Chapter 2
Emerging Contaminants in Wastewater and Surface Water

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Abstract Currently, severe contamination of water bodies has led to the scarcity of usable water for drinking and other purposes. The heavy emergence of pollutants in the aquatic environment ranging from ng/l to mg/L is just a consequence of drastic and speedy anthropogenic activities. As compared to developed countries, developing countries, in general, face a more serious impact of alleviating contaminants in water bodies owing to the lack of adequate studies on the current status of water contamination as well as the fate and impact of ECs in wastewater and surface water. Further, the occurrence of pollutants (generally, organics) in wastewater is increasing non-regulated manner above the safe limits. These are not only harmful to aquatic flora and fauna but also for terrestrial lives and recently have been observed by advanced analytical detectors. These trace compounds are termed emerging contaminants (ECs) derived from pharmaceuticals (PhACs), personal care products (PCPs), endocrine disrupting compounds (EDCs). In this book chapter, we would thoroughly discuss the above-mentioned individual types of emerging contaminants in detail and also present the survey on their local distribution aqueous matrix in India. Finally, we would elaborate on the possible solution to tackle this problematic situation of ECs dumping into wastewater and surface water.

Keywords Emerging contaminants · Pharmaceuticals · Personal care products · Nanomaterials

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2.1 Introduction

Nowadays, fresh and clean water has become scanty across the globe as surface water is no more able to be leveraged directly for various domestic or commercial purposes. Heavy pollution of surface water has made it absolutely of no use. The major contribution to water pollution is the accumulation of emerging contaminants (ECs). ECs are predominantly organic and inorganic compounds for examples chemical ingredients of pharmaceuticals, cosmetic products, taste and odor compounds, surfactants, X-ray contrast media, and steroid hormones. Their direct consumption has a fatal impact on human health in form of lethal and incurable diseases like cancer. Excessive presence in the aquatic environment ranging from ng/l to mg/L is just a consequence of drastic and speedy anthropogenic activities (Verlicchi and Zambello 2015). For the last few decades, several kinds of ECs are getting dumped in the aquatic bodies of our ecosystem through various outputs such as waste sludges from wastewater treatment plants, domestic outlets, industrial units, sewer leakage, agriculture, and surface runoffs from rural and urban zones, and manure waste. Even, groundwater is also severely contaminated across the globe (Bu et al. 2013; Zhang et al. 2015). Predominantly, wastewater treatment plants are of major concern because they directly dump the emerging ECs into water bodies just by overlooking their proper treatment. This serious issue has alarmed the research fraternity engineers and civil authorities to look into the matter to take some quick action as the level of these hazardous pollutants has trespassed their permissible limit in wastewater and surface waters. Therefore, the supply of clean and safe water to urban as well as rural populations has become an extremely challenging task. Even, thorough treatment of wastewater has been proven a tedious task for its further recycling to reuse.'

Ironically, conventional water treatment plants are only sensitive towards water nutrients, bacteria, heavy metals, pesticides, petroleum hydrocarbons, and other primary pollutants (Pal et al. 2014). Overall, the present water treatment plant only focuses on primary pollutants whose impact on human health and animal is known.

However, as compared to developed countries, developing countries, in general, lack adequate studies on issues related to ECs (Rehman et al. 2015). India is one among them. In contrast, the production and consumption rate of compounds in ECs categories in India is growing day by day.

The occurrence of pollutants (generally, organics) in wastewater is increasing in a non-regulated manner above the safe limits. These are not only harmful to aquatic flora and fauna but also to terrestrial lives as recently observed by advanced analytical detectors. These trace compounds are termed as ECs.

Generally, the organic and inorganic trace pollutants found in wastewater have the following broad categories they are derived from.

(i) Pharmaceuticals (PhACs)
(ii) Personal Care Products (PCPs)
(iii) Endocrine Disrupting Compounds (EDCs)
(iv) Per- and polyfluoroalkyl substances (PFASs)
(v) Artificial sweeteners (ASs)
(vi) Flame retardants (FRs)
(vii) Nanomaterials (NMs)

Out of all the above-mentioned categories of ECs, PhACs, PCPs, and EDCs are found in very high concentrations in the aquatic system throughout the globe. This emerging pollutant disturbs the bacterial biomass and hence the biological activity in wastewater and surface water. Especially, nanomaterials consisting of inorganic metal oxides cause malfunctioning in bacterial activity hindering the removal of emerging pollutants in wastewater treatment plants (Wang et al. 2012). It is to be noted that though there are specific groups of ECs as discussed above still there is no clear discrimination amongst the groups of ECs. The compositions of ECs subgroups are overlapping each other.

In this book chapter, a thorough discussion is dedicated to the major ECs i.e. PhACs, PCPs, and EDCs in detail in subsequent sections along with their carcinogenic impact on animal and human health.

2.2 Emerging Contaminants (ECs) in Wastewater and Surface Water

As a consequence of population explosion, ECs are easily circulated over surface water and even reach the groundwater from open resources of water. Disposal of municipal sludge is also a very challenging task as it is considered as the principal source of the liberation of emerging pollutants from open aquatic ecosystem where industries and domestic outlets (as point sources) are directly connected to water bodies without significant treatment of wastewater to make it free of emerging pollutants. The emerging pollutants are categorized into three above said major groups of chemicals. Firstly, PhACs are further subdivided into different categories viz. antibiotics, analgesics, steroids, and nonsteroids, etc. Secondly, Personal care products (PCPs) are identified as cosmetic and health care chemicals available in the market, for example, galaxolide, tonalide, etc. Endocrine-disrupting compounds (EDCs) are groups of compounds or chemicals that show an adverse impact on human endocrine systems by causing androgenic or estrogenic activities even at low concentrations, for example, estradiol, phthalates, etc.

After executing a thorough review of reports on emerging contaminants found in surface water and wastewater, the following major classes falling in the above discussed categories are formed as per their abundant quantity in the aquatic system (Luo et al. 2014; Subedi et al. 2015; Semblante et al. 2017).

