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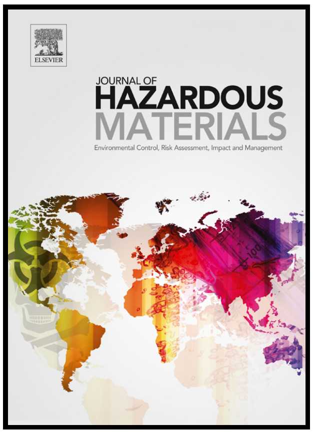

Selected Emerging Contaminants in Water: Global Occurrence, Existing Treatment Technologies, Regulations and Associated Risk

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Selected Emerging Contaminants in Water: Global Occurrence, Existing Treatment Technologies, Regulations and Associated Risk

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Abstract

Emerging contaminants (ECs) in aquatic environments have recently attracted the attention of researchers due to their ubiquitous occurrence and the potential risk they may pose to life. While advance analytical methods have improved global reporting in water matrices, additional information is needed to compile data on their occurrence, existing legislation, treatment technologies and associated human health risks. Therefore, the present study provides an overview of the occurrence of selected ECs, including personal care product, antibiotics, NSAIDs, EDCs and psychiatric drugs, the existing regulatory framework and their toxicological effects on human health. The water matrices under review are the treated wastewater, surface water, groundwater and, in a few cases, drinking water. The study also highlights different treatment technologies available, and evaluates their performance based on the removal efficiency for different classes of ECs. For removal of almost all ECs considered, ozonation integrated with gamma radiation was reported highly efficient. Risk analysis was also performed for selected ECs including diclofenac, ibuprofen, naproxen, carbamazepine, estrone, 17 β-estradiol, bisphenol A, sulfamethoxazole, erythromycin and triclosan. The human health risk analysis indicated the highest number of locations with potential risk due to the EDCs, with South America, Europe and Asia having multiple risks due to estrone and Bisphenol A. The results of this study will give a better insight into the current situation of ECs in the global water matrices, the performance assessment of treatment technologies and the risk analysis will describe the need for more robust regulatory structures around the world to prevent the occurrence of such contaminants in the aquatic environment.

Keywords: Emerging contaminants, Global water matrices, Wastewater treatment, Risk quotient, Guidelines

Abbreviations

ECs	Emerging Contaminants
EDCs	Endocrine Disrupting chemicals
NSAIDs	Non-Steroidal Anti-Inflammatory Drugs (NSAIDs)
PPCPs	Pharmaceutical and Personal Care products
E1	Estrone
BPA	Bisphenol A
E2	17-βestradiol
MOFs	Metal Organic Frameworks
CDM-74	Carbon derived from Zn based MOF-74
MAF-6	Zn based MOF
MBR	Membrane Bioreactor
CWs	Constructed Wetlands
EU	European Union
WHO	World Health Organization
NHMRC	National Health and Medical Research Council
USEPA	United States Environmental Protection Agency

1. Introduction

Water is among the most essential items for sustaining life on the planet. However, as a consequence of population explosion and economic growth, reduced discharge in rivers for extended periods due to climate change (Sjerps et al., 2017), the rapidly accelerated production and utilisation of chemicals (Bernhardt et al., 2017), and enhanced sensitivity of analytical techniques, the amount of chemicals present in water is also increasing rapidly (Sjerps et al., 2016). To provide an example of the scale of this issue, within the European Union (EU) there are more than 100,000 registered chemicals (EINECS) (Schriks et al., 2010), of which 30,000–70,000 are in daily use. Furthermore, it is estimated that nearly 300 million tons of synthetic compounds annually used in consumer and industrial products, partially end up in natural waterways (Schwarzenbach et al., 2006). Following the increasing concerns, researchers from eight countries at United Nations Environment Assembly, 2020 called for the establishment of a global body to direct the efforts to monitor chemical waste in the environment (Adeleye et al., 2022; Snow et al., 2018).

Environmental contaminants in water have a long history, focusing initially on legacy contaminants like organic pollutants and heavy metals. Subsequent to this, the development of more sophisticated analytical methodologies has enabled the identification of emerging contaminants (ECs) in the environment at low concentrations (Adeleye et al., 2022; Snow et al., 2018). Emerging contaminants are pollutants which are present in the environment for an extended period, yet have only been recently identified and characterised. Alternatively, ECs are a class of compounds that have recently been identified in aquatic environments and their presence in water is a potential threat to the environment, humans, and aquatic life (Gumbi et al., 2017). Pesticides, pharmaceuticals, personal care products, endocrine disrupting chemicals (EDCs), microplastics, and flame retardants are some of the few examples of contaminants of emerging concern (Houtman, 2010). Since most of the pesticides have been regulated, they are also categorised as priority micropollutants (Glassmeyer et al. 2017; Peña-Guzmán et al. 2019; Sousa et al. 2018). In 1962, the release of American biologist Rachel Carson's book "Silent Spring" was one of the first and most significant steps in making humanity aware of the existence of such unregulated contaminants and paying attention to their harmful impacts. In that work, Carson raised concerns over the extensive use of biocide dichlorodiphenyltrichloroethane (DDT) and other persistent contaminants for agricultural practices. Though the concentrations of these contaminants were in the range of ng/L to µg/L but a continuous exposure to them can have a negative impact on the health of the ecosystem and its sustainability (Carson, 2002; Houtman et al. 2010).

Emerging contaminants can enter the environment through various pathways. If considering chemicals that are ingested into the living body viz, illicit drugs and pharmaceuticals, are incompletely utilized by the body and are passed in faeces and urine further (Zuccato et al., 2006). Others, like personal care or cleaning products are disposed of via drainage system (Daughton and Ternes, 1999). Furthermore, where infrastructure is available these contaminants are transported to wastewater treatment plants (WWTPs) via sewage system (Chiavola et al., 2019). As outlined by Wen et al. (2021) the treatment technologies for ECs are majorly classified in two broad categories of conventional and advanced treatment processes. The technologies utilized by current WWTPs are not able to completely remove the ECs, this was possibly due to the complex structure and non-biodegradability of these compounds and also due to their low concentration of occurrence (Alvarino et al., 2018; Sheng et al., 2016). The natural attenuation processes, which encompass mechanisms including sorption, dilution, volatilisation, photolysis, and biodegradation, offer a comparatively straightforward and cost-effective approach to remediation. However, these processes may exhibit reduced efficiency and efficacy in certain contexts (Barbosa et al., 2016; Rout et al., 2021). Nevertheless, the removal of ECs via activated carbon and biochar had the centre of focus in research related to EC removal technologies (Bedia et al., 2018; Sophia A. and Lima, 2018). Additionally, high solubility in water and the polarity of ECs reduced the removal efficiencies through physical techniques like sedimentation and flocculation. Whereas over the past few decades, conventional and advanced treatment techniques have gained more attention (Chen et al., 2021), regardless of the high energy and cost requirements of these processes. In light of this hybrid systems have been identified as potential replacements for conventional technologies, with a view of capitalising on the relative strengths of different techniques (Ahmed et al., 2021).

It is evident that a number of ECs have been identified in the drinking water systems, yet the extent of their potential risks to health is unknown. Moreover, the contamination of global water resources due to the presence of emerging contaminants is quite clear. In China (Bao et al., 2020; Hao, 2020; Lin et al., 2017), Malaysia (Shehab et al., 2020), US (Barber et al., 2015; Karalius et al., 2014), Austria (Brueller et al., 2018), Philippines (Katrina and Espino, 2020), India (Joshua et al., 2020), Germany (Gerhardt, 2019), Netherlands (Belfroid et al., 2002), Mexico (Calderón-Moreno et al., 2019) and many more ECs have been identified in different water matrices. These findings imply that the occurrence of ECs in water is a worldwide issue.

The concentration of ECs in water is primarily influenced by the pattern of water usage, catchment characteristics, per capita consumption, environmental persistence and others (Patel et al., 2019; Tran and Gin, 2017). Recent studies highlighted the unregulated, untreated, or partially treated discharge of ECs in the environment, due to lack of strong regulatory structure and insufficient data about the toxicity and fate of the ECs. Addressing the recent concerns some global agencies have started to work on the establishment of interim aquatic guidelines. Moreover, agencies like the United States Environmental Protection Agency (USEPA) (Contaminant Candidate List 4, 2016), European Union (EU) (European Union Directive 2013/11/EU, 2013), World Health Organization (WHO) (WHO, Guidelines for Drinking-Water Quality, 2011) and other responsible bodies have developed a list of priority pollutants consisting of contaminants that can have adverse effects on human health and aquatic biota.

So far, the existence of ECs from different water matrices has been the subject of numerous studies but, most of them have only examined a particular class or geographical region. Additionally, only a handful of studies have assessed the potential toxicity by comparing the concentration in environmental matrices and the available toxicological data. For example, Morin-Crini et al. (2022), Parida et al. (2021), Ramírez-Malule et al. (2020), and Sousa et al. (2018) have recently conducted comprehensive reviews of the existing literature on the occurrence of ECs in the global water matrices. Although these studies have covered diverse geographical regions worldwide, they have collectively failed to provide sufficient information regarding the potential risks these compounds may pose to human health. Contrary to this, Baken et al. (2018) and Sharma et al. (2019) recently carried out the risk assessment of ECs present in water with the limitation being the extent of the geographical area focused in the studies. Therefore, to bridge this knowledge gap, present work was conducted with an aim of providing a comprehensive review of existing literature on the occurrence of different group of ECs, including antibiotics, NSAIDs, EDCs, psychiatric drugs, and personal care products in the global water matrices, majorly consisting of treated wastewater, surface water, groundwater and lastly few cases of drinking water. Furthermore, the potential risks to human health were calculated on a global scale for the concentrations of selected ECs in surface water, groundwater and drinking water matrices, expressed as risk quotients (RQ). In particular, the drinking water equivalent limits were compared with the maximum detected concentrations in water to derive the estimated RQ. In particular, the drinking water equivalent limits were compared with the maximum detected concentrations in water to derive the estimated RQ. Additionally, the study also assessed the potential conventional and hybrid treatment technologies to bring down the concentration of ECs in treated water. Also, a review is conducted about the performance of different technologies and the cost associated to get a better idea about the economical implementation of any technology at larger scale.

2. Emerging contaminants

For the convenience of the readers, following sections few major classes of EC's are discussed in terms of their occurrence and respective impact on organisms.

Endocrine disrupting compounds (EDCs): Back from 1990s, evidence has been accumulating that some natural and artificial chemicals in the environment can unsettle the endocrine (hormonal) functionality of the organisms that are exposed by imitating or obstructing the action of hormones (Colborn et al., 1993). Exposure to these chemicals may result in adverse health effects, collectively termed as endocrine disruption. The impacts of these can be observed in a wide range of biological processes viz. fertility, development, growth and reproduction. Among the EDCs estrogenic compounds like 17 β-estradiol (female sex hormone) have been given the highest attention. In this respect, the most prominent effect observed is the intersexuality in the male fishes in different parts of the world (Houtman et al., 2007; Jobling et al., 1998; Kirby et al., 2004; Solé et al., 2003; Vethaak et al., 2005). The endocrine system of humans is similar to vertebrates like fish, and thus the exposure to EDCs may also present certain health risks for humans. Moreover, it has been postulated that there is a correlation between environmental contaminants and human reproductive health, particularly in relation to declining sperm counts, breast cancer, testicular cancer, and increased occurrence rates of other reproductive disorders, including male infertility (European Environment Agency, 1997; Sharpe and Skakkebaek, 1993). However, despite the apparent correlation between the two variables, a causal relationship has not yet been definitively established (Daston et al., 2003).

Pharmaceuticals: Pharmaceuticals are today one of the keystones of modern Western society. Without pharmaceuticals, many of our current standards of living would not be possible. A great number of pharmaceuticals are utilised today which include antibiotics, pain killers, lipid regulators, anti-depressants, X-ray contrast media etc. (Richardson, 2008). The release of pharmaceutical compounds in the environment has been acknowledged by researchers for decades. Despite this long-standing awareness, the full significance of this phenomenon has remained underappreciated for an extended period. One contributing factor may be the tendency for the regulation of pharmaceuticals to be overseen by health agencies, which may possess limited expertise when it comes to the intricacies of environmental issues(Daughton and Ternes, 1999). An estimate suggests that as much as 65% of all pharmaceuticals sold are never actually consumed (Ruhoy and Daughton, 2008). Moreover, a considerable quantity of pharmaceuticals, such as anti-inflammatory drugs and antibiotics, are not effectively removed by sewage treatment. These substances are commonly used in the veterinary sector to treat cattle in feedlots, where they can directly contaminate surface water through runoff during precipitation. A number of evidence are available reporting the inefficacy of drinking water treatment technologies in eliminating pharmaceutical compounds, with their presence in the drinking water in trace levels (Cooney, 2009; Versteegh et al., 2007).

Personal care products: Personal care products are defined by their active ingredients, which are used for the preservation of cosmetics, toiletry, and fragrance products. The aforementioned ingredients are employed to alter the olfactory, visual, physical, and gustatory characteristics of these products (Daughton and Ternes, 1999). There can be a variety of personal care products like polycyclic musks used as fragrances then the parabens present in the shampoos, creams etc. to prevent bacterial decomposition. Moreover, disinfectants like clorophene and triclosan are used at large scales. For instance, triclosan is used in a variety of products ranging from hand soap and toothpaste to socks and toys (Petrović et al., 2003). Furthermore, benzophenone present in sunscreen has caught the eye of many environmental scientists and biologists. The worldwide occurrence of personal care products in effluents and surface waters has been reported regularly (Daughton and Ternes 1999; Rahman et al. 2009). It has been observed that some of these compounds can accumulate in exposed organisms (Houtman et al., 2004) while some are believed to have possible adverse effects such as mimicking hormonal activity (parabens, UV blockers), extreme bioaccumulation (musks) and toxicity (UV blockers) (Daughton and Ternes, 1999; Rahman et al., 2009).

Pesticides: The use of pesticides in agricultural and horticultural practices, including the application of fungicides, herbicides, insecticides, bactericides, and defoliants, plant growth regulators, has been a topic of concern for surface water quality for many decades. Following the Second World War, relatively nonpolar and substantially persistent pesticides, such as aldrin, chlordane and DDT led to significant increases in crop security and the production of food. But the bioaccumulation possibility of these compounds led to adverse effects on the ecosystem, as evident from the findings of the "Silent Spring" by Rachel Carson (Carson, 2002). Pesticides nowadays are polar and relatively less persistent. After application, these can reach surface waters through runoff, drift, drainage etc. Due to the long history of pesticide usage, the European Union has established regulations limiting the amount of pesticides permitted in drinking water: 500 ng/L for cumulative concentration of pesticides and 100 ng/L for individual compounds (Houtman, 2010).

Perfluorinated compounds: Perfluorinated compounds, such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), are notable for their unique chemical properties: they are both lipophobic and hydrophilic, exhibiting a high degree of repellence to water, lipids, and oil. These substances are employed as repellents for water, dirt, and grease, as well as sprays and coatings and for textiles, leather, and in PTFE (Teflon) non-stick cookware. The growing concern about perfluorinated compounds can be attributed to their apparent persistence, their tendency to accumulate within organisms, as well as their documented toxicity, which includes interference with development and carcinogenicity (Mclachlan et al., 2007; Skutlarek et al., 2006). A number of studies have indicated the presence of perfluorinated compounds in aquatic environments across the globe (Dalahmeh et al., 2018; Eschauzier et al., 2013; Essumang et al., 2017; Kumar et al., 2023; Stroski et al., 2020)

Microplastics: The term "microplastics," defined as plastic particles less than 5 mm in size, has emerged in the past few decades as a significant environmental contaminant. These microscopic particles are derived from diverse sources, including the disintegration of larger plastic fragments, and synthetic fibres derived from textiles and microbeads present in personal care products. Once released into the environment, these micro compounds are found to be present in a wide range of habitats, including both marine and freshwater ecosystems, as well as terrestrial and even atmospheric settings (Thompson et al., 2004; Barnes et al., 2009). The ubiquitous presence of microplastics in the environment is a cause of concern due to their ability to serve as carriers of dangerous substances, such as heavy metals and persistent organic pollutants (POPs), which can adhere to their surfaces (Rochman et al., 2013). The ingestion of these particles by organisms across different trophic levels from fish to zooplankton and even humans can lead to various adverse effects, including physical blockages, the absorption of toxins by the organism's body, and the possible biomagnification of these toxins through the food chain (Cole et al., 2011; Wright et al., 2013). A number of studies have documented the presence of microplastics in some of the remotest regions of the earth. These include the Arctic and the deep ocean trenches, which suggest a wide distribution and ubiquity of these pollutants (Obbard et al., 2014; Van Cauwenberghe et al., 2013).

