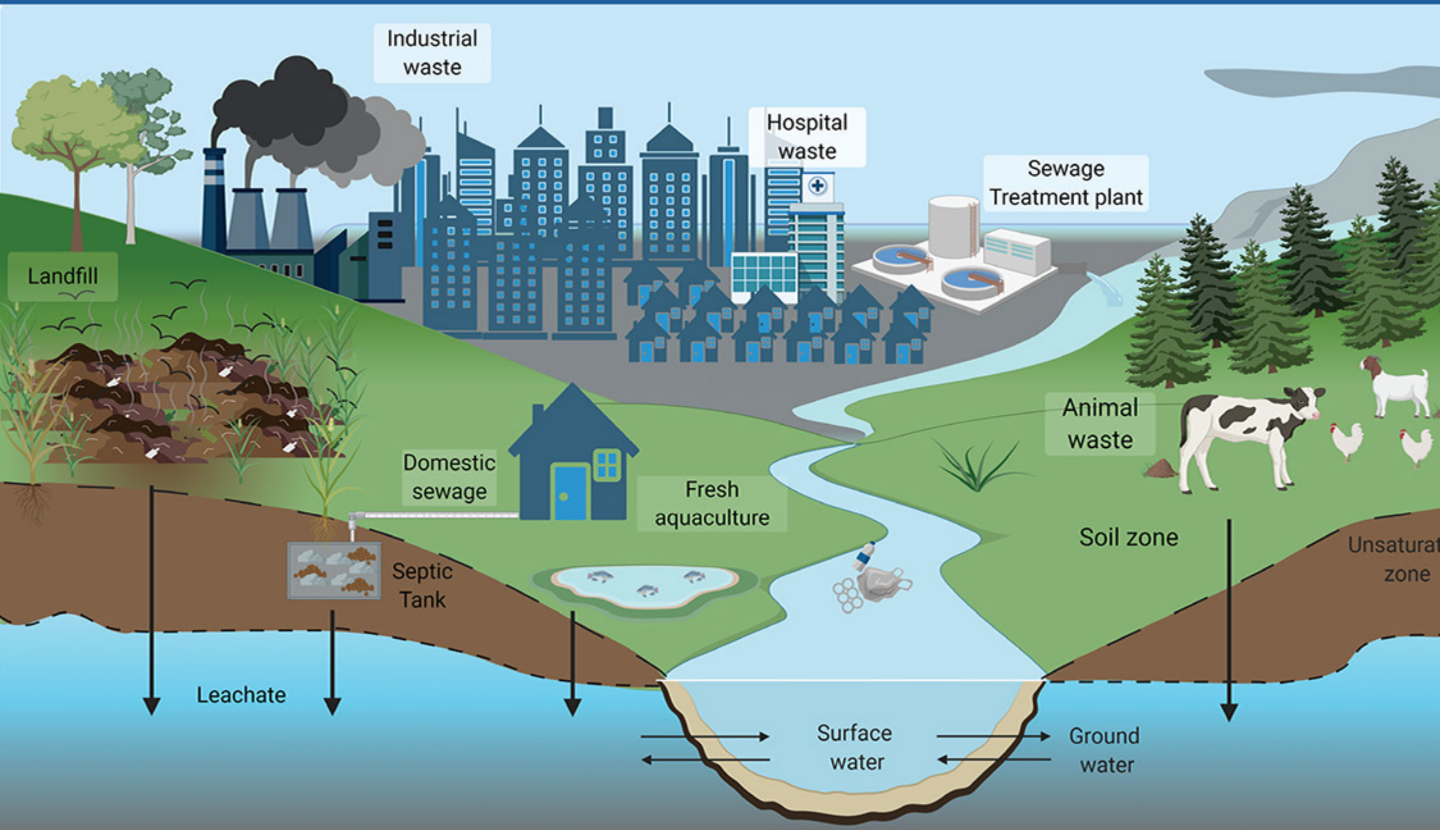
Emerging Contaminants in the Environment