(i) Antibiotics
(ii) Antifungal/antimicrobial agents
(iii) Nonsteroidal anti-inflammatory drugs (NSAIDs)
(iv) Anticonvulsants/antidepressants
(v) Artificial sweeteners
(vi) Beta-adrenoceptor blocking agents
(vii) Lipid regulating drugs
(viii) Steroidal hormones
(ix) X-ray contrast media
(x) UV filters
(xi) Stimulants
(xii) Anti-itching drugs
(xiii) Insect repellents
(xiv) Plasticizers
(xv) Pesticides
(xvi) Metal oxides and composites
(xvii) Perfluorochemicals (PFCs)

2.3 Pharmaceuticals (PhACs)

PhACs are a set of developing ecological contaminants that are broadly and progressively being utilized as a part of human and veterinary medication. They include compounds of environmental concern like antibiotics, legal and illicit drugs, analgesics, steroids, β-blockers, anticonvulsants, antihypertensive, etc. (Luo et al. 2014).

The formation of the above subcategories is based on a mass number of observations by researchers. They have examined their pros and cons over human health and the environment. This classification was performed while keeping four main points into consideration i.e. (i) consumption across the globe (ii) observation frequencies (iii) effect on surroundings (iv) quantity of analytical data.

Keeping all the critical points in view, Table 2.1 has been prepared which ensemble the major classes of pharmaceutical chemicals depicting potential risks on human health and other organisms (Minh et al. 2009; Kurunthachalam 2012; Bu et al. 2013; Luo et al. 2014; Stefanakis and Becker 2015; aus der Beek et al. 2016; Singh et al. 2016; Tiwari et al. 2016; Pavithra et al. 2017; Bai et al. 2018; Gogoi et al. 2018; Nag et al. 2018; Brown and Winterstein 2019).

PhACs include organic compounds like antibiotics, legal and illicit drugs, analgesics, steroids, beta-blockers, anticonvulsants, antihypertensive, etc. (Luo et al. 2014; Pal et al. 2014; Zhang et al. 2015; Taheran et al. 2018). Pharmaceuticals have been defined as substances that are primarily being used for therapeutic, preventive, and diagnostic purposes. Recreational drugs, such as cocaine and caffeine, have been excluded from the present analysis. Other substances, such as homeopathic, minerals, proteins, and immunologic substances, also were not included. If not otherwise indicated, the terms "pharmaceuticals" and "pharmaceutical substances" refer only to the actual active pharmaceutical ingredients. These pharmaceutical pollutants are found to be bio-accumulating in nature as they are very much active in the biological system. Their persistence in the body occurs due to their specific mode of action. Therefore, they are traced in wastewater, surface water, and drinking water which ultimately cause bio-resistant properties in bacteria present anywhere. Even the metabolites of pharmaceutically active compounds have been causing a lethal impact on the ecosystem gradually. Due to their very minute concentration, they have been unnoticed and never been prioritized by Governmental guideline makers to treat wastewater for their removal. That's why they have been termed pseudo-persistent pollutants which accumulate into the environment at trace level (Archana et al. 2017). This situation has been continuing for few decades and no assessment has been executed seriously except a few years back, few reports got surfaced and were noticed for the risk assessment of pharmaceutical ingredients and their derivatives. Recently, more than 160 different pharmaceutical compounds have been detected in water bodies supremely, wastewater treatment plant effluent in the concentration range of ng L^{-1} to low $\mu g\ L^{-1}$ (Archana et al. 2017). These pharmaceutical drugs are not only affecting human beings but also wildlife tremendously (Archana et al. 2017). So far, extremely inadequate information is collected about the toxicological effect of pharmaceutical drugs on terrestrial and aquatic lives, especially in the Indian subcontinent. The exact fate of bioaccumulation of PhACs and their impact on water-bodies and surroundings are therefore quite unpredictable. It is only assured once the consolidated database of PhACs distribution throughout the country is available.

2.3.1 Sources of PhACs

There are various inlets of PhACs through which PhACs are dumped into surface water. Amongst all, sewage effluents are realized as a prominent source of PhACs and their metabolites. Generally, sewage effluents consist of the domestic pharmaceutical left out, discharge from hospitals, and even sometimes from pharmaceutical manufacturing plants. According to a report, Patancheru Enviro Tech Limited (PETL) WTP near Hyderabad received 1.5 MLD effluents from ~90 bulk drug manufacturers in the vicinity in Patancheru. This was found to record the highest levels of PhACs ever reported in wastewater from anywhere else across the globe (Balakrishna et al. 2017). Sometimes the overflow from WTPs also contributes to the contamination of surface water. Even the untreated sewage discharged from cruise and boats also contributes to PhACs contamination in the riverine system. For example, sewage effluents received from typhoon shelters were found highly contaminated with several kinds of antibiotics like β-lactams, fluoroquinolones, macrolides, sulfonamides, tetracyclines, trimethoprim, and amphenicols (Minh et al. 2009). Large scaled animal husbandry and horticulture have been also noticed to pollute the surface water due to excessive use of antibiotics to cure animals (Kaval et al. 2015). Despite the ban on the use of antibiotics at several places like Europe, there are still some regions where a low dose of antibiotics in feed as growth promoters is given to animals. Besides, there are many reports on the use of antibiotics including oxytetracycline and streptomycin on horticultural crops in some countries (Kaval et al. 2015). Leachates from landfills might be the smoother route for pharmaceuticals disposed of household and clinical wastes entering the surface water and even groundwater.

2.3.2 Occurrence of PhACs in Indian Environment

Analgesics, anticonvulsants, antidepressants, antiepileptics, antihypertensives, and β-blockers are commonly observed in water systems owing to higher solubility in water and slower metabolic rate (Brown and Winterstein 2019). The antiepileptic gabapentin has been recorded with the highest median concentration in the aquatic system followed by metformin, lamotrigine, desmethylvenlafaxine, hydrochlorothiazide, sulfamethoxazole, and hydroxycarbamazepine with (>100 ng/L) concentration.