Flame Retardants: Flame retardants are a class of synthetic chemicals employed in the manufacture of a wide variety of materials, including plastics, textiles, and foams used in the production of computer cases, televisions, clothes, and upholstered furniture. The objective of their use is to inhibit combustion in the event of fire (Houtman, 2010). Previously, the primary compounds utilized for this purpose were polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDE). These substances possess structural similarities to the "classical" contaminants, namely polychlorinated biphenyls (PCBs), and exhibit analogous behaviour in the environment as well. It has been documented that Brominated flame retardants are present in the tissues, blood, and breast milk of both wild and captive animals, as well as humans (Rahman et al., 2001). This is a cause for concern, as previous research has identified several potentially toxic properties of these compounds and related products. These include their capacity to disrupt the thyroid, hormonal systems (Legler, 2008); toxicity to the nervous system; and the possibility that they may also be carcinogenic (Richardson, 2009). Due to their low solubility in water, these compounds tend to sorb to river sediments, rather than accumulating in water bodies at high concentrations (Rahman et al., 2001).

3. Methodology

3.1. Data collection

The review was compiled using literature sourced from google scholar, web of science, ResearchGate, and others with the keywords "emerging contaminants, water and name of the continents or top countries contributing to the majority of the area in each continent." The primary set of literature was grouped according to the continents to which the study region belongs. The broad categories of ECs considered in this study were antibiotics, NSAIDs, EDCs, psychiatric drugs and personal care products. Furthermore, the discussed removal efficiencies for different classes of emerging contaminants were directly taken from the previously published research articles. Moreover, the risk was calculated for three age groups including infants, children and adults. The use of age-specific assessments of exposures has been previously employed in order to reduce uncertainty in risk assessment (de Jesus Gaffney et al., 2015; Yang et al., 2017).

3.2. Estimation of human health risk

For the risk analysis, the ten most commonly occurring contaminants from the abovementioned categories were selected. The worst-case scenario of possible health risk due to the presence of selected ECs in water matrices around the world was estimated in terms of risk quotients (RQ). In this study, an age specific RQ for each selected contaminant was estimated by dividing the maximum measured concentration in water by the provisional guideline value (Eq. 1) (Schriks et al., 2010; Sharma et al., 2019).

$$RQ = \frac{MC_D}{DWEL} \qquad (1)$$

Here, MC_D is the maximum detected concentration in water and DWEL is the drinking water equivalent level. The DWEL values for all three age groups were calculated using Eq. 2,

$$DWEL = \frac{ADI(or\ RSD) * BW}{DWI * AB * FOE} \qquad (2)$$

Where ADI/RSD (μg/kg/day) is the acceptable daily intake/risk specific dose. The values of ADI or RSD for each contaminant were obtained from various agencies like WHO, USEPA, EU, National Health and Medical Research Council (NHMRC) etc. BW and DWI is the average body weight (kg) and drinking water intake (L/day) for respective age groups (Leeuwen, 2000) (Table S1 and S2). AB, the gastrointestinal absorption rate was assumed to be 1 and FOE is the frequency of exposure (350/365 days) (Sharma et al. 2019). An RQ value of greater than 1 showed the possibility of human health risk and an RQ value of less than or equal to 0.2 indicated no appreciable risk, whereas values ranging between 0.2 to 1 indicated the need for a more detailed assessment (Schriks et al., 2010; Yang et al., 2017).

4. Treatment technologies

Considering the treatment mechanisms and the aspects of the processes involved, the wastewater treatment techniques can be classified into four main categories: physical, chemical, biological, and hybrid methods. Primarily, these techniques are incorporated into water and wastewater treatment plants with the objective to produce safe water suitable for drinking and disposal respectively. The following sections provide a detailed insight into functionality and principles of the existing wastewater treatment technologies.

4.1. Physical treatments

Physical treatments relate to the removal of the ECs from wastewater without altering the biochemical properties of the contaminants present in water, given that such techniques avoid the use of any chemical or biological agents. Usually, physical treatments act as predecessors to the advanced treatment technologies i.e., chemical and biological treatments in a multistage treatment setup. Screening, sedimentation, aeration, membrane-based filtration are few of the most commonly employed physical treatment techniques (Samsami et al., 2020). The most highlighted advantage of these techniques is their technically simple and flexible approach which allows high adaptability of such techniques in various treatment strategies (Ahmed et al., 2021).

4.1.1. Effect of pre-treatment processes on ECs removal

When considering different classes of emerging contaminants, the effect of pre-treatment processes such as sedimentation and flocculation on ECs in wastewater may vary. For instance, due to their high solubility in water, the majority of pesticides and pharmaceutical contaminants will remain soluble in water and will have a removal efficiency of less than 10% (Ahmed et al., 2016). Whereas in case of microplastics a removal efficiency between 35% to 59% is reported after pre-treatment (Sun et al., 2019). Burns and Boxall, observed that roughly 65% of the microplastics are eliminated during the primary treatment stage (Burns and Boxall, 2018). Additionally, microplastics can be trapped during the gravity settling and the grit removal phase. Studies conducted by Gies et al. (2018) and Bayo et al. (2020) reported that during the primary treatment stage the microplastic removal efficiency can be 92% and 74% respectively. Similarly, Long et al. (2019) studied the influence of the shape of microplastics on the removal efficiency in the primary treatment stage, the findings reported that fibre and pellet shaped particles were removed up to 79% and 83% respectively, whereas for granules and fragments efficiency was found to be 91%. Overall, it should be noted that more advanced techniques are required for the proper removal of ECs from the water.

4.1.2. Effect of adsorption on ECs removal

Adsorption in the past has been considered a powerful technique for the removal of ECs considering the strong binding ability of the majority of the emerging contaminants such as pharmaceutical and personal care products (PPCPs), NSAIDs and others. The main advantages of adsorption over other strategies are low cost, regeneration of the adsorbents, technically simple and many more (Eniola et al., 2022). As the adsorption process is influenced by the properties of both the adsorbent and the contaminant, with contaminant properties such as charge, structure, size and solubility determining the binding of contaminant species to the adsorbent surface. A variety of natural and synthetic materials have been used as sorbents for the removal of ECs from water, including zeolites, agricultural waste, clay, polymers etc. Some of the most common and effective have been summarised.

4.1.2.1. Natural materials

Clay minerals are the most commonly used adsorbents for water treatment, numerous studies in the past reported the use of different clay materials for the removal of ECs from water. For example, Theibault et al. (2015) in a study used sodium smectite for the removal of doxepin and tramadol by adsorption. The Langmuir adsorption isotherm analysis revealed that ECs adsorbed on the clay bed reached 223.5 and 263.4 mg/g for tramadol and doxepin, respectively.

Another natural (synthetic in some instance) absorbent commonly used for the removal of ECs is zeolite (Gupta and Suhas, 2009). A study presented by Maetucci et al. (2012) investigated the efficiency of adsorption for different organophilic synthetic zeolites (Y, ZSM-5, and MOR) for removal of carbamazepine, erythromycin, and levofloxacin. Zeolite Y performed best with removal efficiency of 100, 42, 45 mg/g respectively. Overall, the study found that various materials have varying effects on different drugs, which may be attributed to differences in their interactions and structures.

4.1.2.2. Agricultural waste

Agri-wastes are generated by agricultural activities and the food processing industry in some cases. Rice husks, soybean shells and coconut shells are examples of agricultural wastes. These products contain functional groups such as cellulose, starch and lignin in their composition. These active surface groups on various agricultural waste products used as sorbents make these products a potential alternative to commercial sorbents (Sulyman et al., 2017).

Liu et al. (2013) used rice straw to remove clofibric acid and carbamazepine. The absorbent showed significant results with adsorption of 14.3×10^3 mg/g for clofibric acid and 4.01 mg/g for carbamazepine. In a similar study, Isabel grape bagasse waste (a residue from grapefruit processing, mainly in wineries) was evaluated for its ability to remove diclofenac sodium from water. From the reported results, the Langmuir q_{max} was found to be 76.9 mg/g, with the percentage of diclofenac sodium ranging from 16.4% to 22.8%. Generally, sorbents based on agro-waste have proved to be a promising alternative treatment for wastewater containing ECs (Antunes et al., 2012).

4.1.2.3. Synthetic and modified adsorbents

To enhance the adsorption capacity the physicochemical characteristics of the absorbent materials are many times altered (Eniola et al., 2022). For example, Cabrera-Lafaurie et al. (2014) modified the zeolite Y by introducing surfactants and transition metals; to enhance the adsorption of carbamazepine and salicylic acid this increased the adsorption for salicylic acid from 0.03 to 3.9 mg/g. A Titanium oxide pillared clay (Ti-PILC) having improved microporosity and surface area than natural montmorillonite was also developed to enhance the removal efficiency for various ECs. This improved Ti-PILC showed removal efficiency for 82.68, 23.05, 20.83 and 4.26 mg/g for imipramine, diclofenac-sodium, paracetamol and amoxicillin respectively (Chauhan et al., 2020). Another sorbent was synthesised by Eniola et al. (2020) to develop a modified nanocomposite ($CuFe_2O_4$/NiMgAl-LDH) with magnetic properties and a sheet-like layered structure, by incorporating metal oxide nanoparticles with an LDH. The modified sorbent was tested against oxytetracycline, and the performance compared with NiMgAl-LDH and $CuFe_2O_4$ (the precursors). The adsorption capacity was found in the order $CuFe_2O_4$ (106 mg/g) < NiMgAl-LDH (116 mg/g) <

$CuFe_2O_4$/NiMgAl-LDH composite (192.5 mg/g). The composite's adsorption capacity for ECs increased due to modifications made to the functional group and metal ions on its surface.

Bhadra et al. (2020) reported the use of metal-organic frameworks (MOFs) to synthesise nanomaterials containing metals and non-metals. As compared to non-pyrolyzed MOF carbon drive from MOF (CDM-74) (i.e. carbon derived from Zn based MOF-74) showed a higher adsorption for N, N-diethyl-3-methylbenzamide (DEET), chloroxylenol, and oxybenzone due to high porosity and acidic functionality of the carbon-derived form of MOF. Similarly, An et al. (2018) developed a porous carbon from MAF-6 (Zn based MOF) that demonstrated an exceptionally high adsorption for ibuprofen and diclofenac.

Ravi et al. (2020) was the first to evaluate the removal of caffeine and carbamazepine using a phosphate (-PO_3OH) based organic absorbent. Two synthesised materials showed high microporosity around 19.6% and 32.5% and surface area of 714 and 581 m^2 /g. In the past years, new sorbent materials were synthesised at a comparatively high rate, this might be due to high stability, surface area and pollutant binding ability of the same. The efficiency of these materials largely depends on parameters such as time, pH, temperature, and nature and concentration of the contaminant. The solution pH and surface charge of the adsorbent plays a vital role in binding of the pharmaceutical pollutants on the material surface (Eniola et al., 2022).

4.1.3. Membrane technology

The most commonly used membrane technologies for water treatment includes microfiltration, ultrafiltration, nanofiltration and reverse osmosis. This classification of techniques is purely based on the pore size characterization of the membranes used. For example, for microfiltration the pore size is about 0.04–0.1 μm and is 0.001-0.02 μm of ultrafiltration. Microfiltration is a process used to remove bacteria and viruses. Whereas nanofiltration can eliminate divalent salts and metal ions, pesticides, and other substances from the effluent. Reverse osmosis and nanofiltration are more energy-intensive than micro and ultrafiltration. However, they can produce better quality effluents (Khanzada et al., 2020).

4.1.3.1. Microfiltration

The microfiltration membrane process has been in use since the 19th century and has proven to be an efficient technique for the treatment of water containing various pollutants (Anis et al., 2019). These membranes can be used alone or in combination with other treatment methods, such as advanced oxidation for a better removal of emerging contaminants (Ba et al., 2018). A study recently reported the capability of microfiltration membranes in removing the ECs such as pharmaceuticals via electro-oxidation. The study revealed that as the permeate flux of the membrane filter increased linearly from 74-216.4 L/m^2 /h, the microfiltration membrane successfully degraded sulfamethoxazole with a removal efficiency of 85% (Yu et al., 2020).

4.1.3.2. Ultrafiltration

Ultrafiltration is a low-pressure membrane technology that is used for the removal of a variety of organic contaminants (Kim et al., 2016). Yoon et al. (2007) evaluated the interaction mechanism between the ultrafiltration membrane and 24 different emerging contaminants including the EDCs and pharmaceuticals in different water matrices i.e. drinking, wastewater and others. The source and chemistry of the water affected the adsorption of the targeted ECs. The study also compared the retention capacity of the ultrafiltration membrane with the nanofiltration membrane, and the latter was found to have the better adsorption capacity. Additionally, the study also reported that out of 27 targeted contaminants, 14 and 8 showed 100% retention on ultra and nanofiltration respectively and the retention for the remaining compounds was in the range 40-75 %. Similarly, a study modified the ultrafiltration membrane by ingesting with Cu_2O photocatalyst and tested it over ibuprofen. The results of the study revealed that the membrane successfully removed 85% of the ibuprofen with rate of removal of 32.63×10^{-3}/min under visible light conditions (Singh et al., 2019).

4.1.3.3. Nanofiltration

Nanofiltration (NF) membranes have been used to remove various ECs. It uses a pressure gradient as the driving force (Licona et al., 2018). A study evaluated the performance of NF 90 (a commercially available nanofiltration membrane) for the removal of five pharmaceuticals namely: ibuprofen, acetaminophen, dipyrone, caffeine, and diclofenac. As per the results reported the targeted drugs showed greater than 88% rejection with ibuprofen and diclofenac showed a rejection of more than 90%. Maryam et al. (2020) tested the removal efficiency of two nanofiltration membranes NF10 and NF 50, the authors reported that the breakdown of ECs from a mixture might reduce the removal efficiency of the membranes. For all the targeted compounds NF10 provided less than 10% removal efficiency. Whereas NF 50 on the other hand showed removal efficiency in the order of paracetamol (49%) < ibuprofen (81.2%) < diclofenac (99.7%), but in case of mixture the removal efficiency for diclofenac abruptly reduced to 23%.

4.1.4. Reverse osmosis

Reverse osmosis (RO) is a technology widely used to produce fresh water from seawater and brackish water. Also, it has been used to decontaminate wastewater (Goh et al., 2019). As reported by Kimura et al. (2004) RO was successful in removing some of the pharmaceutically active compounds and some uncharged EDCs. The results highlighted that for carbamazepine the cellulose acetate membrane had 85% rejection, while for polyamide membrane it reached 91%. Khan et al. (2004) reported that RO can be highly efficient in the removal of emerging contaminants like pharmaceuticals. Furthermore, the commercially available RO membrane (BW30) is evaluated for the removal of ibuprofen, dipyrone, diclofenac, caffeine and acetaminophen. The range of removal efficiencies for different pharmaceuticals at different conditions were ibuprofen (99.05-99.15%), dipyrone (98.88-99.03 %), diclofenac (99.10-99.71%), caffeine (86.44-96.1%) and acetaminophen (89.47-95.85%). The study reported respectively lower rejection for Caffeine and Acetaminophen might be due to the highly hydrophilic nature of both the compounds (Licona et al., 2018).

