melts at 297.5 °C and 117.0 °C, respectively. Solubility in water is $8.85x10^2$ mg/L at 25 °C and log K_{ow} = 2.47.

(iii) Triclosan (TCS): Triclosan is an aromatic ether derived by replacing phenol at C-5 by a chloro group and at C-2 by a 2,4-dichlorophenoxy group responsible for antimicrobial activities against bacteria and fungus. It is used in variety of personal care products such as toothpastes, household products, soaps, shampoos, detergents, deodorants, toys, and surgical solutions. It appears as white to off-white crystalline powder with slightly aromatic odor. The boiling and melting points stand at 120 °C and 55-57 °C, respectively. In water solubility is 10 mg/L at 20 °C making it slightly soluble in water and readily soluble in alkaline solutions and many organic solvents; soluble in methanol, alcohol, acetone. The log K_{ow} is 4.76. It is stable under storage condition and decompose at 280 to 290 °C.

Benzophenone Methyl paraben

Ethyl paraben Triclosan

2D chemical structures of PCPs

5.2 Literature Review

In the modern scenario, personal care products typically include in fragrances, sun-screen agents, lipsticks, shampoos, hair colors and cosmetic products (Boxall et al., 2012) which are being used extensively all over the world. Research on these consumer chemicals have accelerated in the past years showing major concern over their presence in natural environment. From the review, maximum studies are related to surface water. In North America, countries like Canada and United States have reported the presence of triclosan (an antimicrobial agent) in water and sediment in various rivers (Lalonde et al., 2019; Lyndall et al., 2016). In Canadian surface waters, the concentration and df (6 to 874 ng/L, df=65%) was higher than the Minnesota waters (30-150 ng/L, 16.4%). Further, sediment concentration of TCS in Minnesota ranged from 4-284 ng/g with low df of 9.5% (Lyndall et al., 2016). However, in Southern America in Brazil, higher concentration of TCS (50.3–788.8 ng/L) were reported in water along with estimations of parabens (MP = < LQ-265.0 and EP=N.D-144.6 ng/L) (Reichert et al., 2020). The df for TCS and MP was 100% while EP were found in 93.2% of the samples. In case of Europe and Asia (especially China), larger number of recent studies were undertaken related to parabens, triclosan and benzophenone. In Poland, among five investigated paraben species MP was found most frequently (Df=100%) with highest concentration in river water 1598 ng/L, while EP ranged from 0.8-27.5 ng/L (Czarczynska-Goslinska et al., 2017). Mandaric et al. (2017) found EP only in winter season with df 67% and maximum concentration as 171 ng/L in Adige River basin, Italy which was highest among reviewed studies from Europe (Table 5.1). MP and EP were also detected in river waters of U.K with mean concentration of 10.8 ± 2.5 and 1.8 ± 0.3, respectively. Most of the recent studies in Europe were focused on the benzophenone and its derivatives which is commonly used as a UV-filter in cosmetic products (Serra-Roig et al., 2016; Mandaric et al., 2017; Díaz-Cruz et al., 2019;

Chiriac et al., 2021; Petrie et al., 2016). Maximum concentration of BP3 (5720 ng/L) in water was reported from Adige River basin, Italy in summers while minimum concentration estimated was 10.1 ng/L in Besòs River, Spain (Mandaric et al., 2017; Serra-Roig et al., 2016). However, Mandaric et al. (2017) found very low concentrations of BP3 (N.D-14.3) in winter. Higher concentration (54.5− 5607 ng/L) of BP3 was also reported in sea water from Black Sea coast, Romanina with 100% df (Chiriac et al., 2021). Chiriac et al. (2021) found BP3 in sediment too with concentration ranging from (16.4− 975 ng/g) with high df=92.8%. The benzophenone derivatives (BP3 and BP1) were also reported in sediment (N.D-39.5 and 30.5–185.1 ng/g, respectively) from two other locations such as Adige River basin, Italy and EVROTAS river Greece but at lower concentrations than the Black Sea coast sediments (Mandaric et al., 2017; Díaz-Cruz et al., 2019). However, BP1 was found with much higher df (=100%) than the BP3 (=17%) in these studies (Table 5.1). TCS was reported from UK waters at a mean concentration of 101 ng/g which comparable to Minnesota in U.S (Petrie et al.2016; Lyndall et al., 2016). In China, Pearl River was found with all four chemical species as discussed above in water, SPM and sediment (Hu et al., 2021; Zhao et al., 2019; Chen et al., 2021). Concentrations of BP3, EP, MP and TCS are shown in Table 5.1 in different environmental matrices. The df for all these compounds were 100% except for BP3 which reported with df>95%. However, concentrations were much lower than those detected from European countries except for MP whose maximum concentration (220 ng/L) in water were comparable to the above discussed studies. Further, Pearl River was detected with lowest concentrations for BP3 and TCS. Only Zhao et al. (2019) and Chen et al., 2021 reported EP MP and TCS in SPM, respectively. Further, TCS was detected from sediment and water with higher df (75-100%) from two rivers in Taiwan i.e., Jiaosu River and Dian-Bao River. The concentration varied from 3 – 68 and 2.7 – 51 ng/L in water while <LOQ–

13 and <LOQ–11 in sediment, respectively. Similarly, Feng et al. (2019) and Zhao et al. (2021) discovered EP and MP from water and sediment from two rivers in China at 100% but comparatively at lower concentrations reported by the former (reported lowest EP value) (Table 5.1). Highest concentration for MP and EP were reported from (854 ng/g and 92.8 ng/L) SPM and water. From Beijing River system, China too, relatively high concentrations for EP and MP were also observed in water (0.54-294 and 6.5-920 ng/L; df= 74.4% and 100%, respectively) (Li et al., 2016a). While, Sun et al., (2016) recorded highest concentration of BP3 (BLD-96.5 ng/L) and TCS (BLD-532 ng/L) in river water from Jiulong River estuary, China. From Africa, BP3, EP and MP were identified from river water in Gauteng Province, South Africa (Archer et al., 2017). The study recorded highest concentration for MP as 26295 ng/g among the studies reviewed and BP3 with concentration (5471 ng/g) while EP was not detected. Another study from Africa was from Egypt which identified MP from drinking and source water (Radwan et al., 2020). The concentration and df varied from < MDL−1780 and 12.8-17.3 ng/L. From the above review, overall lower concentrations were observed from Asia than other continents, however, the df were higher.

In India, parabens and TCS were more frequently studied in the recent years. Ramaswamy et al. (2011) inspected the occurrence of PCPs in rivers from South India. He identified EP, MP and TCS from water and sediment from three rivers namely Kaveri River, Vellar River and Tamiraparani River. The maximum concentration of EP (142, 147 and 58.7 ng/L, respectively) were more or less comparable to Southern Brazil and Italy (Reichert et al., 2020; Mandaric et al., 2017) while MP concentrations (22.8, 14.8 and 3.43 ng/L, respectively) were similar to rivers in China (Zhao et al., 2019; Feng et al., 2019). TCS median concentration reported in these Southern River were 40.7, 8.95 and 142 ng/L in water while mean values in sediment were 16.8, 21 and 16.6, respectively which were also comparable to other studies all over the world. Other studies in

Southern India came from Arkavathi River basin and Coastal area of Ernakulam, Kerala (Gopal et al., 2021; Nejumal et al., 2021). BP and TCS were detected in Arkavathi River water at concentration ranging from 3.43–46.1 and 297–1761 ng/L while EP remained undetected. The concentration of BP (2.3-33.2 ng/L) in Coastal area of Ernakulam were comparable to Arkavathi river. However, the df was higher (100%) than the river (14.3-14.8). The highest concentration of BP was reported in Nagpur, 23–156x10^3, that far exceeds the maximum concentration reported in Adige River basin, Italy (Archana et al., 2017; Mandaric et al., 2017). TCS was also detected in sediments for Nag River, Nagpur ranging from 2–84 ng/g which was higher than rivers in Taiwan but lower than Minnesota. Five recent studied detected these particular PCPs in river water and sediments in Ganga Basin. The most recent is given by Rendedula et al. (2020) in Prayagraj and Varanasi, Uttar Pradesh. The concentrations of EP, MP and TCS (1.59, 0.95-3 and 2.59-7.58 ng/L) were low and were similar to those reported from Pearl River (Zhao et al., 2019; Chen et al., 2020). Df of MP and TCS were above 50% (Table). Chakraborty et al. (2019) reported higher concentration of these species in sediment from river Hooghly (EP= 32–346; MP= 14–423; TCS=1.5- 84 ng/g) than the sediment from China and Taiwan (Feng et al., 2019; Yang et al., 2015) and could be compared to the value reported in the surface sediment from rivers in southern India (Ramaswamy et al., 2011). River Gomti was reported with highest concentration of TCS in water (1100-9650 ng/L) all over the world while sediment values (5.11–50.36 ng/g) were comparable to river Hooghly concentrations (Nag et al., 2018; Chakraborty et al., 2019). The upper Ganga basin also reported TCS with medium concentrations (ND – 139 ng/L) in water and 90% df. However, Sharma et al. (2019) reported lower concentrations and df, <MDL-5.4 ng/L and 21.4%, varying along the entire basin. Most the studies reviewed also reported risk posed by these PCPs to the aquatic organisms especially TCS across the world by calculation RQ or HQ (Hazard quotient)

(Mizukawa et al., 2018; Reichert et al., 2020; Lalonde et al., 2019; Lyndall et al., 2016). Moderate to high risk by derivative of BPs were reported in studies by Díaz-Cruz et al. (2019) and Chiriac et al. (2021) while risk from MP by Radwan et al. (2020). Similar to other rivers in world, in India too, ecological risk from TCS was frequently reported than others (Sharma et al., 2019; Gopal et al., 2021; Ramaswamy et al., 2011; Nag et al., 2018; Singh and Suthar, 2020).