In developing countries, more monitoring results have recently become available, but a concise picture of measured environmental concentrations (MECs) is still elusive. Through a comprehensive literature review of 1016 original publications and 150 review articles (aus der Beek et al. 2016), the authors collected MECs for human and veterinary pharmaceutical substances reported worldwide in surface water, groundwater, tap/drinking water, manure, soil, and other environmental matrices in a comprehensive database. Approximately, 631 different pharmaceutical substances were found at MECs above the detection limit of the respective analytical methods employed, revealing distinct regional patterns. Sixteen pharmaceutical substances i.e. diclofenac, carbamazepine, ibuprofen, sulfamethoxazole, naproxen, estrone, estradiol, ethinylestradiol, trimethoprim, paracetamol, clofibric acid, ciprofloxacin, ofloxacin, estriol, norfloxacin, and acetylsalicylic acid were detected in each of the 5 United Nations (UN) regional groups (Africa Group, Asia–Pacific Group, Eastern Europe Group, group of Latin American and the Caribbean States, and Western Europe and Others Group, which also includes North America, Australia, and New Zealand). For example, the anti-inflammatory drug diclofenac has been detected in environmental matrices in 50 countries, and concentrations found in several locations exceeded predicted no-effect concentrations. aus der Beek et al. (2016) studied the distribution of various PhACs in different regions of the world as shown in Fig. 2.1.

Recently, Philip et al. (2018) analyze the data derived from the monitoring of the presence of PhACs across the country. Unfortunately, it is found that data are scarce regarding the presence of ECs primarily from northeast, north, central parts of the

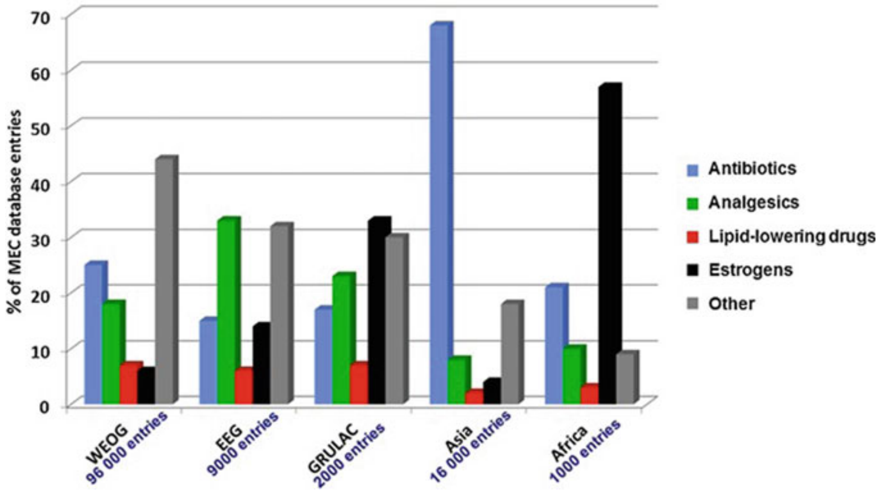

Fig. 2.1 Regional patterns of pharmaceutical therapeutic groups analyzed in each United Nations region. MEC = measured environmental concentration; EEG = Eastern Europe Group; GRULAC = Latin American and Caribbean States; WEOG, Western Europe and Others Group (aus der Beek et al. 2016)

country as visible from Fig. 2.2. Only southern parts have been almost monitored for the presence of ECs in comparison to other parts of the country. However, whatever data are reflected they show the presence of ECs way more than permissible limit almost every part of the country. The drastic accumulation of ECs in water bodies and wastewater systems is attributable to the boom in the application of medicines due to the increase in population across the globe. India stands in the second position in the queue of highest populated countries after China (Kalotra 2014). India is now the largest exporter of generic drugs nearly (20% of gross global exports) as generics rule over more than 70% of the total market share in the Indian pharmaceutical sector which is further scaled to be enhanced in near future. Moreover, multinational companies have been attracted to this giant market of pharmaceutics in the greed of cheap-cost production and flexible environment tribunal guidelines. This is further contributed by efficient and fast techniques, quality research, the abundance of educated personnel, and skilled laborers making the Indian market a fascinating choice for the foreign pharmaceutical majors for their drug production and outsourcing (Kalotra 2014; Bai et al. 2018). Today, the Indian pharmaceutical industry has become one of the leading industries of the nation which has the very high caliber to make right from analgesics to medicine for any fatal disease like cancer and cardiac treatment. Abnormally high concentrations of PhACs are the result of heavy usages and also inefficient wastewater treatment plants (WTPs) to decontaminate the water from these pollutants. Recently, the occurrence of explicitly used PhACs and drugs either in their original or metabolite form raises the concern of the scientific fraternity. Recent reports suggested the significant occurrence of PhACs in