4.2. Chemical treatments

4.2.1. Chlorination

Most chemical oxidation processes have been shown to be highly effective in the degradation of EC in wastewater by oxidising them to a less toxic form. In some cases, bromine and gaseous chlorine/hypochlorite have also been utilised in wastewater treatment. Noutsopoulos et al. reported the use of chlorine for the removal of ECs from water. For pharmaceuticals naproxen and diclofenac, the removal was found to be the highest with efficiency of 95% and 100% respectively (Noutsopoulos et al., 2014). However, for other ECs like nonylphenol, nonylphenol diethoxylate, nonylphenol monoethoxylate, triclosan, bisphenol A, ketoprofen and ibuprofen the efficiency ranged from 34% to 83% (Noutsopoulos et al., 2015). Similarly, (Real et al. (2015) for the case of ECs like amitriptyline hydrochloride, methyl salicylate and 2-phenoxyethanol the rate of reaction of chlorination was three times lower than that of ozonation. Additionally, chlorine and chlorine dioxide are strong oxidising agents that can produce by-products when treating wastewater, and the extent of mineralization achieved can be unsatisfactory (Rivera-Utrilla et al., 2013).

4.2.2. Ozonation

Ozonation is an oxidation process that uses ozone (O_3) to oxidise ECs. This technique shows an impact in significantly reducing the load of ECs in wastewater (Hollender et al., 2009). Ozone can react with ECs directly or indirectly through the formation of secondary oxidants (hydroxyl radicals) as a result of ozone reacting with a particular class of ECs, such as phenols or amines (Rizzo et al., 2019). Ozone is a potent oxidising agent that selectively reacts with aromatic rings and double bonds of ECs having a high electron density like sulfamethoxazole and trimethoprim (Barbosa et al., 2016; Gogoi et al., 2018). At a dose of 5000 µg/L ozone can successfully remove more than 95% of carbamazepine, diclofenac, sulpiride, trimethoprim and indomethacin (Sui et al., 2010). As reported by de Oliveira et al. (2019) the degradation of ECs by ozonation largely depends on the factors viz. temperature, pH and ozone dose and the formation of by-products during the process is still a concerning issue.

4.2.3. Fenton process

Fenton oxidation is another conventional method for oxidation. In this process, hydroxyl radicals are generated after the reaction of ferrous ions with hydrogen peroxide, which are effective in reducing the toxicity of organic contaminants in wastewater. However, this process has some clear limitations, such as the narrow pH range it can operate within, as well as the associated risks and costs of transporting, storing and handling the necessary reagents (Zhang et al., 2019). Another drawback of the process is the accumulation of Fe as $Fe(OH)_3$, and the unintended consumption of OH* to form OH_2* (Ahmed et al. 2016). Considering the related limitation some modifications in the Fenton process were also recommended. For instance, Shen et al. (2019) designed a catalyst similar to Fenton to replace the centred iron matrix for better degradation of ECs like sulfamethazine. Sönmez et al. on the other hand assessed the performance of Fenton process while removing carbamazepine, caffeine and paracetamol from spiked tap water. The study reported the influence of Fe^{2+} and H_2O_2 concentrations on the removal efficiency. The removal of carbamazepine, caffeine and paracetamol at different optimal concentration of Fe^{2+} and H_2O_2 for each compound is reported as 99.77%, 99.66% and 99.11% respectively with caffeine and paracetamol having higher optimal concentrations (Sönmez et al., 2022). A review about the removal of pharmaceuticals of from water by homogeneous and heterogeneous Fenton processes was carried out by Mirzaei et al. (2017). The study reported the removal efficiencies of different Fenton processes ranging from no significant removal in drug manufacturing sewage to complete degradation of antibiotics in distilled water.

4.2.4. Photolysis

Photolysis is the process by which hydroxyl free radicals form when energy from electromagnetic radiation breaks down water molecules. This process can occur with various radiation sources, such as solar and UV radiation (Choi et al., 2020). Recent studies have shown that electro-magnetic energy, together with powerful oxidants such as ozone or H_2O_2, can be used to decontaminate water containing ECs associated with pharmaceutical products (Ali et al., 2017b). A study evaluated the performance of photolysis in removing the selected pharmaceuticals (fluoxetine, carbamazepine, atenolol, and trimethoprim). Reported findings suggested that if water containing targeted ECs is nitrated and exposed to solar or UV light, it can lead to the degradation of compounds via photolysis. The degradation mainly resulting from the oxidation of hydroxyl radicals was lowest for trimethoprim (47%) followed by carbamazepine (50%), fluoxetine (57%) and highest for atenolol (60%) (Hora et al., 2019).

The fate of 16 ECs undergoing photodegradation was studied in controlled conditions under simulated sunlight. The treatment process effectively degraded carbamazepine, trimethoprim, atenolol, ranitidine, diclofenac, warfarin, sulfamethoxazole and ciprofloxacin. These drugs are resistant to wastewater treatment processes. However, some drugs may be transformed into other toxic parent compounds by photolysis. For example, carbamazepine was transformed into acridine, carbamazepine-10, 11-epoxide, and 10, 11-dihydro-10, 11-dihydroxy-carbamazepine and diclofenac degraded into carbazole-1-acidic acid and 8-chlorocarbazole-1-acetic acid. Additionally, acetaminophen irradiation resulted in ethenone. The contaminants degraded at different rates when exposed to light, with some degrading completely in less than 15 minutes and others taking up to 63 minutes. This suggests that exposure to natural sunlight can cause partial or complete degradation of these and other emerging contaminants by photolysis (Ali et al., 2017).

4.2.5. Photo-Fenton

The Photo-Fenton process is a combination of the Fenton process and ultraviolet radiation (Barrera-Salgado et al., 2016). This technique can effectively degrade ECs like pharmaceuticals present in wastewater (Alabdraba et al., 2018). One disadvantage of photo-Fenton is its high catalyst consumption and the production of iron sludge. However, the photo-Fenton method was successful in decontaminating the effluent of a municipal wastewater treatment plant that contained pharmaceuticals (Klamerth et al., 2010). Dong et al.

(2019) in a study reported more than 92% degradation of carbamazepine and ibuprofen under different conditions in a photo-fenton process.

4.2.6. Photocatalysis

Photocatalysis is an advanced oxidation process (AOP) that requires the use of catalysts to facilitate the transfer of energy from photons to water molecules. According to Ahmed et al. (2021), the most extensively investigated photocatalysis technique for eliminating contaminants and microorganisms from wastewater is TiO_2 photocatalysis. Moreover, the use of ZnO has also been reported to oxidise the contaminants like tetracycline and carbamazepine using photocatalysis. However, the highlighted drawback of this material was that at low working pH, it can get corroded. The removal of ECs using photolysis generally follows the order of pesticides < analgesics pharmaceuticals < EDCs and for all other pharmaceuticals it was found to be the lowest (Ahmed et al., 2017).

Figure 1 presents a comparative assessment of removal efficiencies of different chemical treatments in case of different ECs. The figure illustrates that, with the exception of EDCs UV photolysis/H_2O_2 and Photo Fenton were the two most effective methods for removal of ECs. Although, ozonation and UV photocatalysis showed a high removal of EDCs but a relatively lower removal of NSAIDs was observed in case of ozonation while UV photocatalysis was highly underperforming in case of beta blockers and lipid regulators. Additionally, the figure also shows a notable inefficiency of UV photolysis among chemical treatments, with poor removal of lipid regulators, beta blockers, and analgesics (Fig. 1).

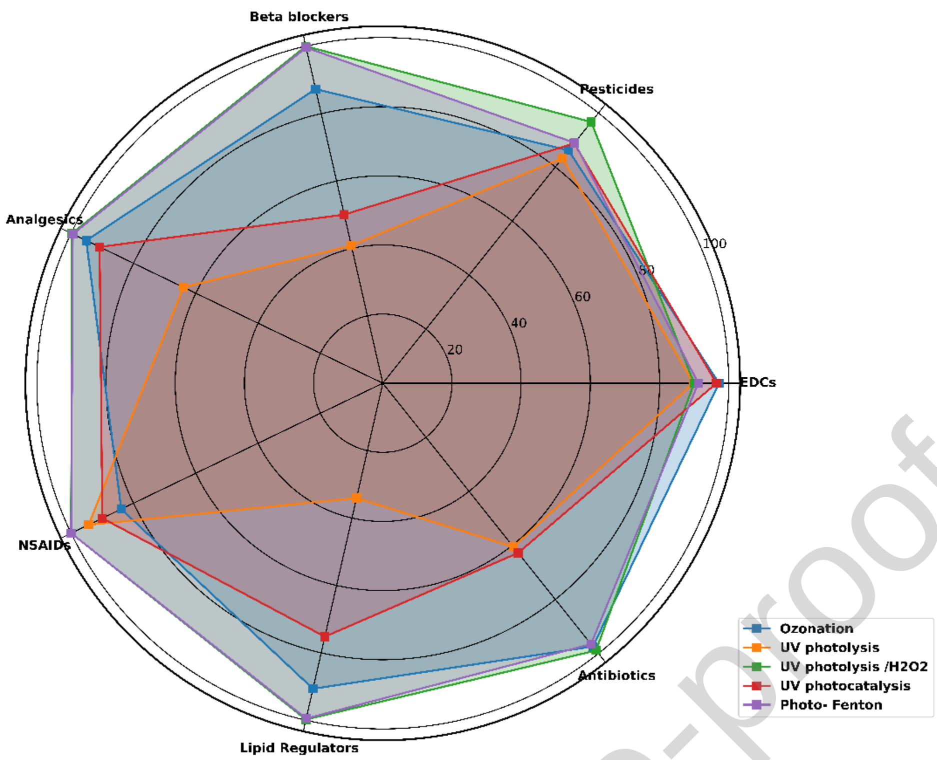

Fig. 1. Efficiency of different chemical treatment processes in removing various groups of ECs from water matrices

4.3. Biological treatments

4.3.1. Aerobic and anaerobic techniques

Aerobic treatment has faster degradation kinetics than anaerobic treatment for the majority of the ECs. The biodegradation and sorption processes are responsible for the removal of pollutants in aerobic systems. The pollutants are mineralized by the activated sludge, resulting in the production of CO_2 and H_2O, and a reduction in the toxicity of the effluent (Fawzy et al., 2018). Akcal Comoglu et al. (2016) investigated the treatment of wastewater contaminated with pharmaceuticals using an anaerobic batch treatment technique. The results obtained suggested that the bacterial biomass and the archaeal present in the reactor were successful in degrading the pharmaceutical contaminants. Furthermore, Zhou et al. (2006) studied the removal of antibiotics from pharmaceutical wastewater using anaerobic and aerobic treatment. The study reported the removal efficiencies for ampicillin and aureomycin as 16.4 and 25.9 % at hydraulic retention time (HRT) of 1.25 day and 42.1 and 31.3 % with HRT of 2.5 day. On the other hand, biofilm airlift suspension reactor showed effective removal of COD, but less than 10 % removal was reported for both the antibiotics. Similarly, Froehner et al. (2010) investigated the removal of hormones, caffeine and bisphenol-A from wastewater following the aerobic and anaerobic treatments. The study reported the removal efficiencies in the range of bisphenol-A (99.9-approx.100 %), caffeine (99.6-approx. 100 %), Estrone (approx. 100 %), 17-β-Estradiol (56.5-66.5 %) and 17-α-Ethinylestradiol (44.1-99.1 %). Shah and Shah (2020) conducted a review of studies on the degradation efficiency of anaerobic and aerobic technology for treating pharmaceutical wastewater. They concluded that hybrid anaerobic and aerobic technology models are the most competent and preferable bioremediation methods for pharmaceutical wastewater.

4.3.2. Bacteria

Park et al. (2017) investigated the influence of ammonia-oxidising bacteria on the removal of ECs from water in a bioreactor. The biodegradability of most of the compounds studied was improved by the presence of the bacteria, including steroidal anti-inflammatory drugs (NSAIDs), analgesics, antibiotics, and antibacterial agents. The results suggest that ammonia-oxidising bacteria in bioreactors will play an important role in the elimination of pharmaceuticals. In another study, the bacterial community has demonstrated an impressive ability to remove ECs (majorly pharmaceuticals) from water. According to the literature, certain species involved in degrading prenolol, bisoprolol, metoprolol, fluoxetine, norfluoxetine, 17β-estradiol and gemfibrozil have achieved removal efficiencies of 90% or more (Ramírez-Durán et al., 2017).

4.3.3. Nitrification and denitrification

Biological nitrification and denitrification play a significant role in removing emerging contaminants (ECs) in addition to managing nitrogen compounds in water systems (Ahmed et al., 2017). Ammonia-oxidizing bacteria convert ammonium to nitrite or nitrate during nitrification, while heterotrophic bacteria use organic carbon sources to reduce nitrate and nitrite to nitrogen gas during denitrification. It is important to note that these processes may incidentally remove some ECs, providing additional benefits beyond standard nitrogen removal (Silva et al., 2018). Phan et al. (2014) investigated the performance of the denitrification process for the removal of different ECs including EDCs, PPCPs and pesticides. The findings further reported that estrone (E1), 17-βestradiol (E2), estriol (E3), 17-ethinylestradiol (EE2), bisphenol A, 4-tert-butylphenol, 4-tert-octylphenol, benzophenone, oxybenze, galaxolide, tonalide and salicylic acid has a removal efficiency of 82-100%. While the pesticides such as fenoprop and atrazine were poorly removed 8-32% and paracetamol and triclosan had a rate of removal reaching 88-98%. According to a study, the rate of removal in denitrification largely depends on the type of contaminants targeted. For instance, in the study carbamazepine, clofibric acid, diclofenac, erythromycin, roxithromycin and gemfibrozil had a lower removal efficiency whereas in the same study, the removal of ibuprofen, ketofenac and metronidazole by nitrification was high as 83-97% (Suarez et al., 2010).

4.3.4. Microalgae

Microalgae have been recognised for their ability to biotreat wastewater. This is due to their ability to grow in nutrient-rich wastewater. They can break down organic carbon into lipids, carbohydrates and other compounds (Mohan and Devi, 2014). Ding et al. (2020) studied the removal of pharmaceuticals using microalgae *Navicula sp.* The study further reported that the microalgae successfully removed 90% of the ECs like carbamazepine, atenolol, naproxen and ibuprofen. Additionally, the study also highlighted that the degradation of bezafibrate, sulfamethoxazole and naproxen was higher in the mixed treatment, which included all the pharmaceuticals collectively, as compared to the separate treatment for individual pharmaceuticals. Conversely, carbamazepine and atenolol demonstrated decreased degradation in the mixed treatment as compared to the separate treatment. Another freshwater microalgae *Chlorella pyrenoidosa* was utilised in the treatment of pharmaceuticals in water. The results suggested that *Chlorella pyrenoidosa*, with a residence time of 7 days, effectively eliminated acetaminophen at a rate of up to 90%, while enrofloxacin exhibited a comparatively lower rate of removal, approximately 70% (de Wilt et al., 2016; Zhou et al., 2014).

Figure 2 shows the performance of various biological treatments in the successful removal of different classes of ECs. From the figure it can be seen that, overall activated sludge-based technique was the least efficient technique with rather lower removal for almost all the targeted group of ECs. On the other hand, biological activated carbon technique was most suitable for the treatment of ECs, considering their high removal efficiencies for all the classes of ECs considering EDCs as an exception. Furthermore, aerobic and anaerobic methods showed a better removal for EDCs but their performance in the case of personal care products was significantly low. In addition, the figure also depicts that nitrification and denitrification were the best performing techniques in the removal of personal care products, while in case of analgesics and antibiotics, the removal efficiency of these techniques was observed below 50% (Fig. 2).