Locations	Matrices	MP	EP	BP & derivatives	TCS	Reference
Adige river basin, Italy	Sediment			N.D-39.5 (17)		Mandaric et al., 2017
	Water		N.D-171 (67)	N.D-5720 (33-100)		
Beijing River system, China	Water	6.5-920 (100)	0.54-294 (74.4)			Li et al., 2016a
Besòs River, Spain		<LOQ		10.1-52.2		Serra-Roig et al., 2016
Black sea coast, Romania	Seawater			54.5− 5607 (100)		Chiriac et al., 2021
	Sediment			16.4− 975 (92.8)		
Canada	Water				6 -874 (0-65)	Lalonde et al., 2019
Dian-Bao River, Taiwan	Water				2.7 - 51 (75-100)	Yang et al., 2015
	Sediment				<LOQ–11 (86)	
Egypt	Drinking and source Water	< MDL−1780 (12.8-17.3)				Radwan et al., 2021
EVROTAS river Greece	Water			0.2 (LOD) to 2031 (88)		Díaz-Cruz et al., 2019
	Sediment			30.5–185.1 (100)		
Gauteng Province, South Africa	Water	26295	N.D	5471		Archer et al., 2017
Greater Poland	Water	1.7-1598 (100)	0.8-27.6			Czarczynska-Goslinska et al., 2017
Huai River, China	Water	11.0–154 (100)	0.23–0.69 (100)			Feng et al., 2019
	Sediment	6.97–18.8 (100)	1.02–2.14 (100)			

Jiaosu River, Taiwan	Water				3 - 68 (100)	Yang et al., 2015
	Sediment				<LOQ–13 (86)	
Jiulong River estuary, China	Water	1.68-68.8(100)		BLD-532 (18-100)	BLD-96.5 (9.1-100)	Sun et al., 2016
Minnesota	Water				30-150 (16.4)	Lyndall et al., 2016
	Sediment				4-284 (9.5)	
Pearl River Basin	Water			0.59–88.6		Hu et al., 2021
	Sediment			4.08–13.3 (>95)		
Pearl river, China	Water	0.25-4.87 (100)	0.56-1.25 (100)			Zhao et al., 2019
	SPM	68.9-220 (100)	25.4-60.6 (100)			
Pearl river, China	Water				1.47–5.62 (100)	Chen et al., 2020
	SPM				0.69–17.5 (100)	
Tibagi River, southern Brazil	Water	< LQ-265.0 (100)	N.D-144.6 (93.2)		50.3–788.8 (100)	Reichert et al., 2020
United Kingdom	Water	10.8 ± 2.5	1.8 ± 0.3	101 ± 9.2	65.7 ± 11.3	Petrie et al., 2016
Yangtze River, China	Water	0.23-42.1 (100)	N.D-5.66 (100)	N.D-45.1 (95.8)	N.D-65.6 (98.3)	Ma et al., 2018
Yellow River, China	Water	1.92-32.6 (100)	0.15–1.11 (88)			Feng et al., 2019
	Sediment	7.07-27.6 (100)	0.61–2.43 (100)			
India						

Arkavathi river basin, Southern India	Water		N.D	3.43–46.1(14.3-14.8)	297–1761 (11.4)	Gopal et al., 2021
Coastal area of Ernakulam, Kerala	Seawater			2.3-33.2(100)		Nejumal et al., 2021
Kaveri River	Water	N.D to 22.8	5.93 to 142		40.7	Ramaswamy et al., 2011
	Sediment				16.8 ± 22	
Tamiraparani River	Water	N.D to 3.43	2.47 to 58.7		142	
	Sediment				16.6 ± 10	
Vellar River	Water	N.D to 14.8	88.9 to 147		8.95	
	Sediment				21 ± 10.5	
Nagpur	Water			23–156*10^3		Archana et al., 2017
River Nag, Nagpur	Sediment				2–84	Kachhawaha et al., 2021
Ganga Basin	Water				<MDL-5.4 (21.4)	Sharma et al., 2019
Ganga in Rishikesh-Haridwar	Water				N.D – 139 (90)	Singh and Suthar, 2020
Ganga lower basin	Sediment	14–423	32–346		1.5- 84	Chakraborty et al., 2019
Gomti	Water				1100-9650	Nag et al., 2018
	Sediment				5.11–50.36	
River Ganga, UP	Water	0.95-3 (66.7)	1.59 (11.1)		2.59-7.58 (55.6)	Rendedula et al., 2020

Table 5.1. Recent studies detecting PCPs concentration (d.f) in various environmental matrices across the world.

5.3 Results

5.3.1 Distribution of PCPs in water, bed sediment and SPM

Water

In river water, all PCPs were detected (Fig. 5.1) that were analyzed. The total concentration of PCPs (∑PCPs) varied from 0-320.9 ng/L while mean concentrations ranged from 7.73- 103.1 ng/L. The maximum mean concentration was observed for MP followed by, TCS, EP and BP (Table 5.2). However, df frequency followed the trend as EP (92%)>MP (88%)>TCS (52%)>BP (36%). The maximum and mean concentrations of TCS and BP were found below Federal Environmental Quality Guidelines and Long-term water quality criteria by Canadian Environmental Protection Act, 1999 and Liu et al., 2021, respectively. Guidelines were not available for parabens due to lack of evidence of accumulation and toxicological studies in animals (Tade et al., 2018).

With respect to each stretch, average ∑PCPs in upper stretch was 90.17 ng/L. Only parabens (MP and EP) were detected. Highest total sum of the PCPs for this stretch was observed in Ganga downstream Haridwar (G1) (Fig. 5.4). No compound was detected in river waters of tributary Song (T1). In the middle stretch, all four organic compounds were identified with highest mean concentration measured for MP followed by TCS and EP. Further, the average sum of PCPs was approximately three times higher than the upper stretch (∑PCPs=245.5 ng/L) with MP and EP showing 100% df. However, BP was only identified from two locations (T13 and T4). The highest ∑PCPs (=319.8 ng/L) and number of compounds (=4) were discovered from Gomti (T13) followed by Ganga in Prayagraj (G5=285 ng/L). Further, Gomti also observed highest concentration of EP and BP (102.5 and 13.6 ng/L) in the basin. Many other locations were also found with higher ∑PCPs than its mean (Fig. 5.1). In the lower stretch, average sum of PCPs was comparable to middle stretch. Also, similar trend was followed by the mean concentrations of individual PCP as middle basin. However, the df of MP and EP was 92.3% (Table 5.3) while 53.8% for TCS and BP. Maximum number (all four of them) of PCPs were identified from Ganga (G6), Gandak samples (T9 and T10) and Ganga downstream Patna (G8). These locations also observed relatively higher sum of PCPs (276.2- 303.4 ng/L). Other tributaries of Ganga such as Kosi (T11) and Mahananda (T12) were also found with higher ∑PCPs (Fig. 5.4) with latter showing highest concentration of TCS (=103.6 ng/L) for the basin. The concentrations of BP, MP, EP and TCS were comparable to other mentioned studies in section 5.2 (Gopal et al., 2021; Ramaswamy et al., 2011; Chakraborty et al., 2019; Kachhawaha et al., 2021).