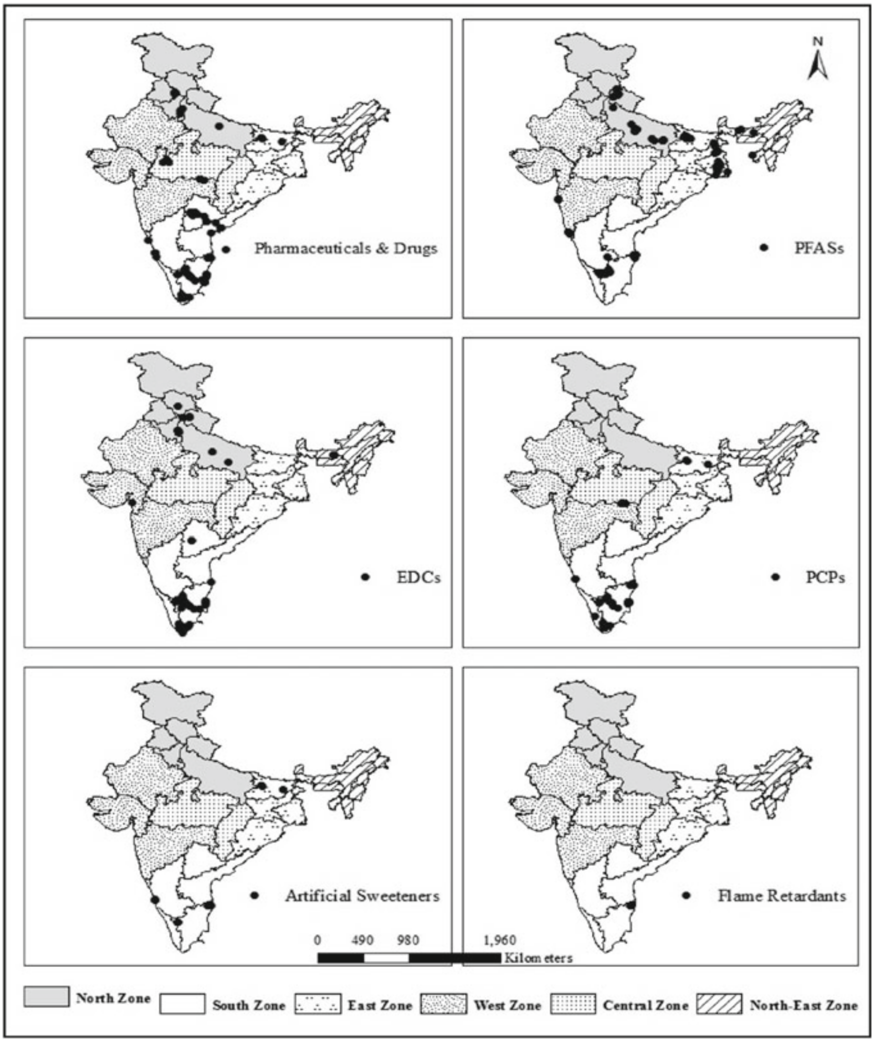

Fig. 2.2 Distribution of different classes of ECs in various Indian environmental matrices reprinted with permission from Philip et al. (2018). Copyright 2018, Elsevier

wastewater and surface water bodies in India. Carbamazepine, atenolol, triclocarban, triclosan, trimethoprim, and sulfamethoxazole, ibuprofen, and acetaminophen are the most commonly found at extremely high concentrations in WTPs and rivers. The concentration of most of these PhACs such as ciprofloxacin, sulfamethoxazole, amoxicillin, norfloxacin, and ofloxacin in WTPs across India might be 40 times higher than that in other countries in Europe, Australia, Asia, and North America (Balakrishna et al. 2017). The pattern of PhACs occurrence in the riverine system is analogous to that of China. This might be due to similar pharmaceutical infrastructure and population compatibility.

Notably, according to a study on antibiotic consumption, India was found to be the largest consumer even more than 75% during the decade (2000–2010). The excessive application of PhACs especially antibiotics has caused the accumulation of antibiotic-resistant genes (ARGs) at an alarming rate almost everywhere across the country. Coming to riverine systems, due to ARGs, the most fatal damage has been caused to holy rivers of the country named Ganga, Gomati, Narmada, Yamuna, Kshipra, etc. (Singh et al. 2016; Gogoi et al. 2018; Nag et al. 2018; Philip et al. 2018). This has caused a distressing situation for riverine life and human health as well as other organisms as flora and fauna belonging to the riverside use the river water for food consumption and various other purposes. The water from these rivers is widely supplied to the urban area of countries for domestic and commercial use. This may be the reason for spreading several kinds of incurable diseases such as cancer, and respiratory malfunctioning. According to a report (Singh et al. 2016), heavy contamination of β-lactam resistance determinant gene (bla_{TEM}) has been observed in the Indo-Gangetic region. It was seen that surface water and sediments of the river Ganga and Gomti Rivers exhibited high numbers of bla_{TEM} gene copies and varied significantly ($p < 0.05$) among the sampling locations. This heavy accumulation of this resistance gene is the exorbitant consumption of antimicrobial of the β-lactam group by humans due to its high efficiency and low cost. The water sample taken from drinking water facility and clinical settings had a considerable number of bla_{TEM} gene copies (13 ± 0.44–10,200 ± 316 gene copies/100 mL). Recently, Biswas and Vellanki (2021) reported the presence of 16 different types of PhACs and PCPs in water samples collected from the 13 locations spanning 575 km along the river Yamuna. Spatiotemporal variations in the occurrence of these ECs were detected during summer and post-monsoon. The appreciably high concentration of ECs was detected during the post-monsoon in comparison to the summer season. This is due to the assimilation of rain runoff from the catchment areas along river Yamuna. The ECs which were found in high concentrations include trimethoprim (8807.6 ng/L), caffeine (6489.9 ng/L), and gemfibrozil (2991 ng/L). The water samples with very high concentrations of ECs were mainly from Okhla barrage (ponding of water from drains traversing Delhi), the confluence of Yamuna with Shahadara drain (industrial and poultry cluster, and Ghazipur dumping yard), and Agra city (industrial clusters). According to a survey (Hanna et al. 2020), there has been a severe accumulation of antibiotic residues and antibiotic-resistant *Escherichia coli* (*E. coli*) in the water and sediment of the Kshipra river. This report analyzed the water samples collected from seven different sites over a long span of 2014–2016 during different seasons. Sulfamethoxazole was detected with the highest concentration of 4.66 μg/L. Even, ARGs were found against various antibiotics including sulfamethoxazole, norfloxacin, ciprofloxacin, cefotaxime, co-trimoxazole, ceftazidime, meropenem, ampicillin, amikacin, metronidazole, tetracycline, and tigecycline. It was found that the presence of antibiotics and anti-resistant genes was directly associated with water quality parameters. In another study (Archana et al. 2017), acetaminophen and ciprofloxacin, caffeine, irgasan, and benzophenone were found present in the influent and the effluent of the sewage treatment plant (STP) and surface water bodies (six major lakes) in and around Nagpur. These ECs were present in the range of 1–174 $\mu g\ L^{-1}$ in collected surface water, 12– 373 $\mu g\ L^{-1}$ in the influent, and 11–233 $\mu g\ L^{-1}$ in the effluent of the STP. They also carried out the ecotoxicity test on the targeted organism. Though they found the hazard quotient (HQ) less than 1 reflecting no hazardous effect of these analytes on the living organism still there is the uncertainty of the extent of effect over long-term exposure as ECs get inhabited in the water bodies for a quite long period.

Unfortunately, the relationship of antibiotics with aquatic dwellers has not been thoroughly explored in the country. Only a few research groups are involved in such studies. The monitoring efficiency must be improved by leaps and bounds and also except exploring the impact in sewage effluents from commercials units, domestics, and surface water systems should also be carefully monitored.

Fortunately, after several reports on the presence of lethal ARGs, the Government of India (GOI) has taken some necessary action but still, their proper implementation is underway. This might be due to improper health infrastructure, inaccessible medical facilities in remote areas, and lack of laboratory facilities for national-level monitoring of antimicrobial resistance.