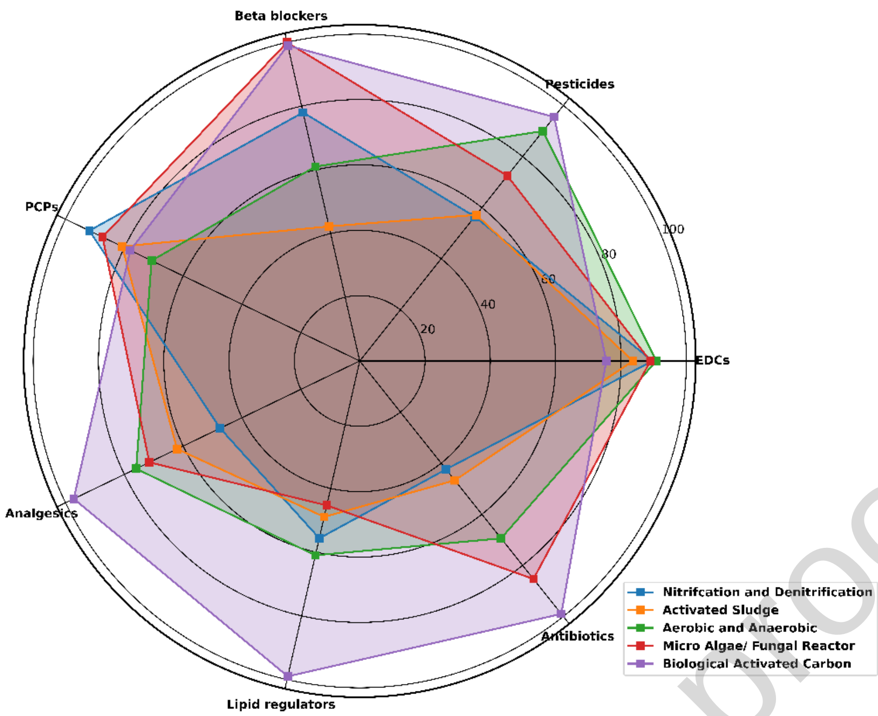

Fig. 2. Efficiency of different biological treatment processes in removing various groups of ECs from water matrices

4.4. Hybrid technology

4.4.1. Advanced oxidation

The inability of the conventional and the recent treatment technologies to properly treat different ECs and the defects in some of the recent developments has led to the utilisation of two or more treatment technologies simultaneously in a single stage for the treatment of wastewater containing emerging contaminants like pharmaceuticals (Eniola et al., 2022). For example, a treatment process integrating biodegradation and photocatalysis has shown effective removal of antibiotics, the study suggested that a hybrid technology can enhance the quality of effluent produced after wastewater treatment (Yu et al., 2020). In another study, Della-Flora et al. (2020) combined solar photo Fenton with adsorption to treat an anticancer drug named Flutamide. Initially, 20% of the drug was removed solely by photo Fenton. The efficiency was taken to 58% by tripling the dose of Fe^{2+} and H_2O_2. Whereas by incorporating adsorption on activated carbon from avocado seeds the targeted drug was completely removed in a contact time of 40 minutes. Similarly, Ling et al. (2020) in a Fenton like process made use of activated alumina-supported CoMnAl metal oxides as co-catalysts to decontaminate the wastewater containing pharmaceuticals.

4.4.2. Membrane bioreactor (MBR)

Membrane Bioreactor is widely regarded as a promising technology for wastewater treatment due to the high removal efficiency achieved with respect to many ECs. It combines a membrane based physical process with a biological process (Tambosi et al., 2010). A recent study developed MBR by incorporating an ultrafiltration membrane with an anaerobic sludge bed digestor. The performance of the bioreactor was evaluated against the treatment of seven ECs namely ketoprofen, fenofibrate, prednisone, fluconazole, loratadine, 17 α-ethinyl estradiol, and betamethasone. The results revealed that despite all being the non-inflammatory drugs betamethasone and prednisone showed high removal i.e.95% and 98% respectively, whereas no significant removal was reported for ketoprofen. Furthermore, fluconazole also showed relatively less tendency of adsorption (Faria et al., 2020). Similarly, Kim et al. (2014) reported that integration of membrane filtration with aerobic digestion of wastewater. As reported out of the 99 ECs investigated 23 compounds showed a good removal efficiency i.e., greater than 90%. The order of removal was, ibuprofen was completely removed and various compounds including metformin, 4-epitetracycline, norfloxacin and others showed a removal of 91-99%, while moderate removal (55-90%) was observed for albuterol. Furthermore, carbamazepine was poorly removed (10-50%) and in the case of thiabendazole, fluoxetine no or less than 10% removal was observed.

4.4.3. Constructed wetland (CW)

Constructed wetlands are systems designed to replicate the processes of natural wetlands in a controlled environment for the purpose of wastewater treatment. This is achieved through a combination of biodegradation (biological), sorption (physicochemical), and oxidation (chemical) interactions between plants, wastewater, and soil. Based on the wastewater flow regime constructed wetlands can be classified into three classes i.e., vertical flow, horizontal flow, and subsurface/surface flow systems. Töre et al. (2012) reviewed the fate of emerging contaminants in constructed wetland-based treatments. The findings revealed that CW effectively removed many ECs with percentage removal for polycyclic aromatic hydrocarbons (60-70%), steroid estrogens (100%), estrone (67.8 ± 28%), bisphenol A (80-100%) and for Linear alkylbenzene sulphonates (30-55%). Similarly, Matamoros et al. (2008) tested a 1-ha surface flow constructed wetland for treatment of 12 ECs in wastewater. The results reported good removal efficiencies (greater than 90%) for all the ECs with the exception of carbamazepine and clofibric acid having removal efficiency range between 30-47%. In another study, Hijosa-Valsero et al. (2011) investigated the removal of antibiotics from wastewater using seven different constructed wetlands. The study revealed that taking into account the soluble water fraction, the only antibiotics that were easily removed were doxycycline (61 ± 38 %) and sulfamethoxazole (60 ± 26 %). Whereas the removal of other contaminants was limited to specific system configurations. Thus, CWs are not an overall solution for the removal of ECs from wastewater considering the seasonal and natural variability.

The performance of three hybrid technologies namely constructed wetland-based (CW based), MBR based and ozonation and gamma radiation-based processes can be seen in the figure (Fig. 3). The figure suggests that different techniques were superior when different ECs were considered. For example, in the case of lipid regulators MBR based techniques were most efficient. While in case of Analgesics Ozonation integrated with gamma radiation was best performing and MBR based techniques had the lowest efficiency. Moreover, when pain relivers are considered both ozonation and MBR based techniques had a better removal efficiency than MBR based methods (Fig. 3).

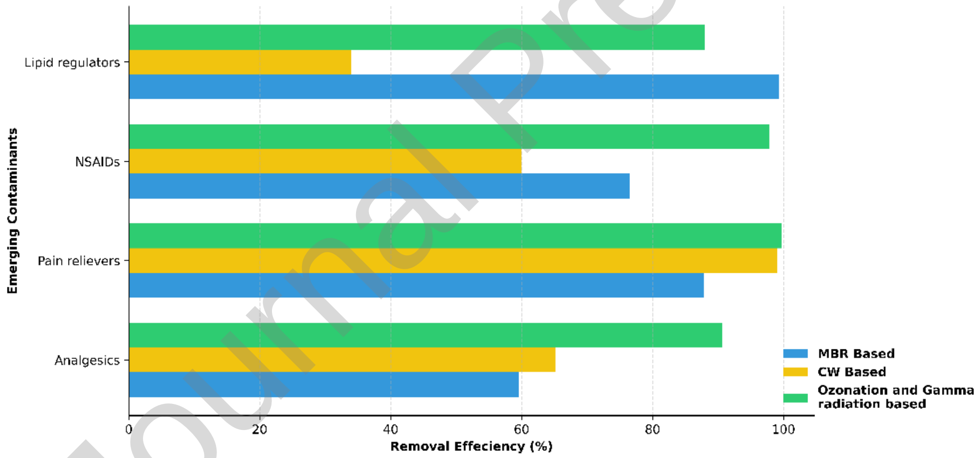

Fig. 3. Efficiency of different hybrid systems in treating various groups of ECs from water matrices

4.5. Cost estimation

The biggest challenge in treating emerging contaminants from water and wastewater using recently developed technologies is the associated cost. For instance, techniques involving adsorbents or photocatalysts can be expensive due to the high cost of the chemicals involved (Eniola et al., 2022). Considering the low cost involved the use of agricultural waste provides an economical alternative for the absorbent materials, but then the cost of pretreatment required for bio adsorbents adds to make the option expensive (Viotti et al., 2019). For photo-Fenton technique, considering a catalyst life of 180 days with 24-hour operation the cost of a photocatalyst for 1 cubic metre was estimated equal to 4.93 euro (Segura et al., 2021). Alternative treatment methods, such as membrane technology, can be expensive due to the high cost of equipment. This can increase the overall operating costs. Additionally, membrane replacement and the extra energy cost due to membrane fouling are significant contributors to the total main operating cost of membrane technology (Jafari et al., 2021). In case of hybrid techniques, the cost of treatment is usually enhanced due to the involvement of multiple treatments in a single stage. Gupta et al. (2021) have estimated the cost of operation for a photocatalysis based adsorption system as 2.2-4.4 USD/cubic metres when this is utilised for the degradation of diclofenac. However, the environmental and human benefits of improved water quality resulting from the higher removal efficiencies of these technologies can offset the high costs of treating emerging contaminants in wastewater. Table 1. Listed the operational costs along with the advantages and disadvantages of various treatment techniques.

Table 1

The operational cost of different treatment technologies utilized for EC removal from wastewater matrix

Treatment Methods	Types	Operational Cost	Advantages	Disadvantages	Applications	Ref.
Physical Methods	Adsorption Membrane Technique	0.98 USD/cubic meter	Technically Simple and minimal generation of by-products	Varying contaminant-adsorbent interactions	Pharmaceuticals Pharmaceuticals and personal care products	(Moran, 2015); (Eniola et al., 2022; Wang et al., 2015)
Chemical Methods	Photocatalysis, Fenton, Photo-Fenton	0.85-10.36 Euro/cubic meter	Universal Applicability	Cost associated with artificial energy generation	Pharmaceuticals and Pesticides	(Segura et al., 2021), (O'Shea and Dionysiou, 2012);

						(Prieto-Rodriguez et al., 2012)
Biological Methods	Aerobic, Anaerobic, Bacteria etc.	0.17-0.53 Euro/cubic meter	More environmentally friendly than chemical methods	High Sludge Generation and Processing	Pharmaceutical and personal care products	(Pajares et al., 2019); (Samer, 2015); (Matamoros et al., 2015; Suman Raj and Anjaneyulu, 2005)
Hybrid Methods	Advanced Oxidation	2.2-4.4 USD/cubic meter	Significant ancillary effect on the removal of ECs	Operational and maintenance cost	Pharmaceuticals	(Gupta et al., 2021); (Rosman et al., 2018)
	Constructed Wetlands	1.33 USD/ sq. Meter/yr.	Low cost and High performance	Chemical precipitation and seasonal dependency	Pharmaceuticals, personal care products and pesticides	(Gkika et al., 2014); (Garcia-Rodríguez et al., 2014; Töre et al., 2012)

5. Occurrence of emerging contaminants in water matrices

Generally, the majority of the ECs discussed in the previous section can enter the water matrices through various natural or anthropogenic sources. The sources of ECs to the environment can be both direct point sources like effluent discharge from hospitals, industries, WWTPs etc., or it can be indirect sources like atmospheric deposition, catchment runoff, septic tanks and waste dumping sites. The presence of a variety of emerging contaminants in water sources around the globe has been documented on a widespread basis, as illustrated in the provided figure (Fig. 4).

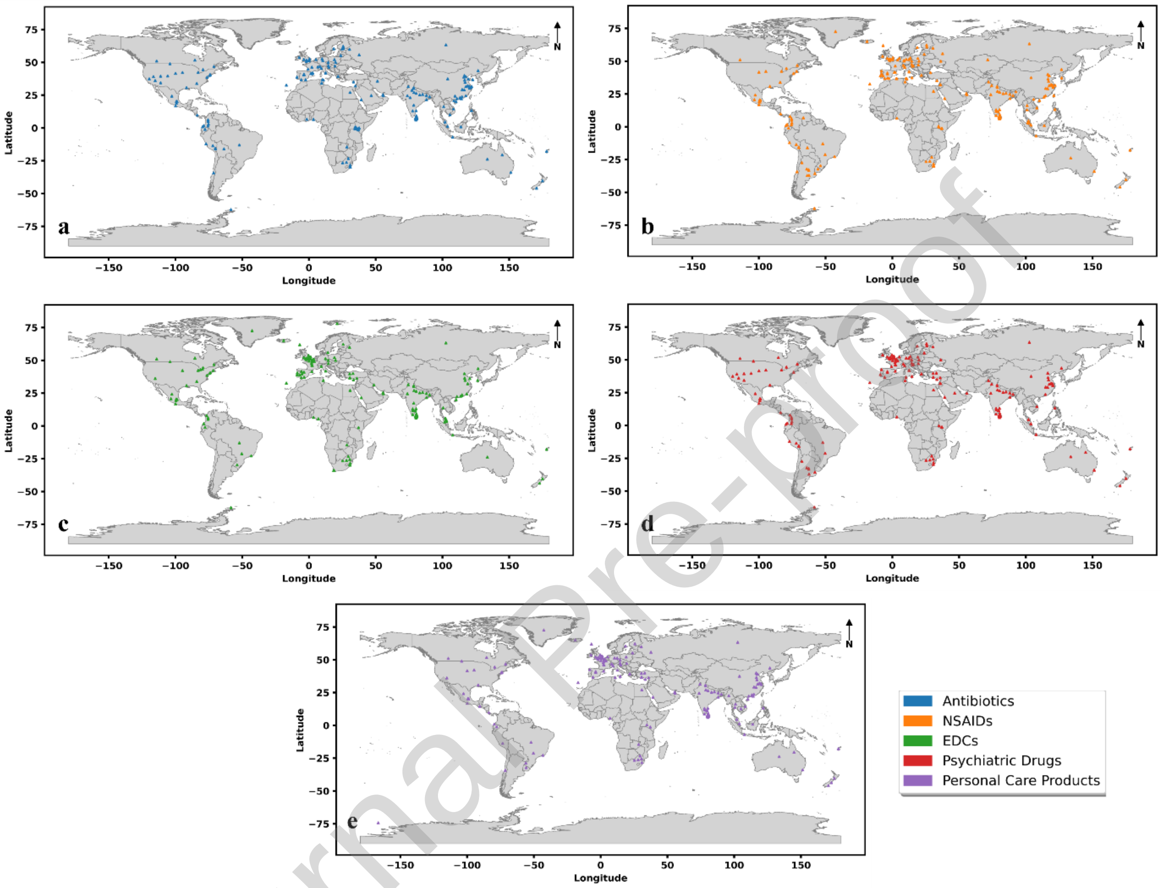

Fig. 4. Occurrence of different ECs in water sources around the world (a) antibiotics, (b) NSAIDs, (c) EDCs, (d) psychiatric drugs, and (e) personal care products

5.1. NSAIDs

The non inflammatory drugs have shown a high persistence in the global water, this can be due to their high utility in daily life. In this study three drugs were studied i.e., diclofenac, ibuprofen, and naproxen. From the review, it was seen that the maximum concentration for NSAIDs diclofenac (836 µg/L), ibuprofen (1673 µg/L) naproxen (464 µg/L) was reported in the Asian country of Pakistan (Ashfaq et al., 2017). A high concentration for diclofenac was also observed in Jeddah, Saudi Arabia (14.02 µg/L) (Ali et al., 2017) and KwaZulu-Natal province South Africa (9.7 µg/L) (Madikizela and Chimuka, 2017). Furthermore, Loos et al. (2013) presented a report on the Union wide monitoring of ECs in wastewater of Europe. The study reported the presence of all the mentioned drugs with maximum concentrations of, diclofenac (0.174 µg/L), ibuprofen

(2.129 µg/L), and naproxen (0.958 µg/L). Another study carried out a review on environmental monitoring of the contaminants listed in the EU guidelines (Sousa et al., 2018). According to the study, diclofenac was one of the most studied pharmaceuticals among the lists. Recently González-Alonso et al. (2017) has also reported contamination due to diclofenac in the Antarctic Peninsula region with concentration of the drug as 7.761 µg/L. Miège et al. (2009) and Santos et al. (2009) reported that across Europe naproxen and ibuprofen were most consumed analgesics, with concentration for the drugs ranging beyond 6000 µg/L in the wastewater influents. Pulicharla et al. (2021) reported the presence of ibuprofen in five drinking water treatment plants across Québec, Canada. In this study the maximum concentration for ibuprofen was reported in Lawrence River (0.083 µg/L). Kallenborn et al. (2018) carried out the assessment of pharmaceuticals and personal care products in the Arctic environments. In this study maximum concentration of ibuprofen was reported for Faroe Islands (4.5 µg/L) followed by Ontario (4 µg/L). Whereas for diclofenac the maximum concentration was reported in Longyearbyen, N, Svalbard (1.074 µg/L). A study from Dunedin, New Zealand reported the presence of naproxen (0.005 µg/L) in the fresh waters (Bernot et al., 2019).