	River water (ng/L)				Bed Sediment (ng/g)			SPM (ng/g)			SCB[c]
	Min.-Max.	Mean± S.D	D.F	WQG	Min.-Max.	Mean± S.D	D.F	Min.-Max.	Mean± S.D	D.F	
MP	91.2-116.9	103.1±6.7	88		8.6-70.2	26.9±21.2	64	17.7-44.9	35.6±8.6	100	
EP	62.2-102.5	79.5±8.4	92		7.9-28.8	17.97±6.6	34.62	19.7-24.96	22.2±1.8	100	
BP	2.1-13.6	7.7±2.9	36	5*10^{5}[d]	0-61.98	14.2±16.7	65.385	N.D	N.D	N.D	9300[c]
TCS	90.1-103.6	93.9±4.3	52	380[a], 250[b1]	13.2-15.3	14.2±0.65	42.31	N.D	N.D	N.D	130[b2], 3260[b3]
∑PCPs	0-320	216±83.9			14.4-102.4	43.11±23.3		37.4-68.6	58.4±10.1		

[1]Federal Environmental Quality Guidelines (CC, 2017), [b1] Long term water quality criteria, [b2]sediment quality criteria (SQC) low, [b3]sediment quality criteria (SQC) high, Xinyu et al. (2021), [c] Soil—remediation level, USEPA (2007), [d]AIHA, 2009

Table 5.2. Descriptive statistics for PCPs in river water, bed sediment and SPM.

	Water (µg/L)			**Bed sediment (mg/kg)**		
	U.S (n=3)	**M.S (n=9)**	**L.S (n=13)**	**U.S (n=4)**	**M.S (n=9)**	**L.S (n=13)**
∑PCPs	90.2	245.5	223.6	27.4	31	42.2
MP	104.5(33.3)	102.3(100)	103.5(92.3)	26.9(50)	13.3(22.2)	29.7(76.9)
EP	83(66.7)	79.6(100)	78.9(92.3)	24.8(25)	16.7(22.2)	17.3(46.1)
BP	N.D	7.8(22.2)	7.7(53.8)	10.4(75)	25.2(77.8)	4.9(53.8)
TCS	N.D	92.8(66.7)	94.8(53.8)	N.D	14(33.3)	14.2(61.5)

Table 5.3. Stretch-wise mean concentration of individual PCPs and ∑PCPs with detection frequency given in parentheses.

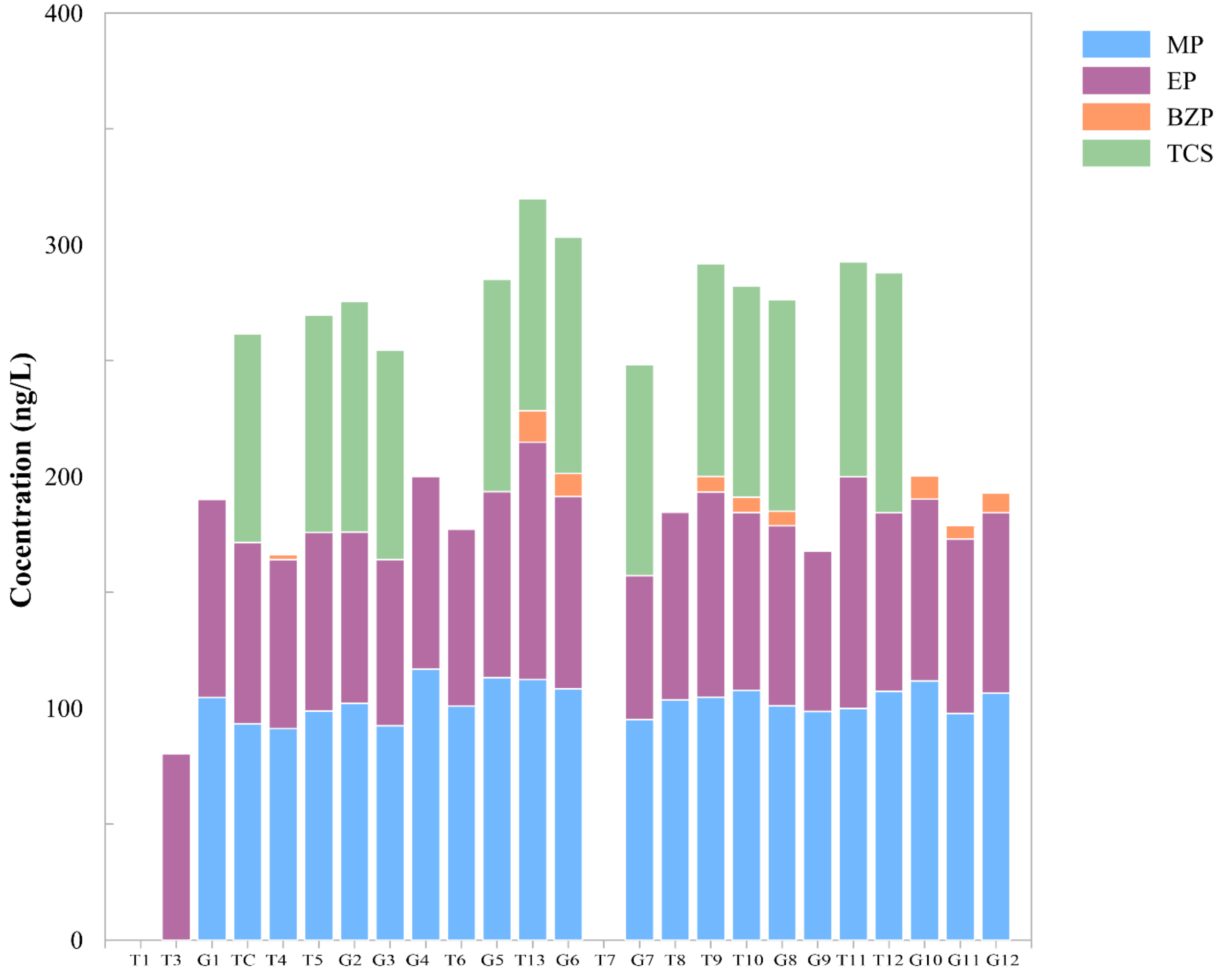


Fig. 5.1. PCPs distribution in river water (x axis indicate locations).

Bed sediment

In bed sediment, all four analyzed PCPs were detected (Fig. 5.2). The average concentration varied from 14.2-26.9 ng/g and the order was followed as MP>EP>TSC=BP. Based on their occurrence of frequency they followed the order as BP (65.4%)>MP (64%)>TCS (42%)>EP (35%). The sum of PCPs ranged between 7.2- 88.5 ng/g. Similar to water, average and maximum value for BP and TSC were below sediment quality criteria (SQC) low, Liu et al. (2021) and soil—remediation level, USEPA (2007), respectively. In the upper stretch, three compounds were detected with BP being most abundant EC followed MP and EP (Table 5.2). However, average concentration was maximum for MP followed by EP and BP in upper basin. The average ∑PCPs was 27.4 ng/g. T1 and T2 were observed with two compounds (Fig. 5.4) and relatively higher ∑PCPs was measured at T2. In the middle stretch, all four compounds were detected similar to water, although higher df was observed for BP (=78%), rest were found in less than 50% of the samples (Table 5.3). The highest ∑PCPs for this stretch (42.2 and 61.98 ng/g) was noticed in Ganga in Prayagraj (G5) and Yamuna (T5) respectively representing only BP as others remained undetected. T5 also showed highest concentration for BP. Maximum number (=3, except for BP) of PCPs were discovered from Gomti (T13) with ∑PCPs exceeding stretch-wise average value. Compared to upper and middle basin, lower stretch, showed maximum mean value for ∑PCPs (=42.2 ng/g) and unlike the other stretches, MP was found with maximum df (=77%) followed by TCS, BP and EP (Table 5.3). Relatively higher total concentration of PCPs (=84.5 ng/g) and methyl and ethyl parabens (63.32 and 21.03 ng/g respectively) were detected from Mahananda (T12). Other locations with higher ∑PCPs were found in Ganga River such as G7 and G9 (57.2 and 63.82 ng/g, respectively) (Fig. 5.4). Similar to water, G8 found all four compound (Fig. 5.2) but relatively at lower concentration with respect to bed sediment values at other locations (except

TCS). Hooghly river in West Bengal (G11) observed highest concentration for TSC (15.3 ng/g) while G10 observed maximum total PCP concentration (=88.49 ng/g) and MP (=70.24 ng/g) in the basin. Densely populated town Bansberia also recorded high ∑PCP (MP+ EP+ TSC=71.6 ng/g).