2.3.3 Effects of PhACs on the Animal and Human Health

Toxicity caused by pharmaceutical substances in the Indian environment is undoubtedly a concerning issue (Kurunthachalam 2012; Philip et al. 2018). Several studies reported that the presence of PhACs in the aquatic system may cause complex biological effects on dwelling flora and fauna by significant alterations in biochemical parameters, hematological indices, enzymological activity, ionoregulatory responses, gene responses, plasma phosphate levels, and hormonal levels (Philip et al. 2018). The extinction of the vulture population from the Indian subcontinent is one of the finest examples of the environmental impact caused by PhACs residues. The exemplary mass extinction of mainly three species of vulture (*Gyps bengalensis*, *Gyps indicus,* and *Gyps tenuirostris*) is due to the consumption of livestock remains that were medicated with diclofenac (NSAID). Generally, high adult mortality and hence lives loss have been related to renal failure and kidney malfunction. These are attributed to in vivo assimilation of commonly used PhACs in high concentrations over a period. According to a study (Stefanakis and Becker 2015), drugs associated with the central nervous system, cardiovascular and anti-infective classes can turn out to be extremely lethal to aquatic life as well as the outer environment. Anti-infectants are also found very hazardous. Moreover, the long-term effect of these ECs is unknown especially at low concentrations in surface water. However, researchers are addressing only the specific classes of PhACs found in high concentrations in water bodies rather than non-specified. However, the effect of these non-prescribed PhACs can be more concerning. Hence there should be proper monitoring of every class of PhACs which can inhabit the wastewater and so surface water. The contamination of groundwater is of primary concern as still, a huge population uses the groundwater as drinking water directly for oral consumption in India. Furthermore, most of the respective scientific studies focus on certain groups such as antibiotics, hormones, or antineoplastics, but other groups such as antiulcerants and non-prescribed drugs also possess a potential negative impact on the environment.

According to reports on the high concentration of PhACs and ARGs in wastewater and surface water, it is concluded that these residues are extremely toxic and lethal to aquatic life too. Devarajan et al. (2015) analyzed the water samples collected from hospital outlet pipes (HOP) and the Cauvery River Basin (CRB) in Tiruchirappalli, Tamil Nadu, India. They analyzed these samples for organic matter, toxic metals, and their ecotoxicity. The analysis report manifested the high concentration of toxic metals in HOP, reaching values (mg kg^{-1}) of 1851 (Cr), 210 (Cu), 986 (Zn), 82 (Pb), and 17 (Hg) whereas in CRB concentrations were lower than that of in the HOP (except for Cu, Pb), with maximum values (mg kg^{-1}) of 75 (Cr), 906 (Cu), 649 (Zn), 111 (Pb), and 0.99 (Hg). As a result of the analysis report, the metal concentrations in both sampling sites were much ahead of the permissible limit recommended by Sediment Quality Guidelines (SQGs) and the Probable Effect Concentration (PEC) for the Protection of Aquatic Life. In this study, the ecotoxicity test with ostracods exposed to the sediment samples presented a mortality rate ranging from 22 to 100% (in sediments from HOP) and 18–87% (in sediments from CRB). The effluents from hospitals and pharmaceuticals outlets are extremely metal and PhACs loaded, and hence it is a major source of pollution of water resources and may place aquatic organisms and human health at risk.

2.4 Personal Care Products

Personal care products (PCPs) consist of generally organic compounds employed in cosmetic and healthcare products which include deodorants, perfumes, shampoos, sun scream, facial cream, sanitizers, cleaning products, and other products with estrogenic activity (Pal et al. 2014; Gogoi et al. 2018).

The following Table 2.2 consists of all possible types of PCPs composed of carcinogenic materials (Bu et al. 2013; Noguera-Oviedo and Aga 2016; Gogoi et al. 2018; Philip et al. 2018).

A list of emerging PCPs in surface water and wastewater (Verlicchi and Zambello 2015; Gogoi et al. 2018; Philip et al. 2018; Wang et al. 2021).

PCPs are dumped from domestic sources and cosmetic industries into surface water and wastewater in their native and derivative forms. The major lethal effect causing concern is the lipophilic nature of their constituents which hinders the metabolism and the lifecycle of flora and fauna in the water ecosystem.

2.4.1 Sources of PCPs

PCPs are most commonly dumped from domestic sources and cosmetic industries into surface water and wastewater in their native and derivative forms. Primarily, three categories of PCPs i.e. musk fragrances, disinfectants, antimicrobials, and preservatives are monitored in water and surface water across the world (Bu et al. 2013). Several reports are demonstrating the finding of these three categories of PCPs in surface water of the Haihe River in China, Michigan Lake in the USA, the North Sea in Germany, etc. (Bu et al. 2013). Notably, PhACs and PCPs can be accumulated in sediments which further act as a source of ECs in the aquatic atmosphere (Bu et al. 2013). The expired or unused PCPs, as well as drugs, even are generally dumped from households into the water which ultimately turns into fatal for animal or humans which consumes the untreated water in any forms (Stefanakis and Becker 2015). Besides Triclosan (TCS) and trichlorocarbon (TCC), paraben is drastically used in PCPs. Their adverse health effects have become a public concern. According to a study Wang et al. (2021), around six types of parabens, TCS and TCC were found in 129 indoor dust samples. They are also observed in 203 urine samples from two different cities in China along with four paraben metabolites. These trace level PCPs like phenols, paraben, and phthalates are almost found in the aquatic system of every part of the world (Santos et al. 2016; Sangeetha et al. 2021).

2.4.2 Occurrence of PCPs in Indian Environment

Primarily, three categories of PCPs i.e. musk fragrances, disinfectants, and preservatives are monitored in water and surface water across the world. Nag et al. (2018) monitored the occurrence of (TCS), the antibacterial agent commonly used in PCPs in water, sediment, and fish samples collected from a stretch of about 450 km of River Gomti, a major tributary of River Ganga, in India. TCS was detected in the range of 1.1–9.65 μg/l while in sediments and fish samples, the level was 5.11–50.36 μg/kg and 13–1040 μg/kg (wet weight basis), respectively. According to this evaluation, TCS uptake via contaminated fish appeared below the permissible limit (50 μg/kg body wt/day) and so there is no health hazard over a certain period. The high concentration of irgasan was monitored at various places in the country varying in seasons throughout the year. An extreme level of PCPs is dumped into the riverine system especially on the occasion of religious gatherings like Kumbh Mela where millions of pilgrims take a bath in holy rivers. Nowadays varieties of UV filters are used in PCPs. Among UV filters, Benzophenone (BPs) and 4-Methylbenzylidene Camphor (4-MBC) are often used to protect the skin and hair from UV radiations. BPs and 4-MBC are directly discharged to water bodies while cleaning and personal hygiene process. Since the conventional treatment plants are incapable to remove the BPs and 4-MBC thoroughly. Therefore, BPs and 4-MBC have been consistently observed in wastewater and off-course surface water in various parts of the country as well as in other parts of the world (Zhang et al. 2021a, b).