5.2. Psychiatric drug

Carbamazepine was continuously detected in water. Highest persistence for the drug was detected in Esmeraldas, Ecuador with concentration more than 80 µg/L (Voloshenko-Rossin et al., 2015). A number of studies have suggested a wide utilization of Carbamazepine in South America. For example, Elorriaga et al. (2013) reported the presence of the drug in wastewater from urbanized locality of Argentina with concentration more than 6 µg/L. Chaves et al. (2021) reviewed the occurrence of emerging contaminants in Brazilian surface water, the study listed the occurrence of carbamazepine in many surface water bodies in the country with maximum concentrations reported in Jundiai River (0.659 µg/L) and Rio Negro (0.652 µg/L). Another study from South Africa has reported a concentration of 3.24 µg/L in water from Msunduzi River, KwaZulu-Natal (Matongo et al., 2015). A concentration of 0.886 µg/L for the compound was reported in the surface water of Rome, Italy (Patrolecco et al., 2015). Glassmeyer et al. (2017) carried out a nationwide inspection of emerging contaminants in the source and treated drinking waters around United States and reported a higher concentration in treated drinking water (586 ng/L) than the source (0.269 µg/L). Asian countries showed a high persistence of the drug in the water with concentrations of 1.933 µg/L (Saudi Arabia) (Picó et al., 2019), 1.455 µg/L (China) (Li et al., 2018) and 0.4841 µg/L of carbamazepine was detected the surface waters of Yamuna River, India (Biswas and Vellanki, 2021). Countries from Oceania have reported relatively lower concentration of carbamazepine up to 0.682 μg/L (Australia)(Scott et al., 2014), and 0.620 μg/L (Waikato, New Zealand) (Moreau et al., 2019).

5.3. Endocrine disrupting chemicals

The presence of different EDCs in water has been confirmed for all the continents around the globe. In this study, the occurrence of three EDCs including two hormones (estrone (E1); 17 β-estradiol (E2)) and one industrial contaminant (Bisphenol A) was reviewed. The highest concentration for all three contaminants was reported in Mexico with concentrations varying from ng/L to 140 $\times 10^3$ μg/L. Recently V´azquez-Tapia et al. (2022) assessed the situation of ECDs in various Mexican water matrices. The study reported the maximum concentration for E1, E2 and BPA in surface water as 1300 μg/L, 2200 μg/L and 140 $\times 10^3$ μg/L respectively. (Kanama et al., 2018) reported concentration for E1 hormone in range of 0.007 μg/L to 6 μg/L in treatment plants receiving influx from the health facilities of Northwest Province, South Africa. In the last decade, a continuous persistence of EDCs in South American water has been reported. For instance, Voloshenko-Rossin et al. (2015) reported the presence of EDCs in Esmeraldas watershed, Ecuador, the maximum concentrations for estrone and 17 β-estradiol were found to be 11.4 μg/L and 2.2 μg/L respectively. Another study from Iguacu River, Brazil reported the maximum concentration for estrone as 0.94 μg/L whereas for estradiol it was 1.42 μg/L (Ide et al., 2017). In a bibliographical assessment of emerging contaminants in the Brazilian environment, Starling et al. (2019) reported the presence of various endocrine-disrupting chemicals in different water systems around the country. Additionally, the study indicated that bisphenol A (BPA) persists at high levels along urban areas and among the identified compounds, 17 β-estradiol and 17 α-ethynylestradiol were found in the highest concentrations in the surface waters. A similar pattern of occurrence was also observed in the countries of Asia and Oceania. Biswas and Vellanki reported the presence of estrone in the Yamuna River, with a detection frequency of 100% and a maximum concentration of 1.782 μg/L (Biswas and Vellanki, 2021). Rivers from western India were found to contain EDCs with range for E1, E2 and BPA varying as 0.026-0.124 μg/L, 0.004-0.028 μg/L and 0.095-0.299 μg/L respectively (Williams et al., 2019). Emnet, reported that E1 was the most detected estrogen in the wastewater effluent of Lyttelton Harbour, New Zealand, with concentration ranging between 0.021-0.114 μg/L (Emnet, 2013). Similarly, in Australia also E1 was most detected among the EDCs in river water with maximum concentration of 0.057 μg/L (Scott et al., 2014). Furthermore, bisphenol A was also highly persistence in the European environment. The maximum reported concentration for BPA lowland aquifers of Berkshire, U.K. was 39 μg/L (Manamsa et al., 2016). Another study from Poland has reported a maximum concentration of 6.88 μg/L for BPA with detection frequency of 100% in the collected groundwater samples (Kapelewska et al., 2018). River pollution by endocrine disruptors in Mira, Portugal have been reported by Rocha et al. (2016) the study reported the maximum concentration of BPA in the river water as 0.3066 µg/L.

5.4. Antibiotics

The condition of antibiotics in global water is not very different compared to the EDCs or NSAIDs, as they have also shown a constant persistence in different water matrices throughout the world. This study has reviewed the situation of two of the most commonly occurred antibiotics in the world namely sulfamethoxazole and erythromycin. The maximum concentration of 309 µg/L for sulfamethoxazole was detected in Esmeraldas, Ecuador (Voloshenko-Rossin et al., 2015). Whereas the African countries have shown the most frequent and high detection of the drug. Kimosop et al. (2016) investigated the discharge load of antibiotics in the hospital discharge of Kenya. The study reported the presence of sulfamethoxazole along with other antibiotics in the discharge from various hospitals around Lake Victoria basin, with the highest concentration for sulfamethoxazole (0.59 µg/L) detected in effluent from Kakamega Hospital. Another study by Kairigo et al. (2020) reported the presence of antibiotics in Kenyan water, highest concentration of 56.6 µg/L was detected for sulfamethoxazole in Mwania river, Machakos. Additionally, the study also reported the presence of antibiotics in the water matrices of Nyeri and Meru County of Kenya with the concentration of sulfamethoxazole in water ranging between 0.3-17 µg/L. Differing from sulfamethoxazole the highest concentrations for erythromycin were detected in the Asian water. According to Xiao et al. (2023) highest concentration for erythromycin were detected in the effluents from south China having a maximum concentration of 7.20 µg/L. Khan et al. (2020) has reviewed presence of ECs in water environments of south Asia. The study reported the concentration of erythromycin in surface water in µg/L as Sir Lanka (6.501); India (0.0387) followed by Pakistan (0.0362) and lastly Bangladesh (0.76×10^{-3}). In Europe, a high occurrence of antibiotics was found in the German groundwater. The maximum concentrations for erythromycin and sulfamethoxazole in groundwater of Germany was found to be 0.3924 µg/L and 0.0422 µg/L (Reh et al., 2013). Lesser et al. (2018) in survey for world's largest untreated wastewater irrigation system in Mezquital Valley, Mexico targeting the presence of ECs reported the maximum concentration of sulfamethoxazole as 6.75 µg/L while for erythromycin it was found to be 1.140 µg/L. The presence of antibiotics in the environmental waters of Oceania has been reported by Watkinson et al. (2009), the maximum detected concentration of sulfamethoxazole was 2 µg/L. A similar study by Moreau et al. reported the maximum concentrations of 0.260 µg/L for sulfamethoxazole in the groundwater of New Zealand (Moreau et al., 2019).

5.5. Personal care products

In this study, the antibacterial compound triclosan (TCS) was considered, as it is the most commonly studied and detected compound in the water matrices around the globe. The highest concentration of triclosan has been identified in the waters of North America. A concentration of 90,000 µg/L was detected in the surface water of Mexico (Díaz-Torres et al., 2013; Vázquez-Tapia et al., 2022). As reported by Kumar et al. (2010) the maximum concentration of TCS in dissolved phase for Savannah, Georgia, USA was 4.76 µg/L. Peña-Guzmán et al. (2019) in a review of ECs in Latin America reported that for Guatemala the concentration of TCS in varied from 18 to 520 µg/L. While for Chile and Costa Rica the study has reported a maximum concentration of 15 µg/L and 0.263 µg/L. Bakare and Adeyinka studied the fate of TCS in wastewater treatment systems across Durban, South Africa, the study reported that the concentration of TCS in effluent ranged from 1.732-6.980 µg/L (Bakare and Adeyinka, 2022). Stasinakis et al. (2008) identified the presence of triclosan in the discharge from Greek wastewater treatment plants with a maximum concentration of 6.880 µg/L. A study by European Commission has reported a maximum concentration of 5.370 µg/L in the wastewater effluents from Luxembourg (SCCS (Scientific Committee on Consumer Safety), 2011). A high occurrence of triclosan was also shown among the Asian rivers. Zhao et al. (2009) investigated the Pearl River in the south China for the presence of TCS. The study further reported that the concentration in river water varied between 0.0006-0.347 µg/L. Another study on Pearl River system reported the concentrations range for TCS in Liuxi, Zhujiang and Shijing river as below quantification-0.0139 µg/L, 0.0045-0.0462 µg/L and 0.0688-0.338 µg/L respectively (Zhao et al., 2010). Similarly, Biswas and Vellanki (2021) identified the presence of triclosan in Yamuna River with a maximum concentration of 0.2698 µg/L. Montagner et al. (2014) have investigated the presence of TCS in six rivers across São Paulo, Brazil, in the study 45% of the samples contained triclosan with concentration varying from 0.0022 to 0.066 µg/L. A review by Starling et al. (2019) has also identified TCS in different water matrices across Brazil. According to Emnet et al. (2020) the concentration of TCS in Lyttelton Harbour, New Zealand was in range of 0.00131-0.1215 µg/L. Close et al. (2021) detected the highest concentration of TCS in groundwater of New Zealand as 0.00203 µg/L. TCS was frequently detected in effluent from Scott base, New Zealand’s Antarctic research site, with concentrations up to 0.043 and 0.807 µg/L, respectively (Emnet et al., 2015). Another study from Oceania has determined TCS in effluents of Australia’s largest wastewater treatment plant near Canberra with concentrations approximately 0.004-0.005 µg/L (Roberts et al., 2016).

6. Challenges in reusing water contaminated with emerging contaminants

6.1. Organic contamination of soil

Wastewater reuse can alter the physio-chemical and biological properties of soils, which in turn can affect the bioavailability and uptake by crops (Minhas et al., 2022). In the past many studies have provided evidence for the ubiquitous occurrence of ECs in soil following wastewater reuse and proved their resistance to various treatment practices (Minhas et al., 2022). For instance, Muñoz et al. (2008) using the life cycle assessment model investigated the impact of 98 ECs and reported a significant impact of 16 of them, out of which 10 are from the category of pharmaceuticals and personal care products. Similarly, a study explained the impacts of wastewater irrigation and biosolid application on the transport of pharmaceutical contaminants in soil. The results suggested that the application of treated effluent has enhanced the transport of some of the pharmaceutical compounds in soil, whereas the biosolids increased the retardation for the same (Borgman and Chefetz, 2013). In another study from the past Topp et al. (2008) mobilisation of ECs like pharmaceuticals and personal care products was studied. The results suggest the accumulation of the targeted compounds in the soil. diclofenac and carbamazepine were detected in the low concentration in the runoff even after 266 days of application of the drugs. Another example of the accumulation of emerging contaminants in soil irrigated with wastewater in China was presented by (Zeng et al., 2008). In the study, Phthalates were detected in the soil sample having concentration in the range of 0.195 $\times 10^{-3}$ to 33.6×10^{-3} mg/g (d.w.) which mainly originated from sewage and wastewater application. In the past few decades, the occurrence of ECs in soil has attracted researchers throughout the globe. Chen et al. (2011) investigated the presence of various ECs in Chinese soil and reported the presence of trichlocarban, salicylic acid, oxytetracycline and tetracycline, having concentrations in the range of 0.3 $\times 10^{-6}$-139 $\times 10^{-6}$ mg/g. Kinney et al. (2006) found the presence of carbamazepine, sulfamethoxazole and ECs in the soil from the USA. Similarly, the presence of doxycycline (62.6–728.4), norfloxacin (< MQL-95.7), trimethoprim (< MQL-60.1) and progesterone (< MQL-24.2) with range in 10^{-6} mg/g was reported in Malaysian soil (Ho et al., 2012). Lastly, Biel-Maeso et al. (2018) studied the occurrence of ECs in soil from Spain. The finding of the study reported the concentration of targeted compounds (mg/g): acetaminophen (n.d.-5.95 $\times 10^{-6}$), diclofenac (n.d.-5.06 $\times 10^{-6}$), carbamazepine, (0.08 $\times 10^{-6}$ –1.36 $\times 10^{-6}$), flumequine (n.d.-5.31 $\times 10^{-6}$) and hydrochlorothiazide (0.38 $\times 10^{-6}$ –1.20 $\times 10^{-6}$).

6.2. Uptake by plants

The presence of organic contaminants in soil can influence the biological balance and further affect plant growth (Gworek et al., 2021). The disturbance is likely caused by the breakdown of a significant number of soil micro-organisms such as microworms, nematodes, and protozoa. This, in turn, affects the processes in soil-plant symbiosis (Grassi et al., 2013). Transport and bioaccumulation of ECs like pharmaceuticals in plants varies with the mode of cultivation i.e., on soil farming and soil less farming also the physical and chemical properties can have a significant impact on the uptake (Carvalho et al., 2014). In the past many studies have been conducted to comprehend the plant uptake of these micro pollutants by different plant species. For example, Kong et al. (2007) conducted a series of experiments in soil-less hydroponic systems to investigate the uptake and toxicity of oxytetracycline in alfalfa (*Medicago sativa L.*). The study suggested that the drug influenced the root and shoot growth by approximately 85% and 61% respectively. In another study, Wu et al. (2010) explored the uptake of five ECs namely diphenhydramine, carbamazepine, fluoxetine, triclosan and triclocarban, in soybean *(Glycine max Merr.)*, under controlled conditions. Analysis carried out after a growth period of 60 and 110 days reported the accumulation of triclocarban, triclosan and carbamazepine in plant roots, shoots and seeds. Whereas diphenhydramine and fluoxetine had a limited accumulation in aerial parts of the plants. Along the same line, another study investigated the potential of veterinary products when present in soil to be taken up by plants consumed by humans. The results indicated the accumulation of targeted contaminants in the soil above the detection limit, for at least 5 months from the application of manure. Additionally, the results of plant uptake by carrot roots and lettuce revealed the uptake of diazinon, florfenicol, trimethoprim and enrofloxacin by carrot roots, whereas florfenicol, trimethoprim and levamisole were present in lettuce (Boxall et al., 2006). Similarly, Winker et al. (2010) studied the uptake of ibuprofen and carbamazepine by ryegrass, supplied with pharmaceutical spiked urine or stream of treated household wastewater. The results reported that carbamazepine was the only drug up taken by the ryegrass. The study further uncovered that about 34 % of the drug was recovered from the shoots and 0.3% from the roots of the plants, whereas 53% of the carbamazepine was still present in the soil. Another study from Turkey, analysed the uptake of tetracycline and related metabolites by *Phragmites australis* (common reed) irrigated with effluent from the slaughterhouse. The trace of tetracycline and its metabolites in the studied plant components increased in the following order: leaves <stems <roots (Arslan Topal, 2015). Recently, Gredelj et al. (2020) investigated the uptake of a PFAA (perfluoroalkyl acid) mixture into *Cichorium intybus L* (red chicory), a common agricultural produce from a major PFAA contaminated zone in northern Italy. The

obtained results highlighted that PFBA showed highest bioaccumulation with roots having the maximum (43×10^{-3} mg/gdw), followed by leaves and head of the plants. Moreover, the concentration in the plant compartments eventually decreased with an increase in PFAA chain length.