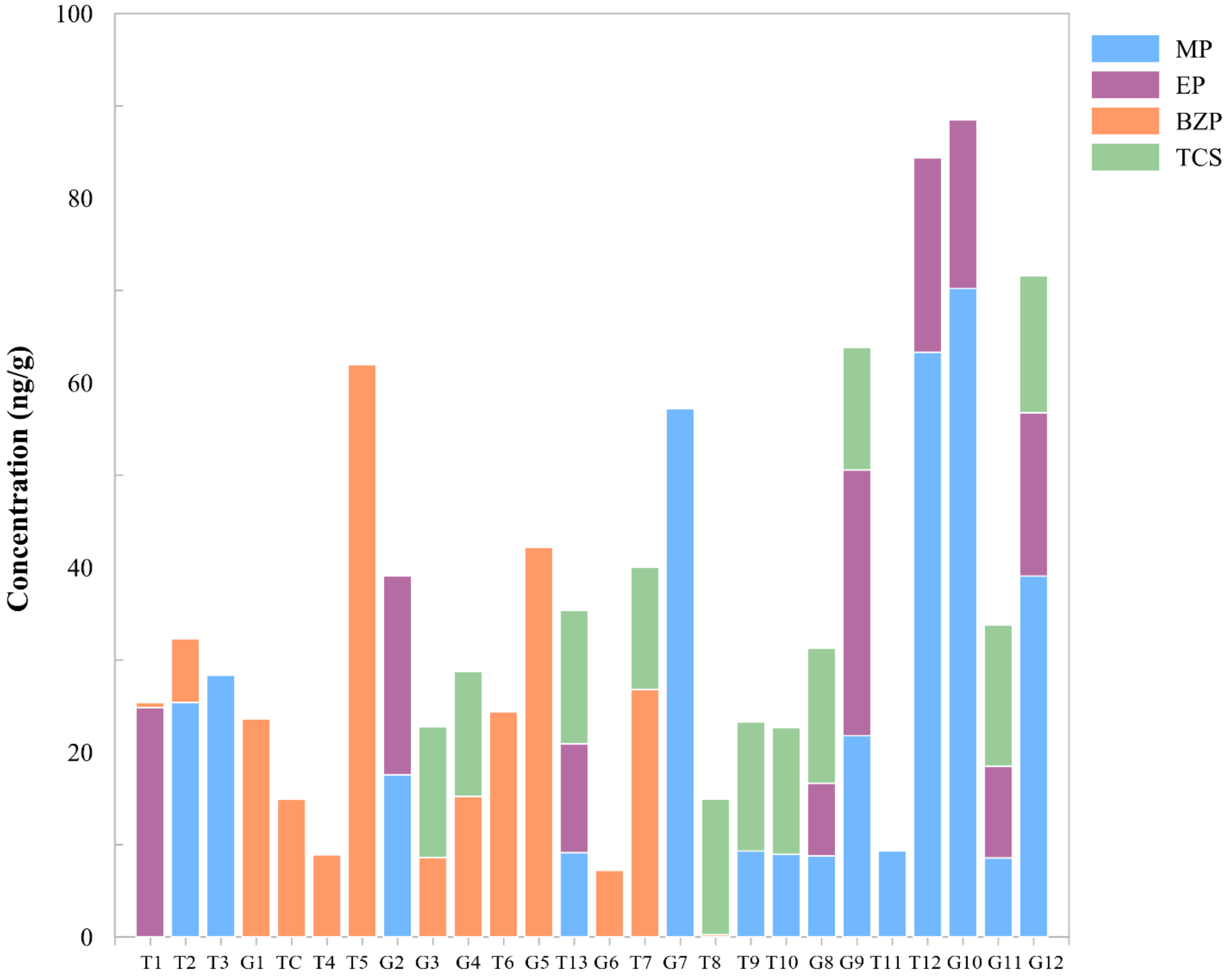


Fig. 5.2. PCPs distribution in bed sediment (x axis indicate locations).

In SPM

In SPM, only MP and EP were detected with 100% df (Fig. 5.3). Based on average concentration maximum was observed for MP (29.7 ng/g) than EP (17.3 ng/g). The sum of PCPs varied from 37.4-68.6 ng/g with highest being observed at G9 which also observed maximum concentration for MP (Table 5.2). Similar to bed sediment, relatively higher concentrations were reported from T3 and G10 (62.95 and 67.3 ng/g, respectively). EP concentrations were not much variating compared to MP (Fig. 5.3).

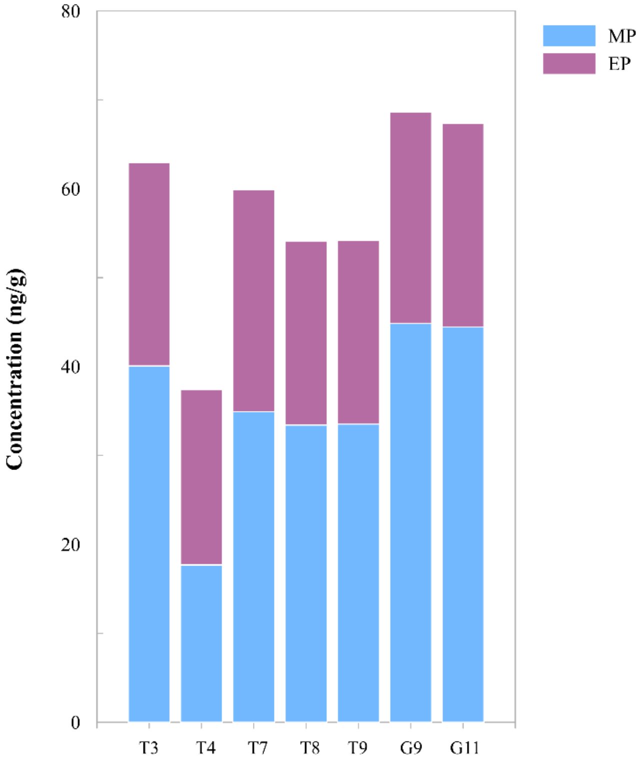


Fig. 5.3. PCPs distribution in SPM (x axis indicate locations)

5.3.2 Influence of tributaries

In water, Chambal (TC) seemed to affect the concentration of parabens and TCS in Yamuna by likely adding to the concentration thereby increasing ∑PCPs levels after confluence

(T5) (Fig. 5.4). Similarly, in sediment the sum of PCPs was increasing in Yamuna (T5 observed higher value than T4) after Chambal joins. However, the concentration in Yamuna (T5) were higher than the Chambal in both bed sediment and water (TC) suggesting additional pollution sources. Further downstream, Yamuna (T6) was found elevating the levels of BP in Ganga bed sediment (G5) (Fig. 5.2 and 5.4) while the concentration of MP and EP were slightly decreasing in Ganga water even after receiving wastewater discharge from Prayagraj. This suggested dilution of MP and EP by Yamuna in Ganga River water at Sangam, Prayagraj. However, the overall concentration of PCP was increasing in each matrix due to city wastewater effluents (Fig. 5.4). In lower basin, concentrations of PCPs were either not detected or remained below detection limit in Ghaghara due to increased volume of water during monsoon which was dominating the effects from local anthropogenic sources (Weizhen et al., 2020). Thus, further diluting the concentration in Ganga River water (G7) after confluence. Similarly in sediment the concentrations of BP were reduced to ~100 times in Ganga due its non- detection in Ghaghara. Due to higher concentrations in Kosi and Mahananda in water and bed sediment, Ganga levels of ∑PCPs and MP (also for EP in water) were elevated after meeting these tributaries.