2.4.3 *Effects of PCPs on the Animal and Human Health*

Although the risk assessment is still underway for several components due to the absence of extensive research still several forms of allergy and mutation are observed in animals and humans as well. Hence an extensive form of research is required to analyze the long-term impact of these ECs. PCPs like triclosan commonly used as an antibacterial agent, shows highly toxic to aquatic flora and fauna such as algae, zooplankton, and fish. It is highly bio-accumulative and has endocrine disruptive properties. According to a report, UV filters used in PCPs are extremely ecotoxic *C. vulgaris* (algae), *D. Magna* (zooplankton), and *Brachydanio rerio* (fish) (Zhang et al. 2021a).

2.5 Endocrine Disruptors (EDCs)

Endocrine-disrupting compounds (EDCs) includes hormones, steroids, perfluorinated compounds, surfactants, and surfactant metabolites, flame retardants, industrial additives and agents, gasoline additives, antiseptics, plastic precursor, food additives, herbicides, insecticide, artificial sweeteners, and nanomaterials that manifest carcinogenic effects on the human endocrine system due to their androgenic or estrogenic activities even at trace level (Table 2.3).

A list of emerging EDCs in surface water and wastewater (Pal et al. 2014; aus der Beek et al. 2016; Tiwari et al. 2016; Kasonga et al. 2021).

These chemicals may disrupt the functioning of vital organs in human as well as animal bodies adversely. United States Environmental Protection Agency (EPA) has declared as external chemicals mess with the metabolism and anabolism of the body's natural hormones which functions in homeostasis, development, reproduction, and behavior. There are three main classes of EDCs; estrogenic mocks the functioning of the body's natural estrogens; androgenic duplicates natural testosterone and last thyroidal disrupts the functioning of the thyroid.

2.5.1 *Sources of EDCs*

A majority of ECs are not produced naturally and their occurrence in the aquatic environment is entirely due to anthropogenic activities. The emergence of EDCs is predominantly accelerated by above mentioned domestic and industrial waste products dumped directly into the water which finally reaches surface water or groundwater because wastewater is further dumped into water bodies without EDCs specific treatment in water treatment plants, unfortunately. The presence of EDCs in the aquatic environment was observed earlier in the 1970s but has received more attention in the 1990s with the use of advanced analytical methods for their detection at very low concentrations. Most of PhACs and sometimes their metabolites were found to exhibit EDC properties. Though they are found in immensely low concentrations (ng L^{-1} or $\mu g\ L^{-1}$) in wastewater they can be very hazardous in long-term exposure to human beings and other organisms.

Phthalates like DBP and DEHP are mainly utilized plasticizers to give flexibility to rigid polymers. These materials are components of industrial solvents, adhesive, wax, ink, pharmaceutical products, insecticide materials, and cosmetics. The direct human exposure of EDCs is mainly through the diet while using canned materials as eateries. The phthalate is not covalently bound to PVC so it can leach, migrate or evaporate into the body and environment and becomes ubiquitous (Tiwari et al. 2016).

2.5.2 Occurrence of EDCs in Indian Aquatic Environment

There are several reports on the occurrence of EDCs in Indian water reservoirs, sediments as well soil (Tiwari et al. 2016; Gogoi et al. 2018; Philip et al. 2018; Kasonga et al. 2021). According to a report (Tiwari et al. 2016), phthalates (PAEs), bisphenol A (BPA), Di-n-butyl phthalate (DBP), and other EDCs were found significantly in surface sediments at different stations across Thane Creek, India. BPA and DBP were detected in the range 0.13 and 0.4 mg kg^{-1} and 16.3 to 35.79 $\mu g\ kg^{-1}$, respectively. According to a study of the androgenic potential of WTPs influents and effluents in the Northern part of the county, the concentration of four EDCs; nonylphenol, hexachlorobenzene, and two testosterone was very appreciable, and hence despite severe treatment, final treated effluent from WTP still had enough androgenic and ecotoxic impact to general public health (Kumar et al. 2008).

Philip et al. (2018) reported the presence of EDCs in all the environmental matrices including air, water, sediment, wastewater, and sludge collected from the North zone, south zone, west zone, and north zone. The ubiquitous presence of five phthalates such as DEHP, DMP, DBP, DOP, and DEP has been reported in bed sediments of Gomti River (Srivastava et al. 2010). The presence of phthalates was also detected in indoor air, outdoor air, indoor dust, outdoor dust, and drinking water samples collected from Jawaharlal Nehru University campus, India.

2.5.3 *Effects of EDCs on the Animal and Human Health*

Their emergence in aquatic bodies can cause disruptive physiological processes, sexual impairment, lesser fertility, and cancer in the human and animal body if directly consumed even in low concentrations. Therefore, even a minute concentration of EDCs can increase the aquatic toxicity manifold and make the water system inhabitable for its dwellers. EDCs are even reported to mock or alter the functioning of hormones and distort the body fluid in the living organism. DEHP was observed to cause a drastic reduction in sperm production, motility, and velocity in goldfish over a monthly exposure, and also there was a noteworthy decrease in 11-ketotestosterone and luteinizing hormone levels over 15–30 days of exposure (Golshan et al. 2015). Zhang et al. (2021b) have demonstrated the impact of DEHP and BPA throughout exposure on rats and found that it can elevate the risk of breast cancer in females. The data manifested that BPA even individually or in combination with DEHP may induce hyperplasia of mammary glands, including the proliferation of ductal epithelial cells and an increase in the number of lobules and acinus after a 30-week exposure. In another study Zhou et al. (2020), the combined exposure to PFOS and BPA can provoke the increment in collagen and interventricular septal thickness (IVS) and damage heart development.