Challenges and Sustainable Practices



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CHAPTER

5 Transport, fate, and bioavailability of emerging pollutants in soil, sediment, and wastewater treatment plants: potential environmental impacts

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5.1 Introduction

Emerging contaminants (ECs) include a wide variety of substances that differ in their chemical structure, toxicity, and environmental behavior. The list of these compounds increases every year as new artificial contaminants and biologically occurring trace compounds such as nanomaterials and microplastics are being detected. Because of this continuous research and discovery, these compounds are classified as "emerging." Nevertheless, there is a discussion about the new term "contaminants of emerging concern" (CECs). CECs may be used in situations where a particular compound has been present in the environment for a long period of time, but until recent times its danger and biological impact have been undescribed (Sauvé & Desrosiers, 2014). The primary source of contaminants in the environment are wastewater treatment plants, which receive effluents from households, hospitals, industrial, and chemical manufacturing, municipal sources, and agriculture (Kahl, 2018a).

Similar to pharmaceutical and personal care products, some other organic contaminants cannot be removed effectively by conventional wastewater treatment processes. (Ghahari et al. 2021). Therefore, advanced wastewater treatment technologies have been developed including activated sludge, activated carbon adsorption, bioelectrochemical methods, enzymatic technologies, hydrolysis, metal-assisted processes, microbial technologies, oxidation processes (coupled or not coupled with biological activated carbon), photolysis, phytolysis, and redox reactions (ionic, acidic, or alkaline), among others, to improve the biodegradation of these contaminants (Souza, Cerqueira, Sant'Anna, & Dezotti, 2011; Wang & Wang, 2018).

Even though removal processes exist, it is estimated that these contaminants are usually present at low environmental concentrations (nanograms to milligrams per liter range), and the development of undesired physiological damages in humans and wildlife need further studies (Archer, Petrie, Kasprzyk-Hordern, & Wolfaardt, 2017). In this chapter, the classification, transport, fate, and bioavailability of emerging pollutants of concern such as antibiotics, resistant bacteria, antibiotic resistance genes (ARGs), steroids, and biocides in aquatic and soil environments will be discussed in detail.

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5.2 Emerging pollutants

CEC include a long list of synthetic or natural chemical compounds, including microorganisms' metabolites with the potential to access the environment and cause known or unknown harmful ecological and/or human health consequences (Calvo-Flores, Isac-García, & Dobado, 2017a; Kahl, 2018b; Raghav, Susana, Mitchell, & Witte, 2020). At present, no universal regulations are established for environmental monitoring (Galindo-Miranda et al., 2019; Thomaidis, Asimakopoulos, & Bletsou, 2013). Some of them eventually survive biodegradation when discharged into the environment. Many others and their metabolites are ubiquitous and persist in the environment (Calvo-Flores, Isac-García, & Dobado, 2017b).

5.2.1 Synthetic hormones and other endocrine-disrupting chemicals

Hormones are a class of signaling molecules produced by glands in superior organisms carried by the circulatory system to regulate physiology and behavior. These compounds can be natural or synthetic and are not readily biodegradable. They become contaminants in wastewater effluents that discharge in surface waters or bioaccumulate in waterborne organisms (Fig. 5.1). Some common examples of these environmental pollutants are 17α-ethinylestradiol, 17β-estradiol, estrone, estriol, progesterone, and diethylstilbestrol (Méndez, González-Fuentes, Rebollar-Perez, Méndez-Albores, & Torres, 2017; Palacios, Cortes, Jenks, & Maki, 2020).

EDCs are considered the most important contaminants of water. EDC list include hormones and other compounds such pesticides, disinfection by-products, bisphenols, fluorinated substances, and phthalates. The presence of EDCs in water has become a public health concern since these chemicals have been associated with harmful health and reproductive disorders in human and animals (Gonsioroski, Mourikes, & Flaws, 2020). These compounds can cause disruption of the endocrine system in some species, even at low concentrations of parts per trillion (ng/L). Endocrine disruption is caused when a compound hinders the normal hormonal processes across multiple molecular pathways. Endocrine-disrupting compounds are a potential risk for fauna and humans as they are presumed to cause diseases like nephrotoxicity, cancers, and metabolic disorders, among others (Lecomte et al., 2017; Raghav et al., 2020).