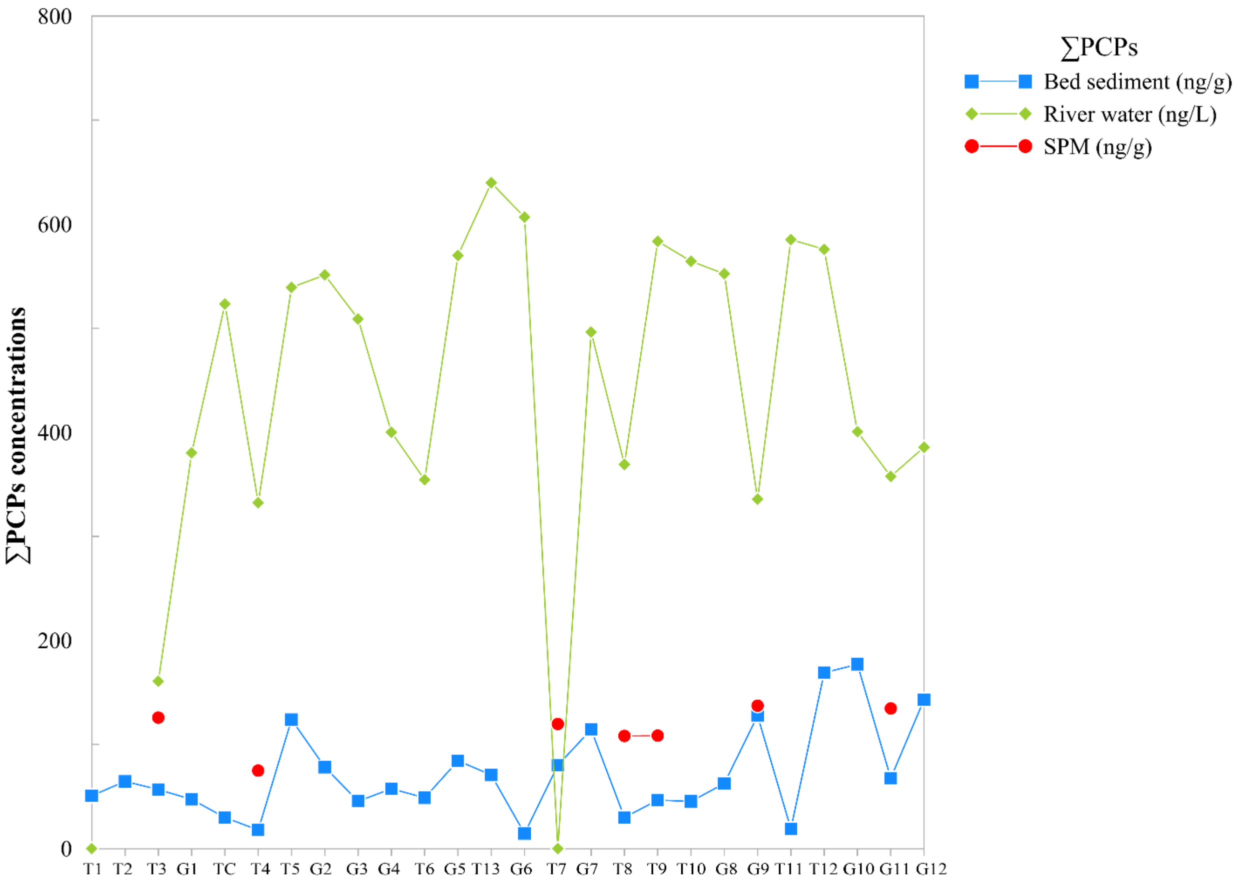


Fig. 5.4. Distribution of ∑PCPs in three environmental matrices along the Ganga River Basin

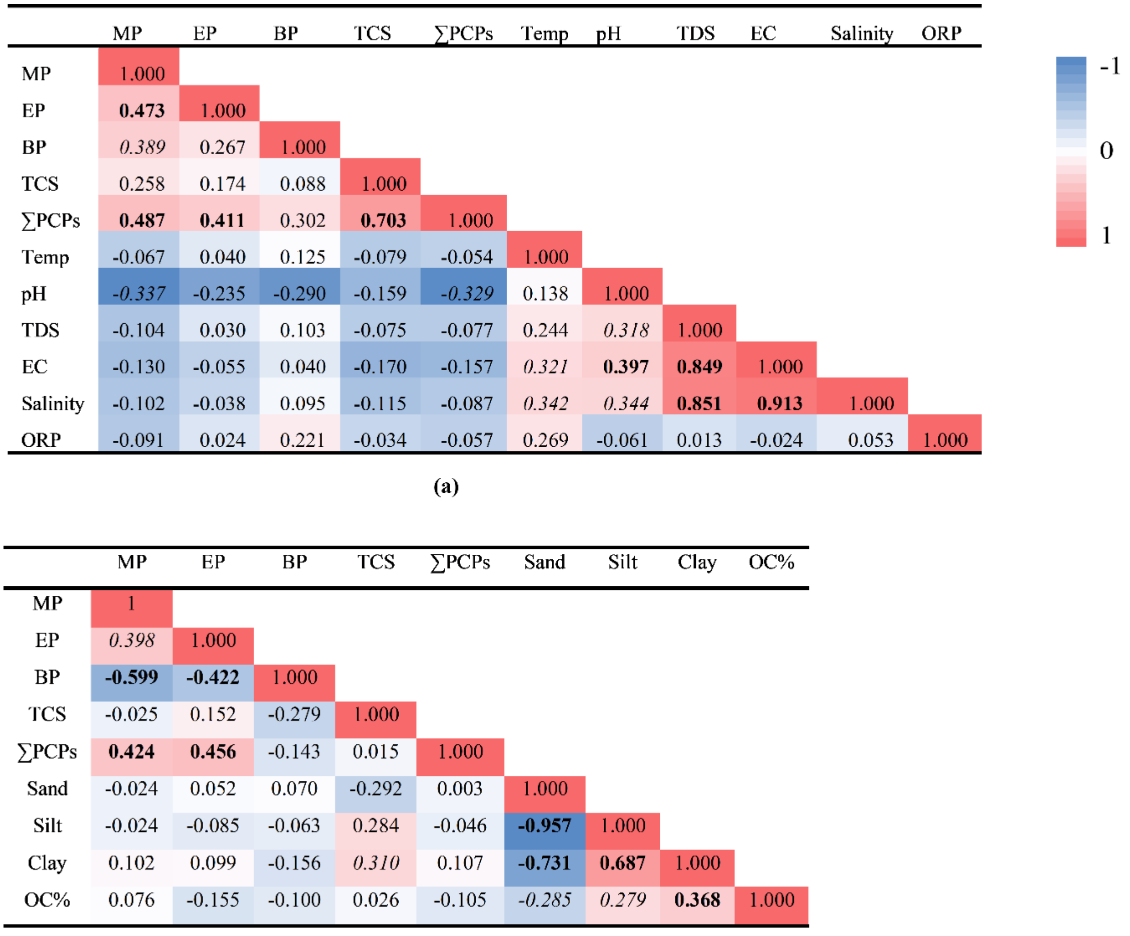
5.3.3 Statistical Analysis

The statistical tests were performed to understand the distribution, influence of tributaries and effect of physicochemical parameters of water, grain size and organic carbon on distribution of PCPs in water and bed sediment.

Correlation

With respect to water, MP showed positive correlation with EP (τ=0.47, p=0.01) and BP (p=0.05) suggesting their similar sources. Many sun protecting serums and suns-creams use parabens as antimicrobial agent while BP as UV-filters (Imamović et al., 2012). Both MP and EP were moderately correlated with ∑PCP (p=0.01) while TCS was strongly correlated (**τ**=0.703, p=0.01) with ∑PCP indicating dominant contribution to the sum of PCPs by these species especially TCS (Fig. 5.5a). Further, strong correlation suggested TCS might act as a pollution marker, because of its high log K_{ow} value and persistence (Sun et al., 2016; Higgins et al., 2011). Thus, presence of TCS could imply the burden of anthropogenic activities resulting in huge inputs especially from wastewater treatment plants (WWTPs). Further, only MP showed significant negative correlation with water pH indicating its distribution is affected by water pH (Tade et al., 2018; Prasad, 2021).

In bed sediment, similar to water MP and EP were positively correlated with each other (p=0.05) and ∑PCP (p=0.01). However, both were negatively correlated to TCS (τ=0.6 and 0.4, p=0.01) indicating their different sources and behavior in sediment phase (Fig. 5.5b). This could also be explained by significant positive correlation of TCS with clay (p=0.05) showing its distribution and behavior was influenced by the finer particles resulting in its accumulation in bed sediment.



	MP	EP	BP	TCS	∑PCPs	Temp	pH	TDS	EC	Salinity	ORP
MP	1.000										
EP	**0.473**	1.000									
BP	*0.389*	0.267	1.000								
TCS	0.258	0.174	0.088	1.000							
∑PCPs	**0.487**	**0.411**	0.302	**0.703**	1.000						
Temp	-0.067	0.040	0.125	-0.079	-0.054	1.000					
pH	*-0.337*	-0.235	-0.290	-0.159	*-0.329*	0.138	1.000				
TDS	-0.104	0.030	0.103	-0.075	-0.077	0.244	*0.318*	1.000			
EC	-0.130	-0.055	0.040	-0.170	-0.157	*0.321*	**0.397**	**0.849**	1.000		
Salinity	-0.102	-0.038	0.095	-0.115	-0.087	*0.342*	*0.344*	**0.851**	**0.913**	1.000	
ORP	-0.091	0.024	0.221	-0.034	-0.057	0.269	-0.061	0.013	-0.024	0.053	1.000

(a)

	MP	EP	BP	TCS	∑PCPs	Sand	Silt	Clay	OC%
MP	1								
EP	*0.398*	1.000							
BP	**-0.599**	**-0.422**	1.000						
TCS	-0.025	0.152	-0.279	1.000					
∑PCPs	**0.424**	**0.456**	-0.143	0.015	1.000				
Sand	-0.024	0.052	0.070	-0.292	0.003	1.000			
Silt	-0.024	-0.085	-0.063	0.284	-0.046	**-0.957**	1.000		
Clay	0.102	0.099	-0.156	*0.310*	0.107	**-0.731**	**0.687**	1.000	
OC%	0.076	-0.155	-0.100	0.026	-0.105	*-0.285*	*0.279*	**0.368**	1.000