6.3. Effects on groundwater quality

Although the reuse of wastewater has continued to elevate following the increase in wastewater production (Khalid et al., 2018), this practice leads to the threat of groundwater contamination (Hashem and Qi, 2021). Considering the groundwater some of the major issues are organic contaminants (Lesser et al., 2018), trace elements (Yang et al., 2021), polyethylene and other micro pollutants present in wastewater may contaminate the shallow aquifers (Panno et al., 2019). Whenever wastewater is applied on land most are absorbed in the topsoil, however, the majority of the hydrophilic and more resistant compounds can reach the aquifer and enhance the groundwater contamination. Supporting this, a study presented by Montesdeoca-Esponda et al. (2021) investigated the occurrence of pharmaceutical contaminants in the groundwater of Gran Canaria Island, Spain. The result reported the presence of nicotine, caffeine, and atenolol in groundwater following the treated wastewater irrigation. The concentrations detected were in the range of <0.0394-4-0.1136, <0.0029-0.0449, and <0.0124-0.068 µg/L respectively. Another study from Plana de Castellón, Spain, studied the occurrence of 42 ECs including antibiotics, UV filters and NAIDs in groundwater following wastewater irrigation. The findings revealed a high presence (µg/L) of bezafibrate (<0.0013–0.012) carbamazepine (<0.0002–0.0019) primidone (<0.0011–0.0075) sulfamethoxazole (<0.0005–0.0061) acetaminophen (<0.0011-0.063) (Renau-Pruñonosa et al., 2020). In a similar study from Pennsylvania presented by Kibuye et al. (2019), the results highlighted the presence of sulfamethoxazole, caffeine, and naproxen in groundwater with detection frequency ranging from 19-40%. Kampouris et al. (2022) presented a case study of antibiotic resistance in the groundwater of Wendeburg, Germany, following wastewater irrigation. The study reported the presence of sulfamethoxazole (0.0982 µg/L-0.4069 µg/L) and carbamazepine (0.1685 µg/L -0.2723 µg/L) in groundwater. However, the concentrations of carbamazepine and sulfamethoxazole in treated wastewater were lower compared to what was detected in aquifers. This could be attributed to the use of a mixture of digested sludge and treated wastewater in these croplands. Turner et al. (2019) investigated the groundwater of Enoggera Catchment (Australia), an area under greywater irrigation. A total of 22 emerging contaminants were detected in wastewater out of which DEET, caffeine and acesulfame were detected in subsurface water whereas the surface water adjacent to the area was having the presence of salicylic acid. Finally, Lesser et al. (2018) carried out a survey of 218 emerging contaminants in groundwater, majorly resulting from the world's largest untreated wastewater irrigation system from Mezquital Valley, Mexico. According to the results, out of 218 pharmaceutically active compounds (PhACs), bis-2-(ethylhexyl) phthalate and dibutyl phthalate were detected in groundwater. Furthermore, carbamazepine, sulfamethoxazole, benzoylecgonine and N, N-diethyl-meta-toluamide were frequently detected in groundwater. Overall, Sulfamethoxazole and carbamazepine are the compounds that have been most frequently investigated and detected in aquifer systems affected by the re-use of wastewater. This is due to their global use, high environmental persistence and low soil affinity. It is important to note that pharmaceutical, personal care products and other persistent ECs have been evaluated in aquifers located in different areas worldwide (Table S3). However, the abundance of these compounds in aquifers of lands irrigated by wastewater has not been extensively studied.

7. Existing regulatory framework

To minimise the adverse effect of different contaminants and or organic pollutants various organisations throughout the world have set some distinct regulatory standards and guidelines. These regulations provide the tolerable limit of compounds in an aqueous environment. Exceeding these concentrations for a long duration can pose a risk to the environment (Kovalakova et al., 2020). As far as the emerging contaminants are concerned there are no rigorous guidelines or standards, which is possibly due to the insufficient information about the behaviour and occurrence of these contaminants in the environment. However, two of the world's biggest environmental agencies the USEPA and the European Parliament Committee have listed various contaminants potentially concerning for the environment, under the Candidate Contaminant List (USEPA) and priority list or watch list (EU) and provided some admissible limit for few of these contaminants.

7.1. EU watchlist

The EU is among the fastest to document some guidelines/measures for the concerning contaminants in water. In the year 2000, the EU launched Directive 2000/60/EC (European Union Directive 2000/60/EC, 2000) to establish a framework and plan of action in the field of water policy. In this Water Directive, the commission had to identify priority substances having significant risk and further set up the European quality standards. The first list of 33 priority substances and 8 other contaminants was launched under directive 2008/105/EC (European Union Directive 2008/105/EC, 2008). This included contaminants like Atrazine, DDT, Naphthalene, Polyaromatic hydrocarbons (PAHs) and many more. Five years later the directive was amended with the launch of directive 2013/39/EU (European Union Directive 2013/11/EU, 2013). Along with the demand for new treatment technologies this directive has also suggested the monitoring of 45 priority substances which included, metals cadmium, lead, mercury nickel and 41 organic substances. Furthermore, this directive has proposed a framework for the development of a Watch List of contaminants for their monitoring throughout the union in the field of water policy. This list was published in 2015/495/EU on 20 March 2015 (Table 2). The watch list considered 10 groups of substances further including 17 contaminants of emerging concerns.

Table 2

Watch List of substance group for union-wide monitoring as per Directive 2015/495/EU

Name of substance/group of substances	CAS number
17-Alpha-ethinylestradiol (EE2)	57-63-6
17-Beta-estradiol (E2), Estrone (E1)	50-28-2, 53-16-7
Diclofenac	15307-86-5
2,6-Ditert-butyl-4-methylphenol	128-37-0
2-Ethylhexyl 4-methoxycinnamate	5466-77-3
Macrolide antibiotics	
Methiocarb	2032-65-7
Neonicotinoids	
Oxadiazon	19666-30-9
Tri-allate	2303-17-5

7.2. USEPA candidate contaminant list

The United States is also actively working to regulate the occurrence of emerging contaminants in the environment. For instance, EPA has published the list of potential contaminants, under the Candidate Contaminant Lists (CCL), which is updated every five years by the EPA. The first ever CCL was published in 1998, it majorly included pesticides, metal contaminants and some other organic contaminants. A list highlighting almost similar contaminants CCL2 was published in 2005. Succeeding to this in 2009 CCL3 was published, including a total of 116 contaminants (104 chemical and 12 microbial contaminants). The list incorporated various pharmaceuticals, biological toxins and industrial emerging contaminants like 17alpha-estradiol, erythromycin equilenin, estrone, PFOS, PFOA and many more. Furthermore, CCL4 published in November 2016 included 97 chemical and 12 microbial contaminants. As a highlight, this list categorised organophosphate flame retardants as compounds of high priority with the requirement of extensive investigation on their impacts (Contaminant Candidate List 4, 2016). Lastly, in 2022 the latest contaminant list CCL 5 was published. This included 66 chemicals from three chemical groups namely, per- and polyfluoroalkyl substances (PFAS), disinfection byproducts (DBPs) and cyanotoxins, and 12 microbes (Contaminant Candidate List 5, 2022).

7.3. Other recommendations

Except for the EU and USEPA lists of priority substances, there is not much legislation available globally about the ECs in the environment. However, the European Parliament Committee on the Environment, Public Health and Food Safety gave a proposal to incorporate some more ECs under the priority list. This proposal recommended amidotrizoate, bisphenol A, carbamazepine, diclofenac, iopamidol etc. for the potential priority substances in water (EPRS, European Union, 2023). In 2011, WHO also amended the Guidelines for Drinking Water Quality to include certain chemicals that were not previously considered. Furthermore, similar to EU and US Australian guidelines for water recycling under National Health and Medical Research Council (NHMRC) provided limits for the ECs in wastewater in the Australian environment. Here NHMRC documented the guidelines for various pharmaceutical and non-pharmaceutical ECs in drinking water. N, N-diethyltoluamide, 4-Nonylphenol (4NP), 4-tert-octylphenol, amoxicillin, azithromycin, sulfamethoxazole, carbamazepine are some of the pharmaceuticals included in the Australian guidelines.

8. Human health risk assessment

The potential risk to human health posed by the presence of emerging contaminants in aquatic environments has been a topic of global concern. In the past decade, many researchers from different parts of the world have assessed the risk to human health due to the presence of ECs in regional water matrices (Schriks et al., 2010; Sharma et al., 2019). Following a similar approach, this study performed an age-specific risk analysis for ten different emerging contaminants, taking into account their intake through drinking water. Therefore, their concentrations in surface water, groundwater and drinking water were considered in the risk analysis.

Figure 5 represents the variation of risk quotients (RQ) for three age groups namely infants (Fig. 5. (a)), children (Fig. 5. (b)) and adults (Fig. 5. (c)). The figure shows that for infants EDCs possess the highest risk with estrone and BPA having most of the points under potential risk. Conversely, diclofenac, 17β-estradiol and sulfamethoxazole exhibit a similar trend, where the majority of data fell under the no appreciable risk category and some data indicated the need for further assessment, accompanied by a few points in the potential risk category. Furthermore, the observed trends for ibuprofen, naproxen, carbamazepine, triclosan and erythromycin indicated a minimal proportion of data falling within the potential risk category (Fig. 5. (a)). The observed trends in RQ for children and adults were largely comparable to those observed in infants, with the only notable difference being a reduction in the risk of each contaminant moving from infants to adults. For instance, in the case of infants and children, sulfamethoxazole has some points showing potential risk, whereas, in the case of adults almost all the points were under the no risk or showed the need for further assessment, decrease in risk among the age groups is also evident in case of BPA where infants are at highest risk and the risk decreases as we move from children to adults.

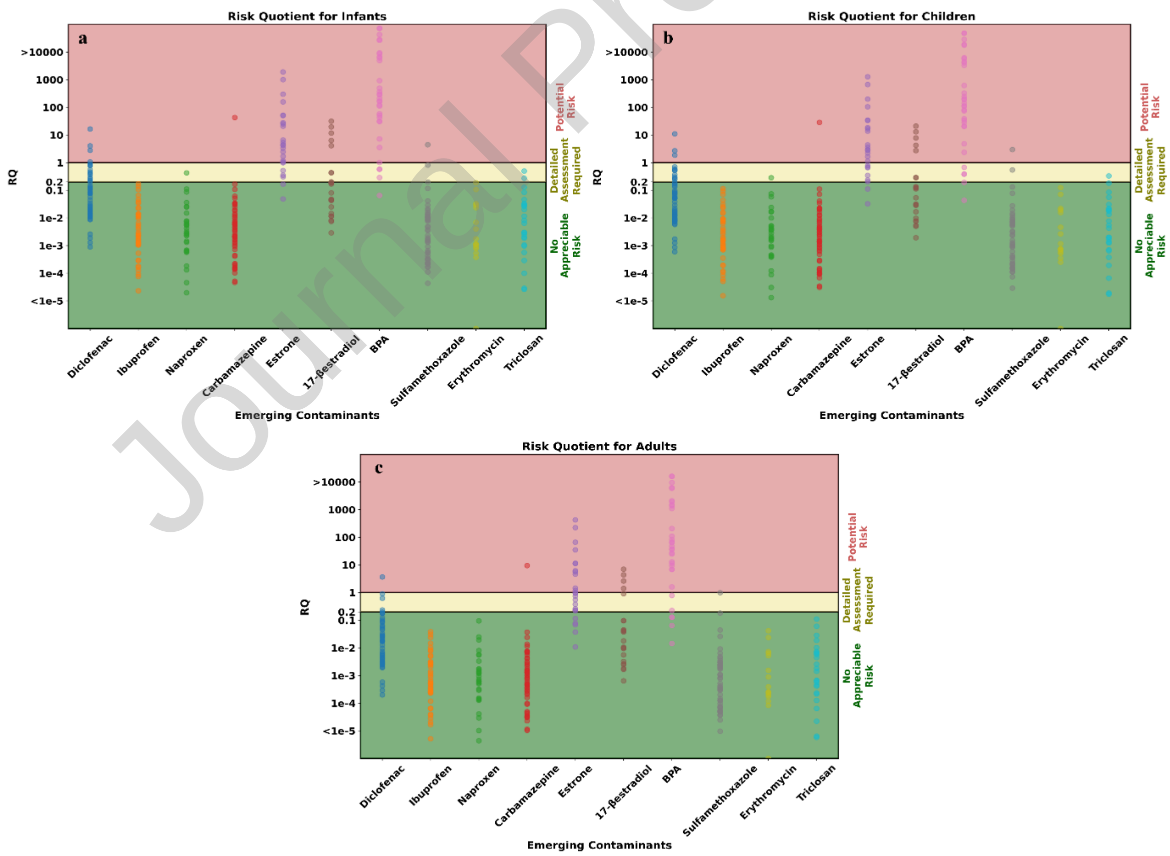

Fig. 5. Categorical spread of risk quotient (a) infants, (b) children, and (c) adults

The identification of location-specific risks associated with considered contaminants can provide a more in-depth understanding of the potential severity of these ECs in the global portable water environment. Figure 6 illustrates the risk posed by various contaminants to infants and children in different locations around the world. Antibiotics (Fig. 6. (a)) exhibit a low risk profile globally, with majority of the locations indicating no potential risk with some exceptions in Africa and South America indicating the need for detailed study and potential risk respectively. A nearly similar trend was followed by carbamazepine beside a few locations in South America showing potential risk (Fig. 6. (b)). EDCs on the other hand showed a high risk in almost all the continents around the world with South America having some locations under potential risk and the remaining indicated the requirement of detailed assessment. Furthermore, as evident from the figure the high risk of BPA is well distributed around the globe, but South America and Asia have also shown some high risk due to estrone, whereas a high risk due to 17β-estradiol can be seen in Africa and South America (Fig. 6. (c)). NSAIDs also majorly had a low risk profile around the world with very few areas indicated potential risk, however, need for further study in case of NSAIDs was observed all over the globe (Fig. 6. (d)). Lastly, triclosan (Fig. 6. (e)) has profile with no appreciable risk beside Asia having the only location indicating the need for further study.

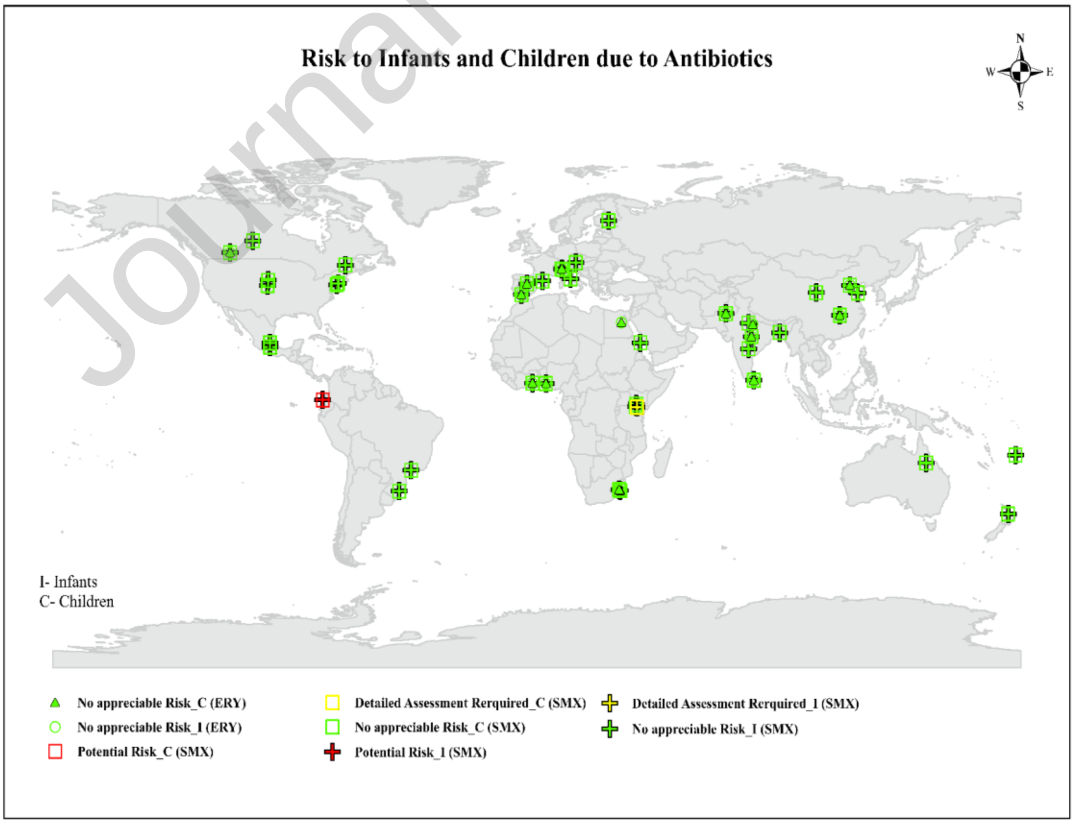

Fig. 6 a. Location-wise characterisation of RQ for infants and children due to presence of antibiotics