2.6 Monitoring and Regulation of ECs in Wastewater and Surface Water

2.6.1 *Regulations and Guidelines*

Since the conventional WTPs can not remove ECs completely as demonstrated by their presence in drinking water, this is a potential threat to public health. The detection of ECs across the globe makes them ubiquitous. Moreover, several ECs are degraded over the period but their constant use and abuse release them into the environment and hence in water. That's why they can be called "pseudo-persistent" (Ebele et al. 2017). Pseudo-persistent PhACs are more fatal to the environment than other organic ECs as they are getting replenished even after decomposition processes such as biodegradation and photodegradation.

Attributing to awareness about the adverse impact of ECs on human and animal health, several countries have imposed strict rules and regulations to monitor and tackle the panic situation throughout the globe. Indian governments have also been establishing several policies and rules over this issue of severe contamination of water bodies and groundwater. Concerning the abrupt usage of antibiotics, GOI has formulated a national policy on the application of antimicrobial drugs. Unfortunately, the implementation was not practiced up to the mark due to various reasons, for example, unorganized health infrastructure, poor medical facilities in remote areas, lack of coordination national level monitoring of antimicrobial resistance.

Later, to pose more restrictions on counter sales of PhACs and drugs, the Drugs and Cosmetic Rule, 1945 underwent amendation realizing Schedule H1 in the year 2013 which incorporated 46 more drugs including 3rd and 4th generation antibiotics, anti TB drugs, and narcotic drugs (Philip et al. 2018). After 1 year this Schedule H1 was implemented in the country in March 2014 by Central Drugs Standard Control Organization (CDSCO). Afterward, authorities took the initiative of 'Chennai declaration' in 2012 to tackle the issue of antimicrobial resistance in the country and made a 5-year strategy to control antibiotic resistance. Onwards, National Action Plan on Antimicrobial Resistance (NAP-AMR) 2017–2021, was actuated in the country along with six strategic rules to combat antimicrobial resistance and contribute towards the global efforts to tackle this public health threat (Oviedo and Aga 2016). Despite all of this, the country is facing the problem of emerging contaminants in surface water and groundwater bodies. This is basically because of inefficient treatment of pharmaceutical industrial effluents, hospital effluents, urban runoff, etc. (as presented in Fig. 2.3) as well as extremely poor sanitation facilities in both rural and urban areas. The abrupt use of PhACs and PCPs is going to result in a panic situation for highly populated countries such as India. The distribution and fate of ECs in the environmental matrices are still unclear due to the lack of comprehensive studies. A few studies have reported the presence of PhACs and PCPs in the rivers but are limited to few sampling locations and target compounds. In India, the capacity of WTPs is considerably less than the sewage produced leading to the discharge of partially treated or untreated sewage being discharged into the surface water bodies.

In nutshell, to tackle this problem, there should be strict rules on the implementation of existing national drug policies. Moreover, an awareness program on the application of PhACs, PCPs, EDCs, and other abusive drugs should be run across the

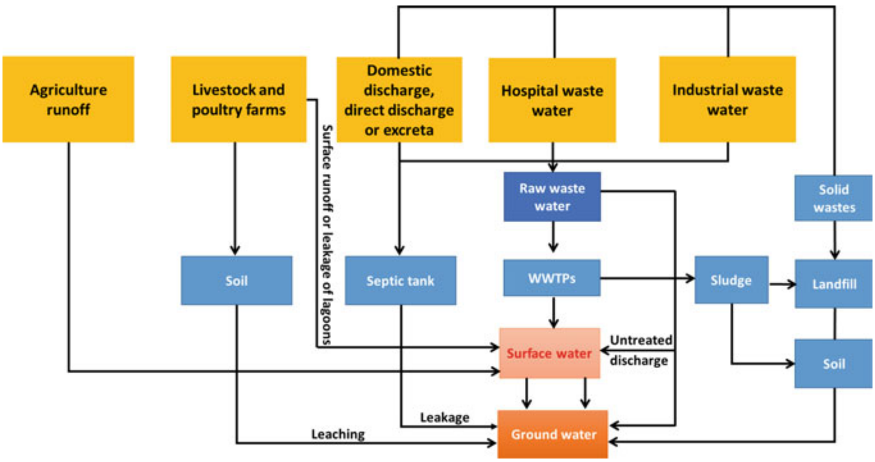

Fig. 2.3 The main sources and possible pollution pathways of ECs accumulation in surface water and groundwater

country. The proper handling of expired and unused drugs is the utmost requirement today through establishing a new regulation over its disposal and counter-sell.

2.6.2 Analytical Methods for Monitoring of ECs

There has been great improvement in analytical tools to achieve better chemical identification and quantification of ECs as well as their metabolites. Conventionally, ultra-violet visible (UV–Visible) spectrophotometry has been employed for the determination of PhACs and other drugs in various types of water matrices. But over the period, there have been advancements in varieties of ECs so new techniques were developed which can even trace the minute concentrations of ECs i.e. ppm or sub-ppm level in surface water, groundwater, and wastewater. The analytical techniques like gas chromatography with mass spectrometry (GC–MS) or GC with tandem MS (GC–MS/MS) and liquid chromatography with mass spectrometry (LC–MS) or LC with tandem MS (LC–MS/MS) are employed for trace level detection of ECs. Amongst, LC–MS/MS is the most preferred analytical technique in ECs detection. LC–MS/MS technique performs the separation and exact detection of co-eluted ECs having similar molecular mass, but different productions. Additionally, MS/MS combination allows better analytical selectivity and sensitivity in complex water samples (Luo et al. 2014; Pal et al. 2014; Rehman et al. 2015; Stefanakis and Becker 2015; Verlicchi and Zambello 2015; Pavithra et al. 2017; Philip et al. 2018; Kasonga et al. 2021).

Besides the trace level detection of ECs, it is also very important to monitor the health impact of these ECs on macroinvertebrates and other organisms in the water. Hershberger assays are generally used to monitor the androgenicity caused by EDCs (Kumar et al. 2008). To make the traditional WTPs capable to treat ECs, they have to be equipped with modern technologies including adsorption, biodegradation, membrane technology, and advanced oxidation processes (AOPs). Further X-rays radiation can be employed for the removal of parabens and EDCs in water. Moreover, the heterogeneous photocatalytic process appears to be more favored for the removal of parabens due to its ability to mineralize parabens in water. However, more work is needed to improve this ability of heterogeneous photocatalysts.