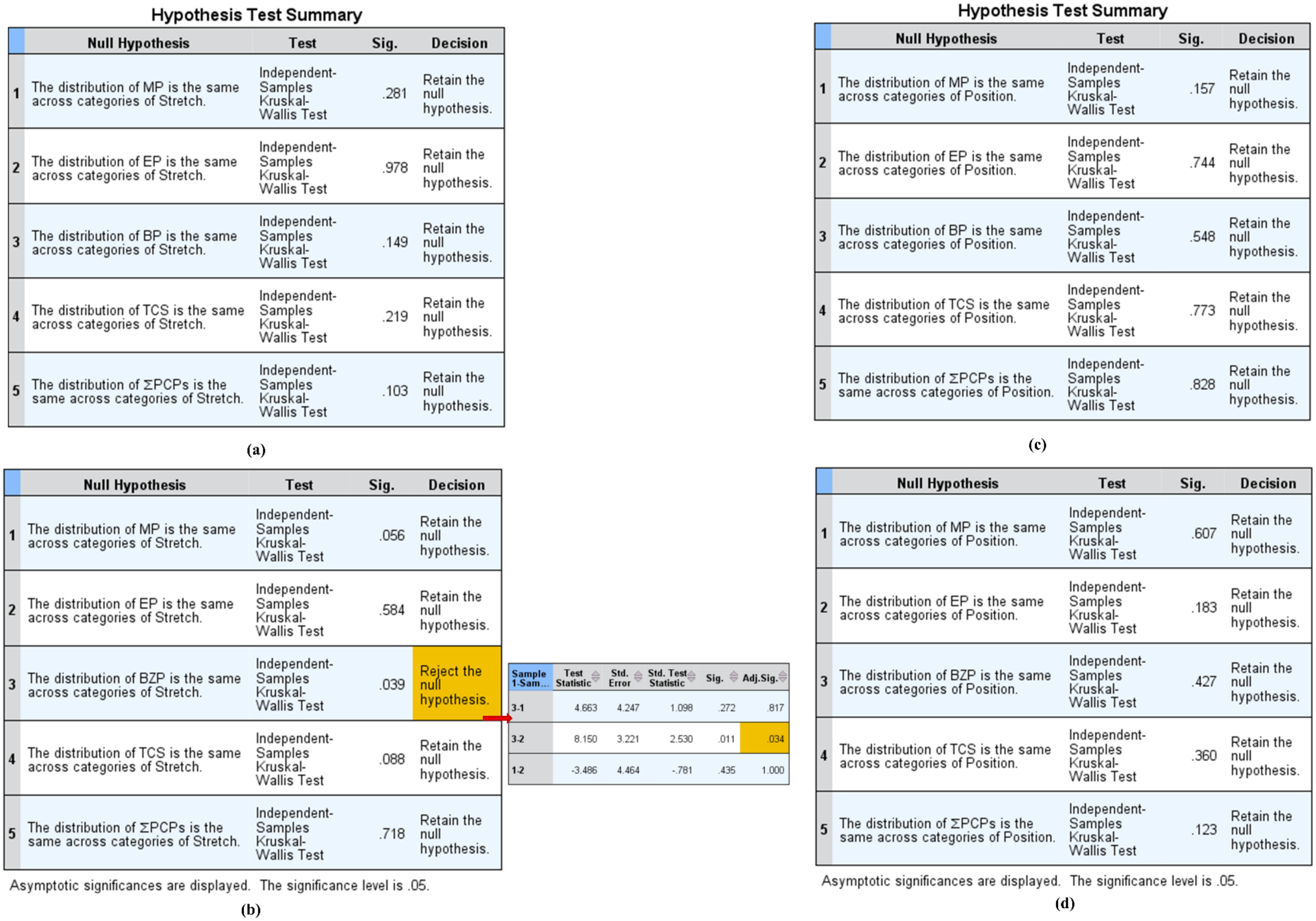
(b)

Fig. 5.5. Kendall's Tau correlation analysis for PCPs in (a) river water (b) bed sediment.

Kruskal-Wallis test

The non-parametric equivalent ANOVA called Kruskal-Wallis was employed to recognize the significant difference between the concentrations of different PCPs in three stretches. A fixed factor as "stretch" with three groups were considered, i.e., upper, middle, and lower designated by 1, 2 and 3, respectively. Fig. 5.6a showed no significant differences between the concentrations of PCPs among three stretches in water. Least variations were observed in EP with higher p value while lowest p value was observed for ∑PCPs. However, in bed sediment (Fig. 5.6b), significant variations were observed for BP as higher mean rank was observed in middle basin than lower stretch suggesting urban influence from middle basin (Chen et al., 2020; Rendedula et al. 2020). This is consistent with distribution of BP which observed highest df and mean concentration in middle basin (section 5.3.1). Lower p values for MP and TCS similar to river water were also observed in bed sediment (p=0.056 and 0.088) with higher mean rank in lower basin.

With respect to tributaries effect in Ganga, no significant differences in PCPs concentrations were found between Ganga and its tributaries for both water and bed sediment (Fig. 5.6c and d). Lowest p values were observed for MP (p=0.157) (Fig. 5.6c) indicating MP might be contributed by tributaries in river water of Ganga as also suggested in section 5.3.2.



Hypothesis Test Summary

	Null Hypothesis	Test	Sig.	Decision
1	The distribution of MP is the same across categories of Stretch.	Independent-Samples Kruskal-Wallis Test	.281	Retain the null hypothesis.
2	The distribution of EP is the same across categories of Stretch.	Independent-Samples Kruskal-Wallis Test	.978	Retain the null hypothesis.
3	The distribution of BP is the same across categories of Stretch.	Independent-Samples Kruskal-Wallis Test	.149	Retain the null hypothesis.
4	The distribution of TCS is the same across categories of Stretch.	Independent-Samples Kruskal-Wallis Test	.219	Retain the null hypothesis.
5	The distribution of ΣPCPs is the same across categories of Stretch.	Independent-Samples Kruskal-Wallis Test	.103	Retain the null hypothesis.

(a)

Hypothesis Test Summary

	Null Hypothesis	Test	Sig.	Decision
1	The distribution of MP is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.157	Retain the null hypothesis.
2	The distribution of EP is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.744	Retain the null hypothesis.
3	The distribution of BP is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.548	Retain the null hypothesis.
4	The distribution of TCS is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.773	Retain the null hypothesis.
5	The distribution of ΣPCPs is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.828	Retain the null hypothesis.

(c)

	Null Hypothesis	Test	Sig.	Decision
1	The distribution of MP is the same across categories of Stretch.	Independent-Samples Kruskal-Wallis Test	.056	Retain the null hypothesis.
2	The distribution of EP is the same across categories of Stretch.	Independent-Samples Kruskal-Wallis Test	.584	Retain the null hypothesis.
3	The distribution of BZP is the same across categories of Stretch.	Independent-Samples Kruskal-Wallis Test	.039	Reject the null hypothesis.
4	The distribution of TCS is the same across categories of Stretch.	Independent-Samples Kruskal-Wallis Test	.088	Retain the null hypothesis.
5	The distribution of ΣPCPs is the same across categories of Stretch.	Independent-Samples Kruskal-Wallis Test	.718	Retain the null hypothesis.

Asymptotic significances are displayed. The significance level is .05.

Sample 1-Sam...	Test Statistic	Std. Error	Std. Test Statistic	Sig.	Adj.Sig.
3-1	4.663	4.247	1.098	.272	.817
3-2	8.150	3.221	2.530	.011	.034
1-2	-3.486	4.464	-.781	.435	1.000

(b)

	Null Hypothesis	Test	Sig.	Decision
1	The distribution of MP is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.607	Retain the null hypothesis.
2	The distribution of EP is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.183	Retain the null hypothesis.
3	The distribution of BZP is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.427	Retain the null hypothesis.
4	The distribution of TCS is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.360	Retain the null hypothesis.
5	The distribution of ΣPCPs is the same across categories of Position.	Independent-Samples Kruskal-Wallis Test	.123	Retain the null hypothesis.

Asymptotic significances are displayed. The significance level is .05.

(d)

Fig. 5.6. Kruskal-Wallis test for PCPs in (a and c) river water and (b and d) bed sediment.