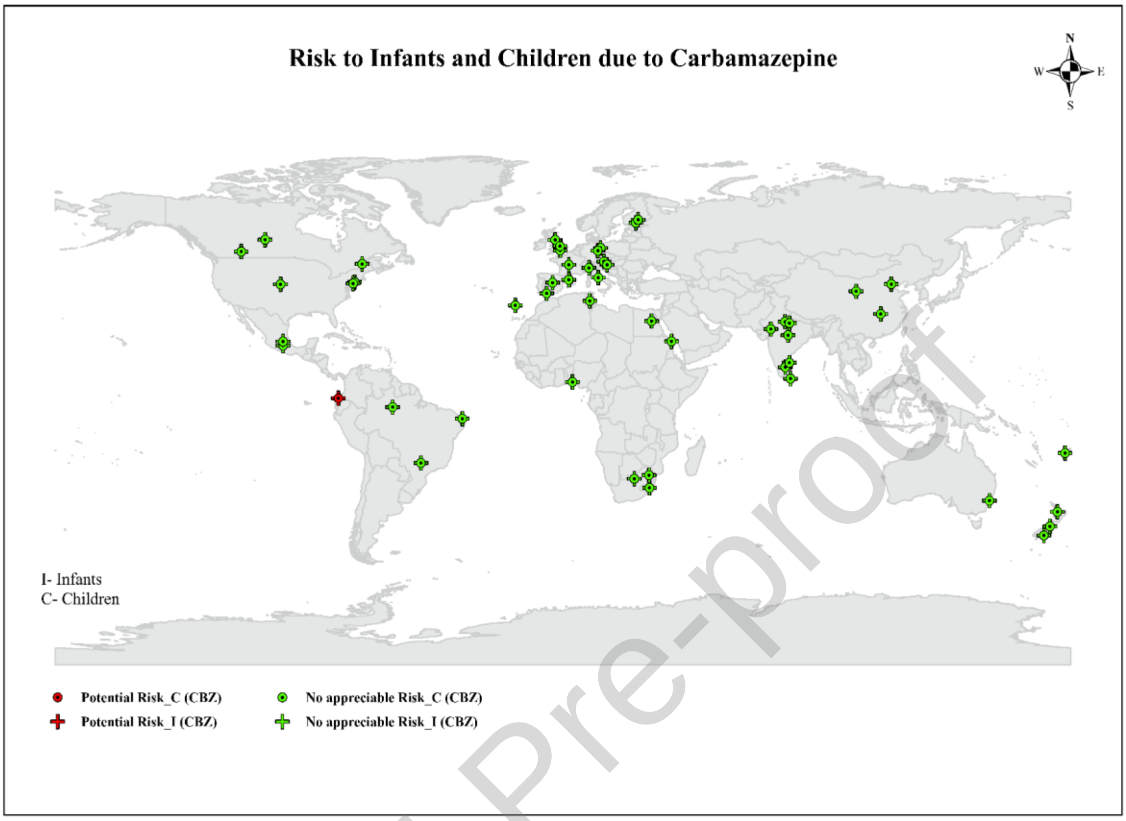

Fig. 6 b. Location-wise characterisation of RQ for infants and children due to presence of carbamazepine

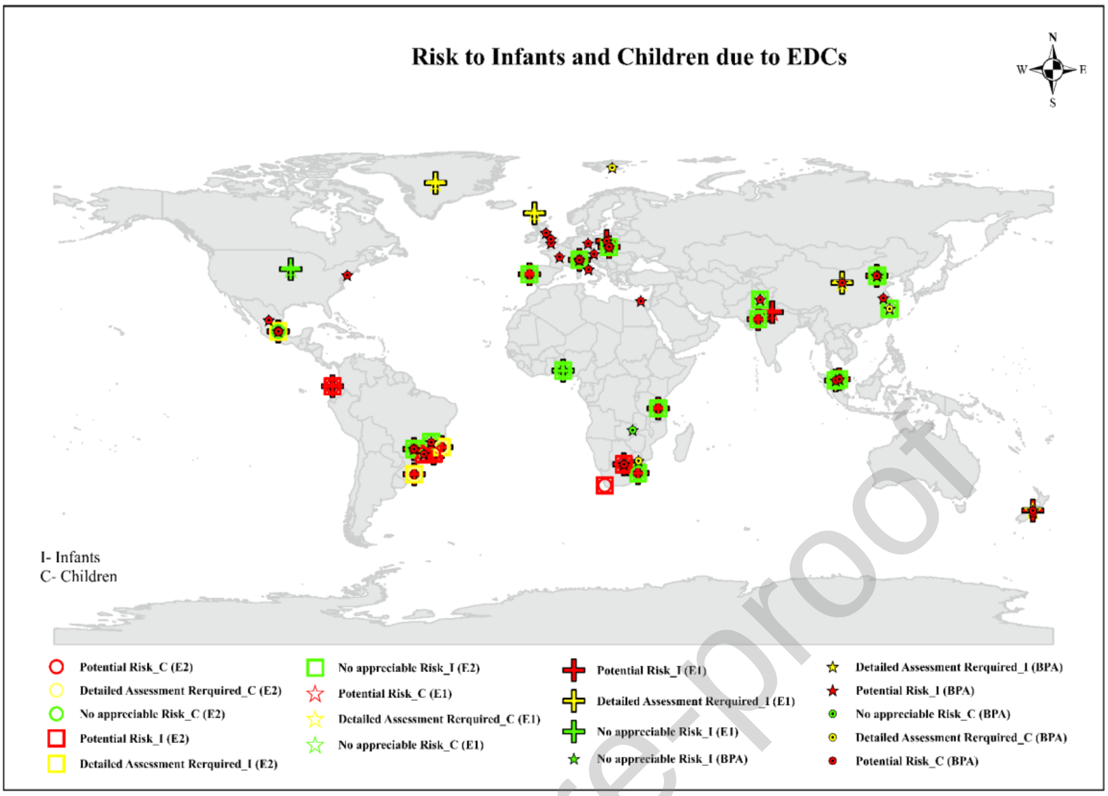

Fig. 6 c. Location-wise characterisation of RQ for infants and children due to presence of EDCs

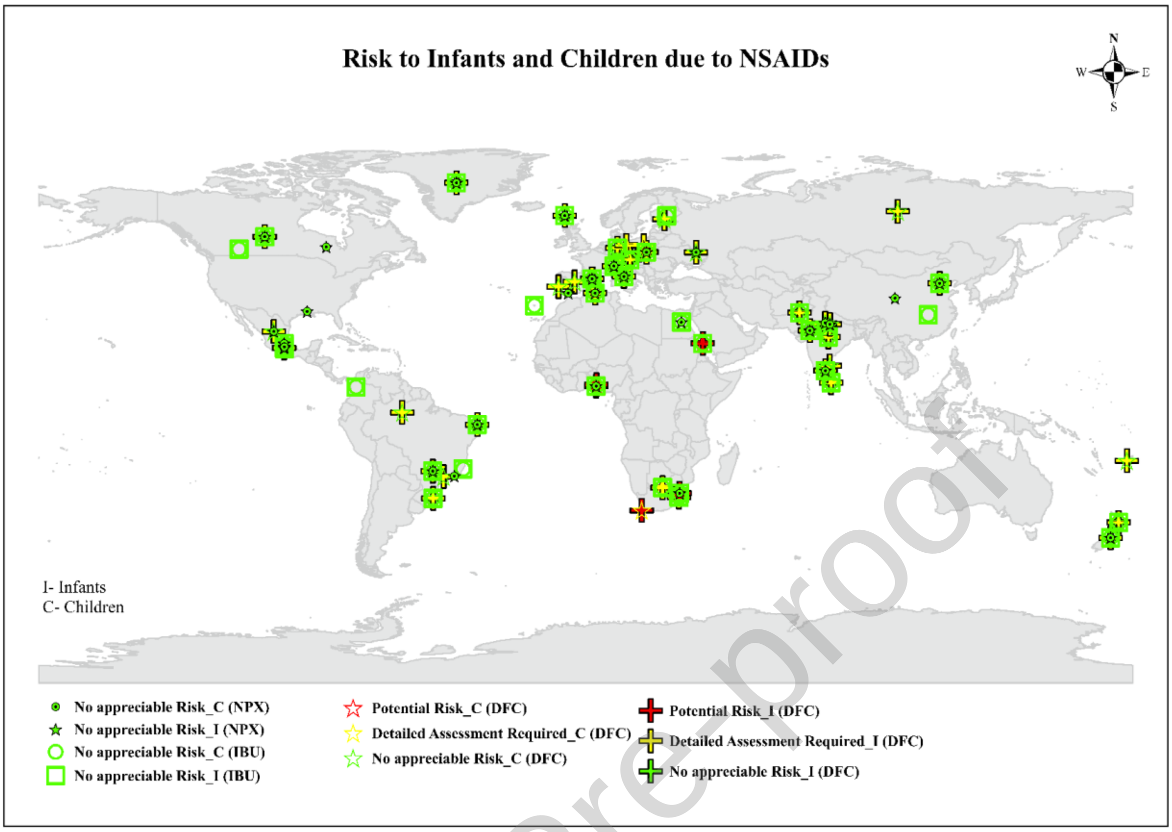

Fig. 6 d. Location-wise characterisation of RQ for infants and children due to presence of NSAIDs

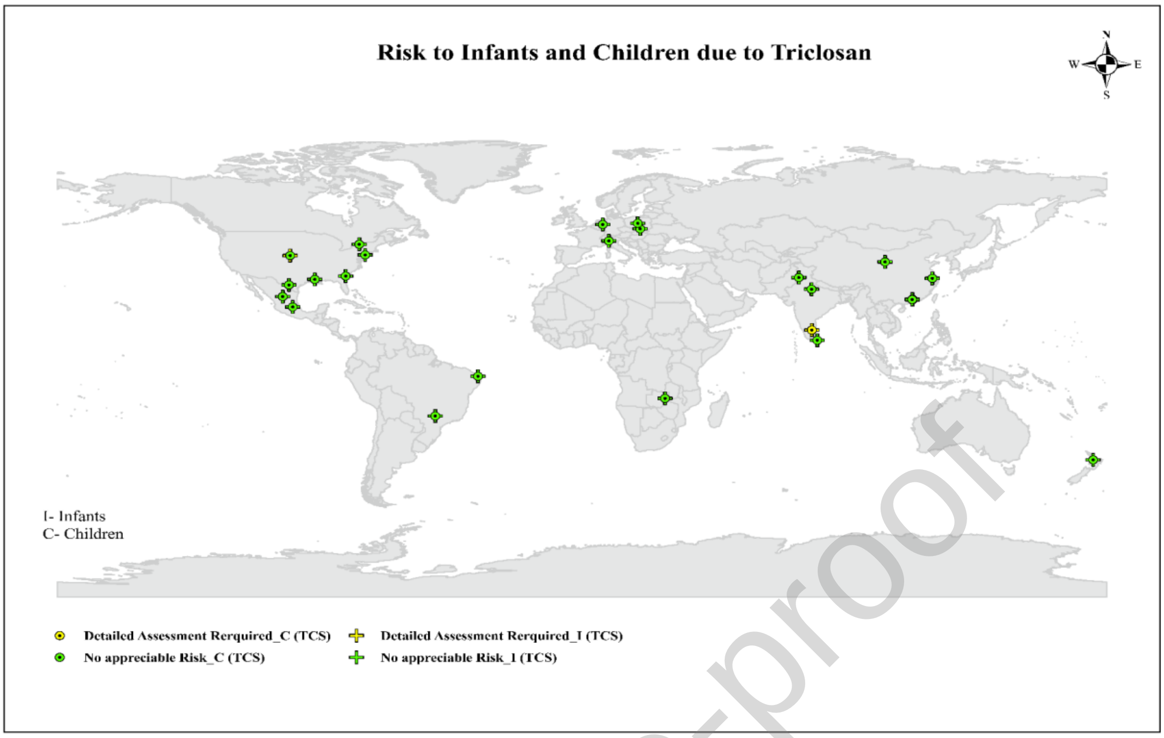

Fig. 6 e. Location-wise characterisation of RQ for infants and children due to presence of triclosan

As discussed earlier, the potential risk was reduced when higher age groups are considered, the same is well evident from the figure (Fig. 7) which depicts the risk any considered contaminant can pose to adults. The overall trend for all the contaminants was almost similar to the case of infants and children. For example, antibiotics and carbamazepine had no appreciable risk at majority of the locations and the very few locations with possible risk were identified in the region of South America (Fig. 7. (a and b)). In the case of EDCs estrone and BPA have more locations characterised as potential risk sites. Europe and South America had some serious risks to EDCs followed by Asia and Africa then Oceania and lastly North America (Fig. 7. c)). Similar to the lower age group NSAIDs in the case of adults also followed a low risk profile, with some locations in Africa showing potential risk and need for detailed assessment for diclofenac. Whereas no potential risk was identified for ibuprofen and naproxen and both the drugs have a completely no risk profile all around the globe (Fig. 7. (d)). Furthermore, no appreciable risk has been identified for triclosan, with all the locations identified as no risk sites (Fig. 7. (e)).

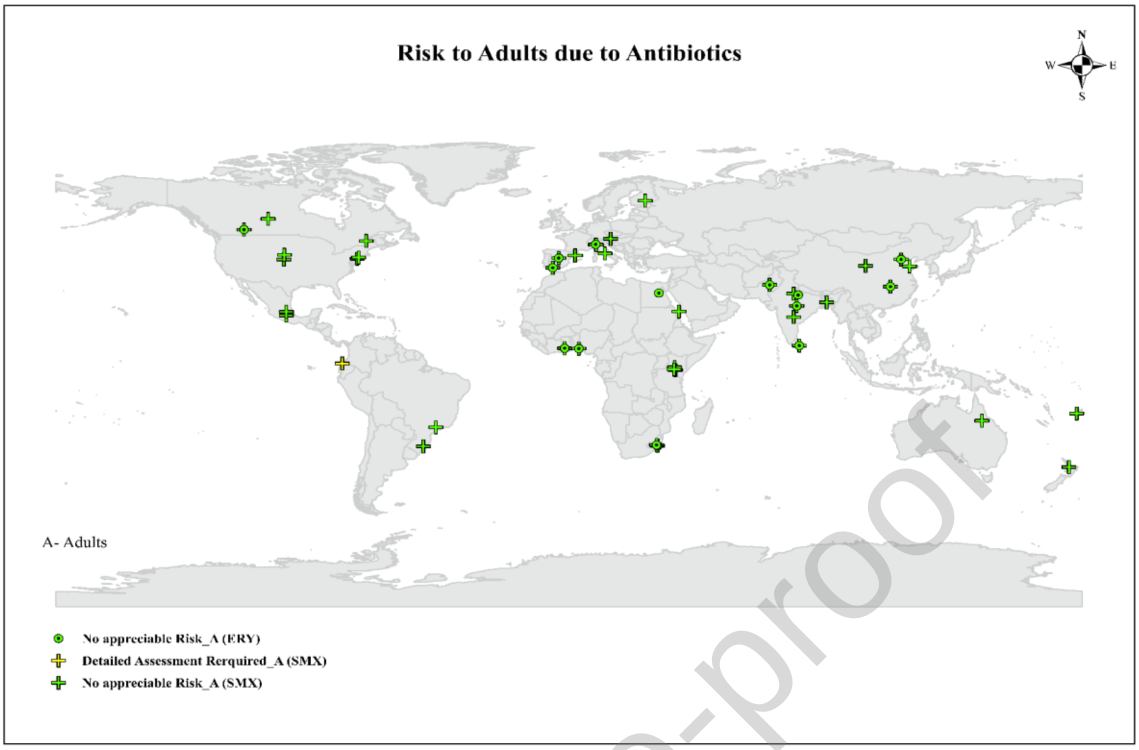

Fig. 7 a. Location-wise characterisation of RQ for adults due to presence of antibiotics