2.7 Conclusions

The emergence of pollutants in wastewater has affected the physiological and reproduction processes of the organism by impairing the functioning biological system inside the body. This has also increased the probability of cancer in human beings and other organisms and developed antibiotic resistance in bacteria. As a result of excessive drugs and their metabolite loading in biota, ARGs have been recorded widely and this can be fatal for the ecosystem which may not be further cured.

So far, any serious research to dive deep over emerging pollutants and their possible effect has not yet been checked thoroughly. Furthermore, the pharmaceutical industry is all overspread in the country but still, the major clusters are concentrated in Maharashtra, Gujrat, West Bengal, Andhra Pradesh, Tamil Nadu Madhya Pradesh, and Goa, but unfortunately, there are very few assessments surfaced to reflect the status of ECs in wastewater and surface water. Hence the authorities and academia responsible for the monitoring of ECs should be more active in fieldwork rather than doing paperwork. Further, time-wise risk assessment and status of all possible ECs in wastewater or surface water present in every province must be updated earnestly on record.

Additionally, WTPs are still not well equipped to treat the wastewater and make it free of ECs. Resultantly, water effluents carrying an abundance of ECs have been carried out to rivers and other open water bodies causing a threat for water bodies as well as human beings.

Therefore, wastewater effluents after treatment from WTPs must be checked for the presence of ECs. WTPs must be equipped with effective detection and removal techniques to ensure the absence of ECs in wastewater effluents. After removal of ECs and mitigating much below the permissible limit wastewater effluents must be discharged to the aquatic system. Additionally, the long-term effect of ECs exposure to the ecosystem must be carefully analyzed to avoid any kind of casualties or incidence of aquatic pollution.

Noteworthy, most of the reported studies reflecting the presence of ECs in diverse environmental matrices including biological samples in India are executed by scientific groups overseas. Various types of possible samples such as influent, effluent, sludge, water, sediment, soil, air, and biological samples were collected from different locations in India and analyzed at laboratories situated abroad. Therefore, a monitoring committee should be established to monitor the time-wise accumulation of ECs into the aquatic system of the country as soon as possible.

Regarding more strict regulation on monitoring of ECs across the country, GOI must make more stringent rules as well as the national authorities responsible to give time-wise report on the risk analysis and status of ECs in Indian aquatic life both surface water and groundwater. Hence there is a suggestion given inspired by the European Union recommendation that each Member of Parliament can submit a monitoring and measuring program to the European Commission, to achieve a good chemical status of the surface water.

Table 2.1 A list of major classes of PhACs depicting potential risks on human health and other organisms

Emerging pharmaceuticals contaminant groups	Contaminants
Human antibiotics and veterinary	Trimethoprim, streptomycin, amoxicillin, lincomycin, sulfamethoxazole, chloramphenicol, Triclosan
Analgesics, anti-inflammatory drugs	Ibuprofene, diclofenac, codein, acetaminophen, acetylsalicilyc acid, fenoprofen, tramadol
Psychiatric drugs (Anticonvulsant)	Diazepam, carbamazepine, primidone, salbutamol
β-blockers	Metoprolol, propanolol, timolol, atenolol, sotalol
Lipid regulators	Bezafibrate, clofibric acid, fenofibric acid, etofibrate, gemfibrozil
X-ray contrasts	Iopromide, iopamidol, diatrizoate
Stimulants	Caffeine, nicotine
Antihypertensive	Triamterene, valsartan, hydrochlorothiazide
Antidepressant	Desmethyl-venlafaxine, antihypertensive, temazepam, venlafaxine hydroxybupropion
Antiepileptic	Phenytoin, pregabalin, lamotrigine, gabapentin
Antihyperlipidemic	Gemfibrozil
Antiarrhythmic	Lidocaine
Drug precursor	Acetophenone

Table 2.2 A list of all possible types of PCPs composed of carcinogenic materials

Emerging PCPs Contaminant groups	Contaminants
Fragrances	Nitro, polycyclic and macrocyclic musks, phthalates (galaxolide, celestolide, tonalide, phantolide, traseolide, musk ketone, musk xylene Cashmeran)
Sun-screen agents	Benzophenone, methylbenzylidene camphor
Shampoos and facial creams	Dimethicone, sodium laureth sulfate, sodium laureth sulfate, cocamidopropyl betaine
Cleansing products	Perchloroethylene, bleach
Toners	Iopamidol, diatrizoic acid
Soaps and detergents	Triclocarban, triclosan

Table 2.3 A list of emerging EDCs in surface water and wastewater

Emerging EDCs contaminant groups	Contaminants
Hormones and steroids	Estradiol, estrone, estriol, diethylstilbestrol (DES), 17-α-Ethinylestradiol
Perfluorinated compounds	Perfluorotoctane sulfonates (PFOS), perfluoroctanoic acid (PFOA)
Surfactants and surfactant metabolites	Alkylphenol ethoxylates, 4-nonylphnol, 4-octylphenol, alkylphenol carboxylates, tributyl phosphate, octylphenols, nonylphenols, di(2-ethylhexyl) phthalate (DEHP)
Flame retardants	Polybrominated diphenyl ethers (PBDEs): polybrominated biphenyls (PBBs), polybrominated dibenzo-*p*-dioxins (PBDDs), polybrominated dibenzofurans (PBDFs), tetrabromo bisphenol A, C10-C13 chloroalkanes, tris (2-chloroethyl)phosphate, hexabromocyclododecane (HBCDs)
Industrial additives and agents	Chelating agents (EDTA), aromatic sulfonates
Gasoline additives	Dialkyl ethers, methyl-t-butyl ether (MTBE)
Antiseptics	Triclosan, chloroprene
Plastic precursor	Bisphenol A, phenol
Food additives	Butylated hydroxyanisole, triethyl citrate
Herbicides	2,4-D, atrazine, bromacil, dDiuron, MCPP, metolachlor, metolachlor ESA, triclopyr
Insecticide	Imidacloprid, carbaryl
Artifical sweeteners	Acesulfame, cyclamate, saccharin, sucralose
Nanomaterials	Inorganic metal oxides
UV-filters	Octocrylene, oxybenzone
Insect repellents	*N,N*-diethyltoluamide

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