Adeel et al. (2017) reported that globally, the discharges of natural steroid estrogens are approximately 30,000 kg/yr, with an additional 700 kg/yr from birth control pill practices. The potential discharge of estrogens to the environment from farm animals is much higher, about 83,000kg/y. The manure produced by livestock is a significant source of hormones into the surface water and soil (Adeel et al., 2017; Lecomte et al., 2017).

Nonetheless, limited information exists regarding hormones consumption worldwide. The content of naturally occurring hormones in food has been considered safe for decades. However, hormone toxicity, including estrone, estradiol and estriol, is significant and poses severe risks to soil, plants, water resources and humans. The toxicity is related to the uncontrolled release of hormones into the environment, causing an adverse and harmful effect in the immune, nervous, and reproductive systems of humans and other organisms. Recently, the human' exposure to hormones, and other endocrine-disruption contaminants, have been associated with health issues in several epidemiological and experimental studies with humans and animals (Adeel, Song, Wang, Francis, &

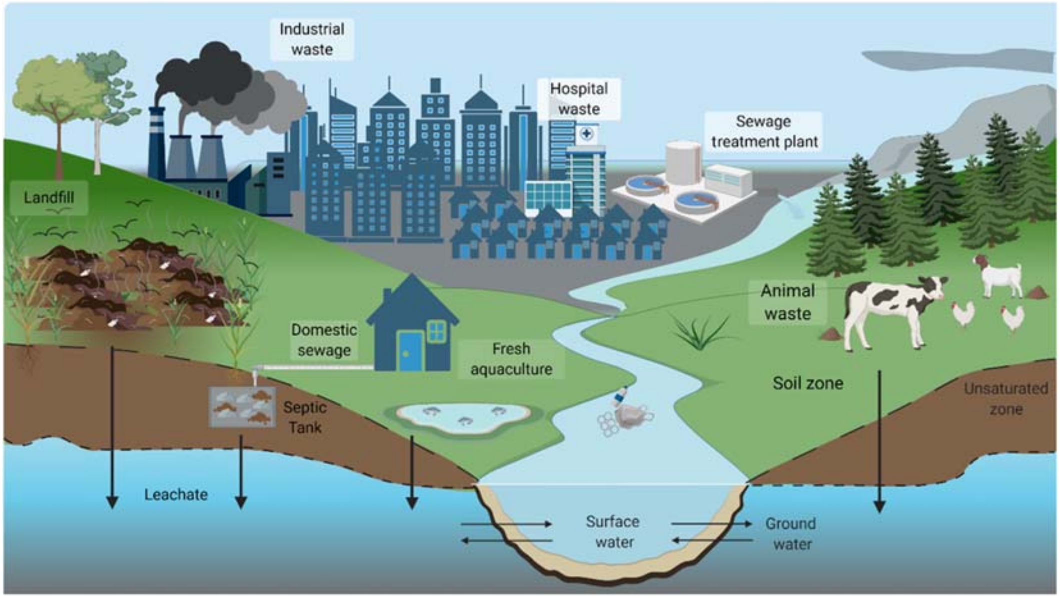

FIGURE 5.1

Pathways of CECs entry to the environment. By observing urban and rural landscapes, evidence can be found about possible entry routes of emerging contaminants into the environment. Wastewater treatment plants collect sewage from industries, commerce, houses, and health care facilities. Eventually, many pollutants are discharged into watersheds due to low degradation of this contaminants (such as sweeteners, stimulants, pharmaceuticals (including antibiotics), and personal care products, among others) by photolytic and biological processes. Furthermore, livestock raising, artisanal domestic sewage systems, manure used as fertilizer, and poor practices in solid waste disposal allow these contaminants' entry into soils and groundwater reservoirs where they accumulate. Created with BioRender.com.