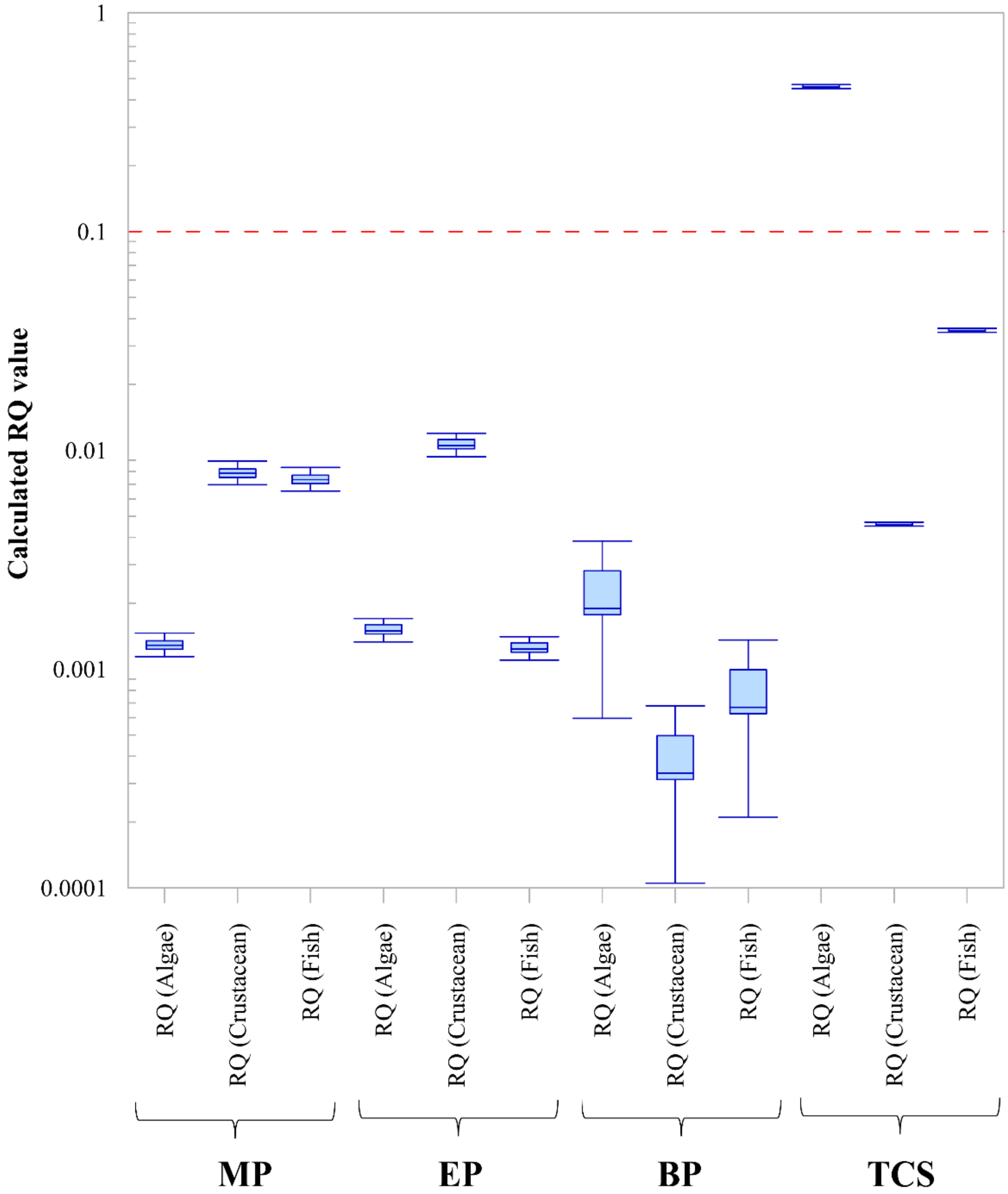
5.3.4 Risk Assessment

For assessing the risk for PCPs, RQ is calculated according to the equation 4.1 and porewater concentrations were derived using equation 4.2. The values of PNEC were used for three groups of organisms and were taken from previous literature (Li et al., 2016a; Gopal et al., 2021, Table 5.4). PNEC value for BP was calculated using previously estimated toxicity data. The organisms include algae (*Pseudokirchneriella subcapitata*), crustacean (*Daphnia magna*) and fish (*Lepomis macrochirus, Danio rerio (Zebra Danio).* According RQ classification, only TCS was posing moderated risk to *Pseudokirchneriella subcapitata* in river water (RQ=0.45-0.52) at each location from where it was detected (Fig. 5.7b). The box plot indicated all values to lie above 0.1 scale. Remaining RQ values were measured below 0.1 indicating low risk for other aquatic organisms in both water and bed sediment (Fig. 5.7a-g).

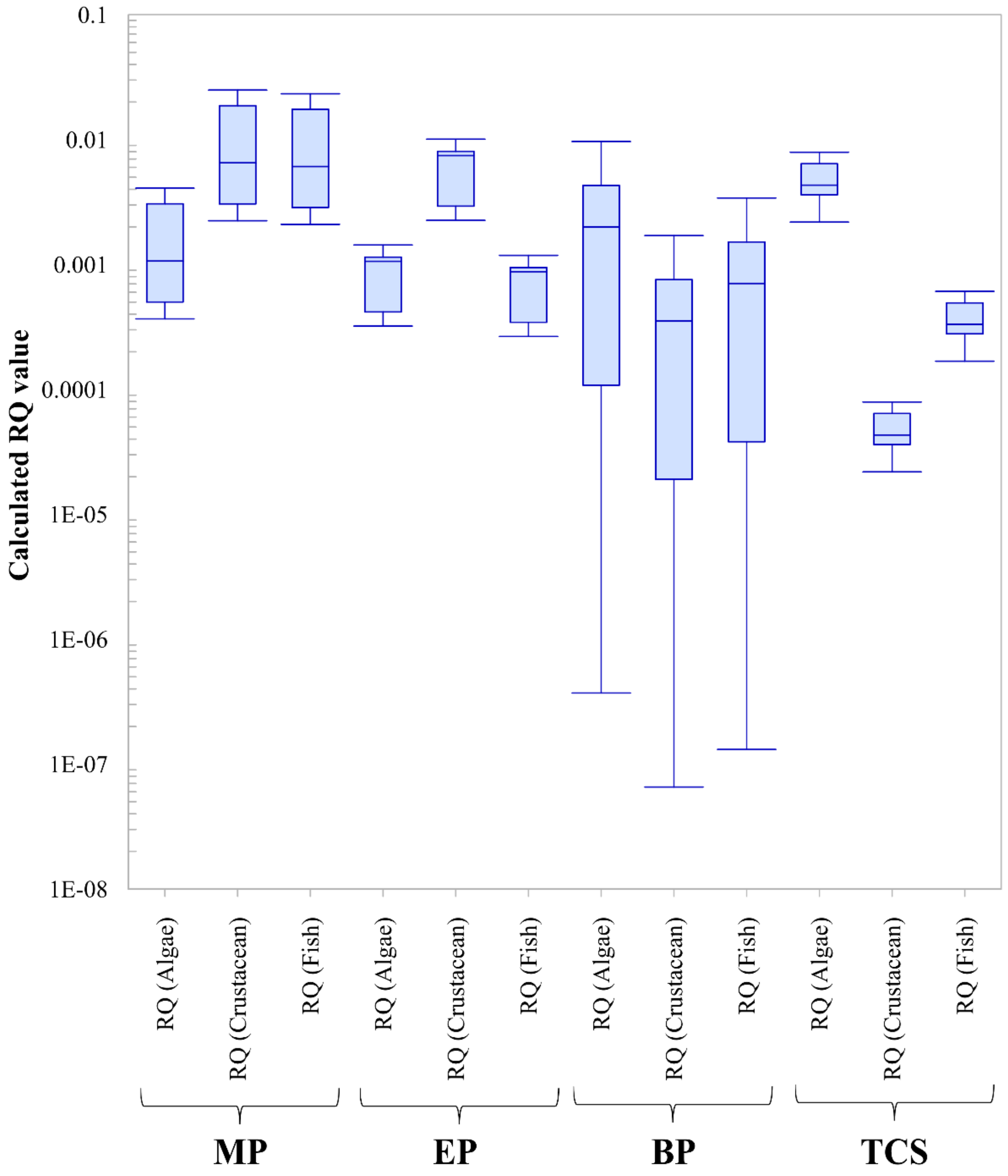
	Species group	**Species scientific name**	**Toxicity data (µg/L)**	**Assessment factor**	**PNEC$_{water(\mu g/L)}$**	**References**
MP	Algae	*Pseudokirchneriella subcapitata*	EC_{50} =80,000	1000	80	Li et al., 2016
	Crustaceans	*Daphnia magna*	EC_{50}=34,000	1000	34	
	Fish	*Oryzias latipes*	E EC_{50} = 14000	1000	14	
EP	Algae	*Pseudokirchneriella subcapitata*	EC_{50} =52000	1000	52	
	Crustaceans	*Daphnia magna*	EC_{50} = 7400	1000	7.4	
	Fish	*Oryzias latipes*	EC_{50} = 63000	100	17.	
BP	Algae	*Pseudokirchneriella subcapitata*	EC_{50} = 3,530	1000	3.5	
	Crustaceans	*Daphnia magna*	EC_{50}=3000	1000	3	
	Fish	*Oryzias latipes*	EC_{50}=10000	1000	10	

TCS	Algae	*Pseudokirchneriella subcapitata*	NOEC =2	10	0.2	Gopal et al., 2021
	Crustaceans	*Daphnia magna*	LOEC=200	10	20	
	Fish	*Danio rerio*	NOEC =26	10	2.6	

Table 5.4. The toxicity data of PCPs to the most sensitive aquatic organisms



(a)



(b)

Fig. 5.7. Box whiskers plot showing RQ calculated for PCPs for different groups of organisms in (a) river water and (b) bed sediment.