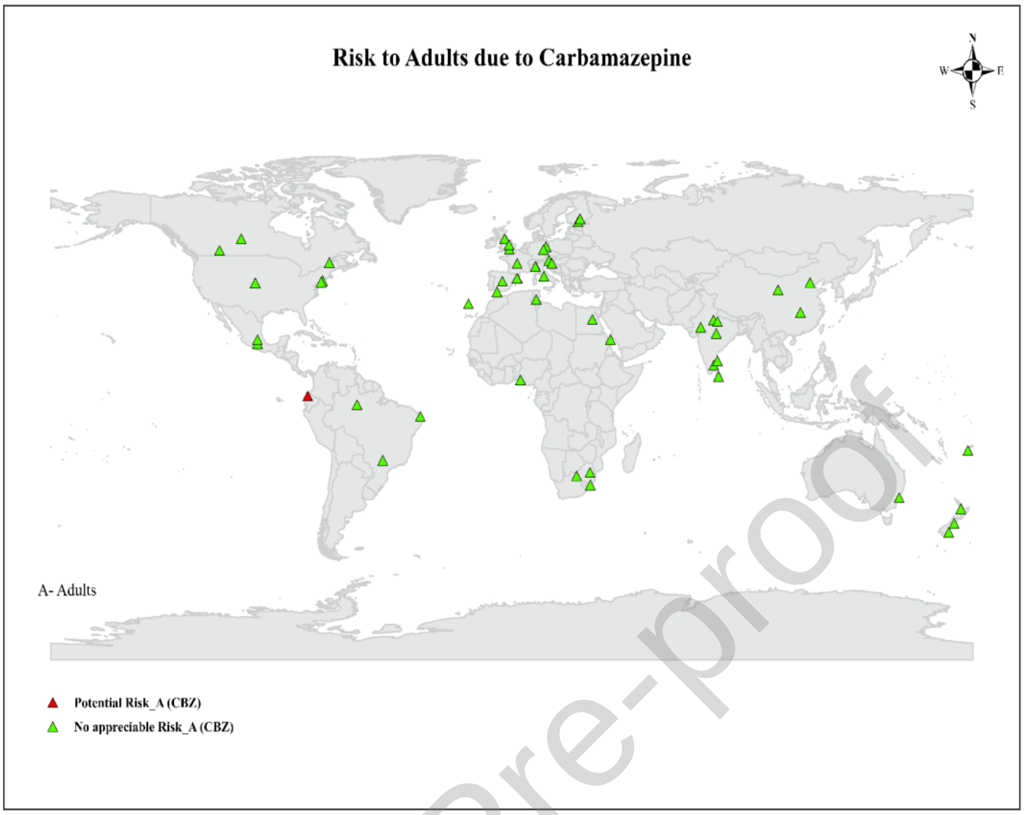

Fig. 7 b. Location-wise characterisation of RQ for adults due to presence of carbamazepine

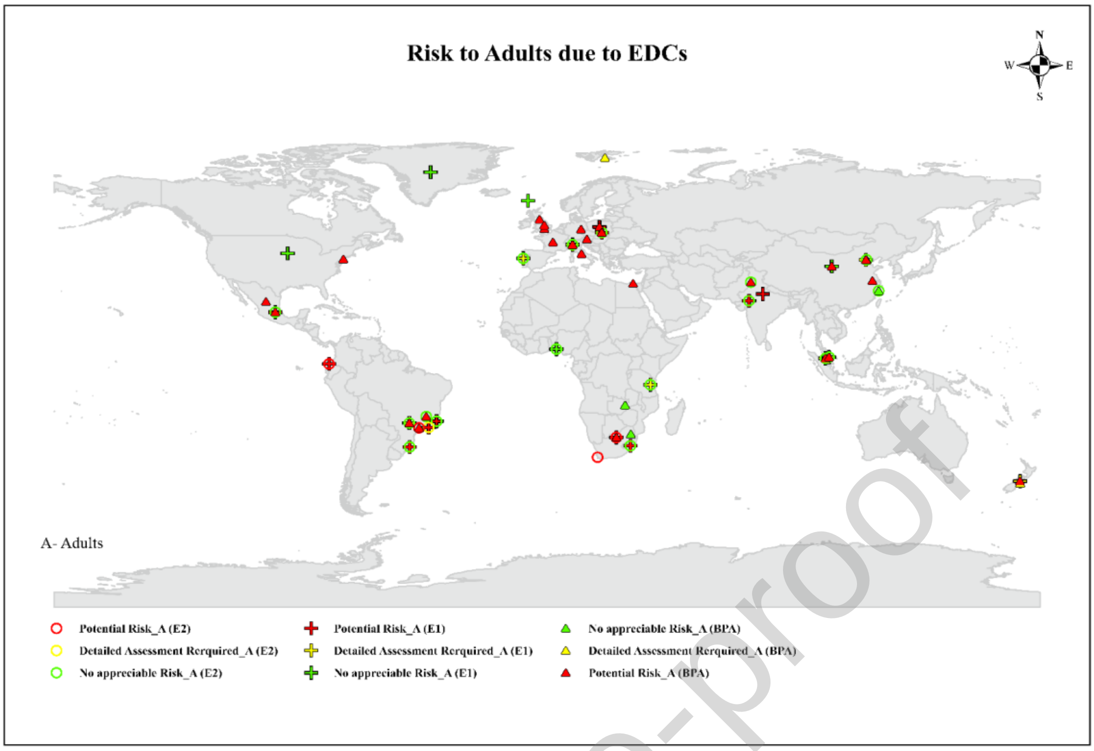

Fig. 7 c. Location-wise characterisation of RQ for adults due to presence of EDCs

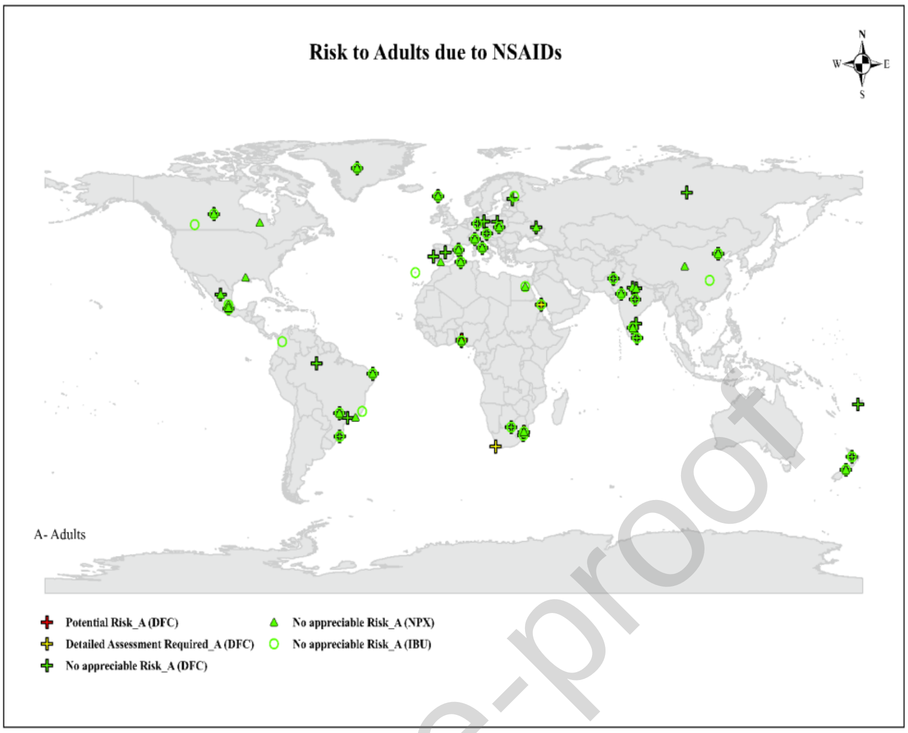

Fig. 7 d. Location-wise characterisation of RQ for adults due to presence of NSAIDs

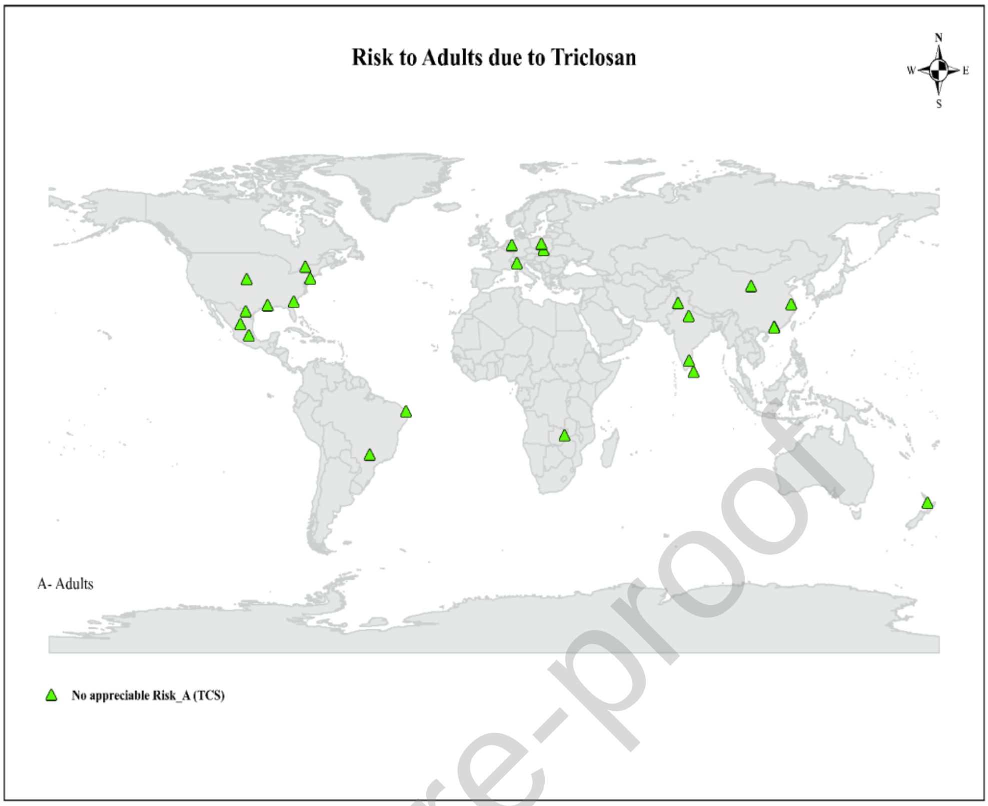

Fig. 7 e. Location-wise characterisation of RQ for adults due to presence of triclosan

9. Summary

The ubiquitous presence of emerging contaminants in water can be due to the continuously increasing use of compounds like pharmaceuticals, personal care products, industrial chemicals and others belonging to the category. The majority of these contaminants enter the global water matrices via different wastewater streams, due to the lack of proper regulatory structure these chemicals are being regularly discharged into the environment without proper treatment. Also, from the study it was found that the efficiency of treatment varies with the considered contaminants. For instance, the biological activated carbon has shown good removal for antibiotics and analgesics but the removal is comparatively less when EDCs are considered. On the other hand, chemical technologies like UV photolysis/H_2O_2 were among the best techniques in the removal of majority of the ECs but the removal efficiency was relatively less when EDCs were considered. This could be due to the complex structure and toxic nature of emerging contaminants which can impact the efficiency of treatment technologies. Furthermore, Ozonation based hybrid systems have shown good removal for most of the emerging contaminants. The present study provides a critical review of the effectiveness of different treatment systems when the removal of ECs is considered. As discussed above the properties of contaminants largely affect the efficiency of treatment so a more detailed assessment of the interaction between different contaminants and treatment systems can provide a better insight into the factors governing the efficiency of each treatment method in case of different contaminants.

The occurrence of ECs is widespread throughout the globe, but some relatively high concentrations of the ECs were detected in countries in Asia and Latin America. The resulting high concentrations of ECs in global water matrices can lead to adverse effects on human health following the consumption of water with the presence of contaminants of emerging concern. Previously, few studies also estimated the potential risk due to the presence of ECs in water (Schriks et al., 2010; Sharma et al., 2019). In this study, the most spatially variable age-pecific risk was found due to the presence of EDCs like estrone and BPA. Although EDCs indicated a potential risk all around the world, a relatively high risk due to multiple contaminants was identified in South American, European and Asian countries. Overall, the study indicated a good resistance to all the considered contaminants except a few. Additionally, some contaminants have also indicated the need for detailed assessment. From the study it was seen that the lack of proper regulatory structure has contributed to the high persistence of emerging contaminants in global water matrices. So, a proper general or local regulatory framework is needed to be developed to mitigate the risk due to presence of emerging contaminants in water.

10. Future scope and limitations

There is a significant deficit of information pertaining to the prevalence of emerging contaminants (ECs) in drinking water on a global scale. Although the topic has recently gained the interest of stakeholders, the majority of studies have focused on pharmaceuticals and personal care products, while other classes of ECs, such as PFAS, PFOS, flame retardants and others, have not been given the requisite attention. The global prevalence of ECs underscores the necessity for the establishment of an effective regulatory framework and the implementation of mitigation strategies to prevent the entry of such chemicals into the global water matrices. To improve the current situation, a source identification for different ECs in fresh water can be carried out on a global scale through the execution of small pilot studies, thereby facilitating the formulation of region-specific remediation plans.

The current study is limited to the occurrence of a few pharmaceutical and personal care products in the water matrices; however, the actual situation may differ considering the broad classes of ECs. Furthermore, the risk analysis was carried out considering the single contaminant separately. A risk analysis considering the mixture of different ECs in water must be carried out to get a clearer understanding of the actual situation.

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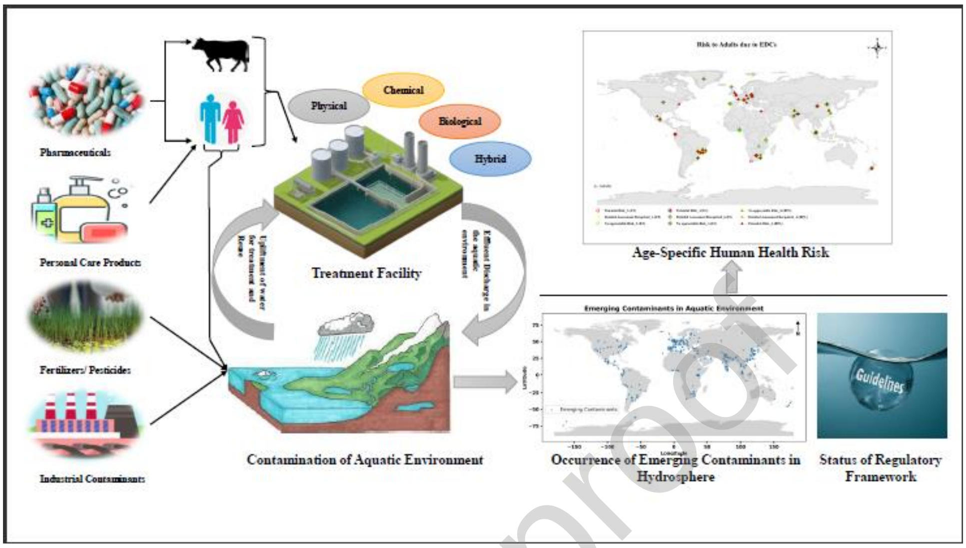
Declaration of Interest

The authors confirm that they have no known competing financial interests or personal relationships that could have biased the work reported in this paper.

Environmental Implications

The research underscores the pressing environmental implications of emerging contaminants (ECs) in aquatic systems. The compilation of global data on the occurrence of ECs provides insight into their extensive presence and facilitates the identification of regions and water matrices most affected. This information can inform targeted monitoring and management strategies in areas with raised contamination levels. The study also emphasises need for more generalised and robust regulatory framework to mitigate the presence of emerging contaminants in environmental water. Moreover, with the risk assessment the study also supports the development of targeted risk management strategies.

Graphical abstract



Highlights

- The occurrence of selected ECs in global water matrices is reviewed.
- EC removal efficiency of existing treatment technologies are discussed.
- Highest human health risk attributed to EDCs found in global water matrices.
- This review will serve as a basis for developing a more robust regulatory framework.