Yang, 2017; Czarny, Szczukocki, Krawczyk, Gadzała-Kopciuch, & Skrzypek, 2019; Kumar et al., 2020; Palacios et al., 2020).

Globally, the incidence of hormone-dependent cancers (HDC) such as breast cancers, endometrium, prostate and ovaries, have increased in all age groups over the past 30 years. Some causes for this increase may be related to the population's ageing, environmental conditions, contaminant exposure, lifestyle and genetic mutations ($< 20\%$). In women, globally, the most commonly diagnosed HDC are breast and cervical cancers; on the other hand, prostate cancer is the most frequently diagnosed cancer in men. Exposure to exogenous endocrine-disrupting chemicals (EDCs), may represent a significant risk factor (Bray et al., 2018; Lecomte, Habauzit, Charlier, & Pakdel, 2017; Raghav et al., 2020).

Regarding water exposures, Bexfield et al. (2019) investigated the occurrence of hormone and pharmaceutical products in groundwater for drinking production across the United States. The study analyzed samples from 1091 sites in Principal Aquifers representing 60% of the volume pumped for drinking-water supply. The results revealed the presence of bisphenol A (plastic), carbamazepine, sulfamethoxazole, and meprobamate (pharmaceutical), and 1,7-dimethylxanthine (caffeine degradation product) in lower than the defined human-health benchmarks. Hydrocortisone showed a concentration larger than a human-health threshold at one site (Bexfield, Toccalino, Belitz, Foreman, & Furlong, 2019).

Some toxic effects due to hormones have been reported. Globally, the incidence of hormone-dependent cancers (HDC) such as breast, endometrium, prostate, and ovarian cancers, have increased in all age groups over the past 30 years. Some causes for this increase may be related to the population's aging, environmental conditions, contaminant exposure, lifestyle, and genetic mutations ($<20\%$). In women, globally, the most commonly diagnosed HDC are breast and cervical cancers; on the other hand, prostate cancer is the most frequently diagnosed cancer in men. Exposure to exogenous endocrine-disrupting chemicals (EDCs), may represent a significant risk factor (Bray et al., 2018; Lecomte, Habauzit, Charlier, & Pakdel, 2017; Raghav et al., 2020).

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Adeel et al. (2017) reported that globally, the discharges of natural steroid estrogens are approximately 30,000 kg yr^{-1}, with an additional 700 kg yr^{-1} from birth control pill practices. The potential discharge of estrogens to the environment from farm animals is much higher, about 83,000 kg yr^{-1}. The manure produced by livestock is a significant source of hormones into the surface water and soil (Adeel et al., 2017; Lecomte et al., 2017).

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In Mexico, in the Cuautla River at the State of Morelos, several ECs including 17 β-estradiol, 17α-ethynylestradiol, BPA, 4-N-nonylphenol, and 4-tert-octylphenol, were determined in surface water during the dry season. According to ecological risk assessment conducted, the estrogenic activity values and environmental risk were elevated even though Cuautla River had only trace concentrations of these pollutants, which could have severe effects on sustainability, as they can modify the growth of plants and cause ecotoxicological and human health problems (Calderón-Moreno et al., 2019).

Roshan & Taghizadeh (2019) reported estrogen levels in the public recreational pools of Shiraz, Iran. They observed a significant increase in the pools relative to filling water. The women-only pool's estrogen concentration was 17.95 pg mL^{-1}, meanwhile the men-only pool increase was 8.96 pg mL^{-1}. The highest estrogen in the women's pools, 30.8 pg mL^{-1}, occurred in hot seasons due to more usage (Roshan & Taghizadeh, 2019). The review of Adeel et al. (2017) indicates an acceptable daily intake of estrogens for humans via food (μg day^{-1}) and predicted-no-effect concentration for aquatic life (PNEC). According to these values, 17 β-E2 is <5 μg day^{-1} for humans on the whole and E1 as <50 μg day^{-1} for women. No more information is available for threshold values of estrogens in environmental or recreational waters worldwide (Adeel et al., 2017).