5.4 Discussion

From distribution of PCPs in three stretches in water, no significant variations were found. However, higher mean rank and sum of PCPs were maximum in middle and lower stretch than upper basin due to larger population density in former two regions than upper basin releasing high loads of wastewater effluents from industries (industrial (including textile mill, tannery industries etc.) residential areas and municipal facilities (Ramaswamy et al. 2011; Zeng et al. 2014; Chen et al., 2020; Peng et al. 2017). Similar to other studies (sections 6.2) higher dfs of both MP and EP were discovered from water as these are the most common preservatives that found application in variety of cosmetic products, pharmaceuticals, food and industrial products (such as cigarettes, varnishes and glue, animal feed) (Stuart et al., 2013; Soni et al., 2005). Due to their ubiquitous usage they have been constantly detected in the environment with less variations (especially in case of MP and EP in this study) regardless of the anthropogenic pressure (urban, industrial and agricultural) (Dominguez et al., 2019; Botta et al., 2018). That is why they are also referred to as "pseudo-persistent" contaminants (Ellis, 2006). In upper basin, higher sum of PCPs detected from G1 could be from municipal wastewater discharge from households, commercial establishments, and industries in Haridwar. River water of Song remained relatively pristine due to lesser inputs of these chemicals or adsorption by the bed and suspended sediment thereby removing them from water (Gopal et al., 2021). In middle basin, Ganga in Prayagraj (G5) was the second most polluted site with respect to sum of PCPs in middle basin, due to municipal sewage and hospital waste dumped into the river from the mega city (Lv et al., 2014; Xu et al. 2007). Similarly, Ganga Kanpur (G3) was also found be contaminated by these ECs. The presence of triclosan which is used as broad-spectrum antibacterial agent in various PCPs (as mentioned in section 5.1) and benzophenone (a UV filter) in rural areas (TC, T5 and G2) could be due to their persistence in the environment as also indicated by TCS correlation with clay resulting in long distance travel in suspension without undergoing degradation resulting in detection in less populated rural areas because of their release upstream along with their local sources (Olaniyan et al., 2016; Higgins et al., 2011). Similarly, in Gomti, the untreated household discharge from rural and small areas with dumping of domestic waste directly into the river with upstream load from major cities like Lucknow and suburban areas could have resulted in detection of all four compounds and maximum total PCPs concentration along the basin (Nag et al., 2018). The highest sum of PCPs in lower basin was discovered from G6 which was identified to be contaminated by direct wastewater flow from households and small establishment in towns and suburban centers located upstream (such as Ballia) contributing to contaminants like parabens, triclosan and benzophenone to the environment. Other densely populated location with presence of four of these PCPs were Gandak (T9 and T10) and Ganga downstream Patna (G8) (Fig. 5.1). Additionally, higher concentration in Kosi (T11) and Mahananda (T12) due wastewater discharge from small cities and towns, also elevating the levels at G10 as discussed in section 5.3.2.

In bed sediment, maximum sum of PCPs was found in lower basin followed by middle basin and similar to water lowest were detected from upper basin indicating increased inputs from larger consumption of personal care products by swollen population downstream (Chakraborty et al., 2019). In the upper basin, both location T1 and T2 recorded higher total PCP concentration due wastewater release from Rishikesh and Haripur Kalan respectively. High tourist activity in the upper zone was also responsible for detection of ECs in bed sediment (Mandaric et al., 2017; Sharma et al., 2019). In upper basin, higher levels of PCPs in T3 were caused by joint effect of low streamflow from pre-arrival of the monsoon in upper basin and tourism.

Similar to water, higher sum of PCPs was measured from G5, T13, G2 and T5 in middle basin. While in lower basin, G11 observed with higher TCS and Mahananda (T12) showed elevated ∑PCP from possible sources as discussed in this section above. However, highest ∑PCP from G10 was due to inputs from densely packed suburban areas with hospitals and domestic establishments in addition to supply from tributary Mahananda. Similarly, higher concentrations at G12 could be explained by crowded cities (Bansberia and Kalyani) situated on either side of the bank of the river releasing large amount of wastewater with higher particle associated compounds (Chakraborty et al., 2019; Lim et al., 2012). Correspondingly in SPM, concentrations were also higher in G12 and G11 in West Bengal. In both bed sediment and SPM, unlike water, concentrations were elevated in Ghaghara indicating accumulation of BP and TCS in sediment phase, while MP and EP were transferred from dissolved phase to suspension. Higher variation of ∑PCPs were observed in river water compared to bed sediment was mainly caused by TCS and BP (as MP and EP values were showing less variations) concentrations. The former was also proposed to be pollution marker indicating enhanced utilization by urban population (Yang et al., 2015). BP was also shown to be an indicator of urban contamination as according to the literatures the compound was mostly reported from urbanized regions. These observations were in river water in this study also (Careghini et al., 2015). In turn, both rural and urban areas were detected with BP in bed sediment. Both the matrix concentrations were also affected by the tributaries confluence as suggested in section 5.3.3.

With respect to partition of compound in water and sediment phase, MP and EP were mostly detected from water while TCS and BP showed higher df in bed sediment. This could be due to low log K_{ow} and higher solubility (section 5.1) of MP and EP while comparatively higher log K_{ow} and hydrophobicity of TCS and BP resulted in partitioning of these compounds in sediment phase (Chiaia-Hernandez., 2013; Zhao et al., 2021). However, in SPM, MP and EP also showed 100% df which could be due to direct exchange from water to suspended particles in surface water (Zhao et al. 2019; Wang et al. 2018).

5.5 Conclusion

The present research showed that risen consumption and manufacturing of PCPs in modern scenario has resulted in more often detection and higher concentration of these compounds (especially MP and EP) like PAHs and PAEs in the environment. Significantly greater BP in middle basin further confirmed the effect of swollen population in both cities and rural areas. TCS was another significant marker in river water which could effectively identify the escalated urban contributions. It was also the representative of ∑PCPs and its enrichment in bed sediment by clay particles could have resulted in its lower availability to organisms thus avoiding metabolism by aquatic species and degradation. Consequently, from risk assessment, only TCS was shown to cause moderate risk to algae in water. Tributaries of Ganga such as Chambal, Kosi and Mahananda were likely adding the PCPs while Ghaghara was diluting the concentrations. Based on physical properties like log K_{ow} and solubility, MP and EP were more frequently detected in water while TCS and BP in bed sediment. Further, similar sources of MP and EP were discovered from both water and bed sediment. Based on the above study, only TCS was found to be the contaminant of concern. Further investigation on its control and specific sources appointment could help the administrative departments in charge of freshwater protection to employ efficient protection measures and set guideline values to keep check on its contamination level from wastewater released by different sources, and scientifically protecting freshwater zone.

Appendix I

Parameters	Min.-Max.	Mean±S.D	BIS limits, 2012
River water			
Temperature(°C)	19.34-33.81	29.47±2.79	
pH	6.41-8.82	7.29±0.45	6.5 to 8.5
TDS (mg/L)	41.8-629	166.41±120.45	500
EC (µS/cm)	60-820	197.56±158.82	300
Salinity (ppt)	0.05-0.7	0.17±0.13	
ORP (mV)	59-253	123.56±44.76	
Bed sediment			
Sand%	18.74-99.41	50.31±22.36	
Silt%	0.59-73.17	47.1±20.41	
Clay%	0-9.5	2.6±2.57	
OC%	0.21-0.68	0.42±0.12	

Table A1. Physicochemical properties of river water and bed sediment.

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