The occurrence of hormones and other EDCs in the drinking water supply, particularly in tap water, is a common finding throughout the world, and it has become a significant concern in the last few decades (Brueller et al., 2018; Gonsioroski, Mourikes, & Flaws, 2020; Wee & Aris, 2019; Cortes Munoz et al., 2013). These compounds are relatively stable and resistant to degradation by water treatment methods. The concern is that they may enter the drinking water systems.

In 2018 Mnguni et al. reported estrone in raw water samples taken from Vaal River's catchment area, south of Johannesburg, South Africa, during the rainy season. The hormone was found at concentrations of 0.90 and 4.43 ng L^{-1}; the significance of these concentrations still unknown. All treated potable water samples from this site presented undetectable levels of the analyzed hormones (Mnguni, Schoeman, Marais, Cukrowska, & Chimuka, 2018).

Further systematic epidemiology studies are needed to investigate the low dose effect and consequences of hormones and other endocrine-disrupting compounds in human health and the environment.

5.2.2 Pharmaceuticals and personal care products

Pharmaceuticals and personal care products (PPCPs) include thousands of various chemicals used for consumer and therapeutic purposes. Pharmaceuticals may be prescription and nonprescription drugs utilized for veterinary and human purposes to prevent or treat animal or human diseases and personal care products are used mostly to improve daily life quality. The list of PPCPs includes analgesics, antidepressants, antimicrobials, antipyretics, cosmetics, disinfectants, fragrances, steroids, stimulants, and many other widely used chemicals daily (Archer et al., 2017; Calvo-Flores, Isac-García, & Dobado, 2017c; Daughton, 2005; Sui et al., 2015). Therefore, obtaining information to assess the risks related with the existence and impact of micropollutants in the environment is crucial (Sodré, Dutra, & Dos Santos, 2018; Sui et al., 2015).

A wide range of PPCPs persists in natural freshwater resources. They usually occur as trace environmental contaminants (mainly in surface and groundwater) due to their widespread, constant, and extended use in a wide range of veterinary and human practices. PPCPs contaminate water systems from various sources: drain water, unlawful disposal of human excreta, industries, leeching from landfills, and sewage. Unexpected physiological effects in wildlife and humans caused by PPCPs in environmental waters are currently unknown. (Fig. 5.1) (Daughton, 2005; Ebele, Abou-Elwafa Abdallah, & Harrad, 2017). However, some studies showed that continuous exposure to subtoxic concentrations of PPCPs can cause unanticipated outcomes and unintentional effects that may induce detrimental impacts on humans and ecosystems (Sui et al., 2015).

Li et al. (2019) analyzed the distribution of 15 pharmaceuticals in soil—water—radish systems and observed that 14 out of 15 compounds could go into radish tissues in which the accumulation varied from 2.1 to 14,080 ng g^{-1} (Li, Sallach, Zhang, Boyd, & Li, 2019). Roberts et al. (2016) reported the differences between removal efficiencies and concentrations in the effluent-receiving environment of 11 pharmaceuticals in Australia's wastewater treatment plants. Removal of most pharmaceuticals was highly variable for various compounds. It was highest for venlafaxine and triclosan compared to carbamazepine, sertraline, fluoxetine, atenolol, sotalol, metoprolol, propranolol, chlorpheniramine, and diphenhydramine (Roberts et al., 2016).

Another study developed in the Nairobi River Basin in Kenia revealed the increased risk of antimicrobial resistance secondary to pharmaceuticals and other chemicals use and bad disposal. Caffeine, carbamazepine, nicotine, sulfamethoxazole, and trimethoprim were the most frequently detected compounds. Eighty-six percent of the total amount of pharmaceutical analyzed along the Nairobi/Athi catchment corresponds to paracetamol, caffeine, and antibiotics such as sulfamethoxazole and trimethoprim (Bagnis et al., 2020).

In other fields, such as the aquaculture industry, the use of pharmaceuticals has important and severe ecosystem consequences. According to the Food and Agriculture Organization (FAO), aquaculture is the fastest-growing food-producing activity worldwide. It now accounts for 50% of the world's fish used for food (Food & Agriculture Organization of the United Nations, 2021). Pharmaceuticals, such as antibiotics, have been widely used in the aquaculture industry for disease prevention and growth promotion; these products can eliminate harmful organisms and inhibit or kill planktons, which is beneficial for simultaneously selected microorganism growth. Continuous use of PPCPs might cause gene mutation in bacteria and antibiotic resistance acquisition (He, Cheng, Kyzas, & Fu, 2016).

5.2.3 Biocides

Biocides are substances of natural origin and/or obtained by chemical synthesis. These compounds are used to eliminate or neutralize a given group of organisms from the environment, such are insects, animals, fungi, or plants. The list includes building materials, hand and surface disinfectants, water disinfectants, pesticides, wood preservatives, and other biocidal products (e.g., antifouling agents; Durak, Rokoszak, Skiba, Furman, & Styszko, 2021). According to some authors, biocides are classified as pharmaceuticals or personal care products (insect repellent; Salimi et al., 2017; Stefanakis & Becker, 2015).

Pesticides are chemical compounds used to eliminate pests, like rodents, insects, plants, and fungi. They are used in public health to control vectors of disease, such as mosquitoes, and in agriculture, to prevent damage of harvests by pests (World Health Organization, 2020). Biocides used in agriculture include fungicides, herbicides, insecticides, nematocides, and rodenticides (Food & Agriculture Organization of the United Nations, 1997).

In recent years, biocides have received increasing attention as environmental contaminants because they may induce acute toxicity in aquatic organisms and the accumulation of toxic substances in the environment may lead to the loss of habitat and biodiversity and are a hazard to human health (Durak et al., 2021). Acute toxicity describes the adverse effects resulting from a single exposure to a biocide via dermal, inhalation, or oral routes. The harmful effects can be seen as clinical signs of toxicity, abnormal body weight changes, and/or pathological changes in organs and tissues, which in some cases might result in death (European Chemicals Agency, 2013).

Worldwide pesticide use had significantly increased by 79% during the period 1990–2018, according to the FAOSTAT database (http://www.fao.org/faostat). The growing human population has put increasing demand on agricultural productivity (FAO, WHO, 2019). Their use is particularly high in tropical countries that provide out-of-season fresh fruits and vegetables in the global market, e.g., banana, pineapple, melon, and coffee. (Ecobichon, 2001; Pesticide Action Network UK 2017). It is important to mention that pesticides are one of the most frequent causes of death by self-poisoning in low- and middle-income countries (World Health Organization, 2020).

The level of biocides in the ecosystem is positively related to biocide chemical characteristics and emission rate, human activity, utilization, and mode of use (Fig. 5.1). Biocides are used in daily life as active substances in body care products or pharmaceutical preparations, and they have already been detected in wastewater treatment plants (Durak et al., 2021; Mielech-Łukasiewicz & Starczewska, 2019).

As mentioned before, the application of pesticides may lead to pollution of the aquatic environment including leaching, runoff, and spray drift, affecting aquatic life directly and indirectly. Pesticides in the water runoff affect human health through the ingestion of contaminated fishes and shellfish or directly by drinking contaminated water. Biocides have critical ecological impacts affecting other living organisms with specific mechanisms, such as biomagnification and bioconcentration (Durak et al., 2021; Hassaan, El, & Nemr, 2020; Mielech-Łukasiewicz & Starczewska, 2019). Biomagnification is defined as the rising level of a chemical or biocide by entering the food chain. The level of pesticides and other chemicals is gradually amplified in tissues and other organs from smaller organisms to high-level predators (i.e., humans). Bioconcentration refers to the transmission of a biocide -or any other compounds- into an organism from the nearby medium and its accumulation in tissues. For example, pesticides such as dichlorodiphenyltrichloroethane (DDT) accumulate in fat tissue in humans and other animals. Environmental degradation of pesticides is led by microbiological interactions in water and soils and by metabolization of the compounds when living organisms consume them as part of their food uptake (Hassaan et al., 2020)

5.2.4 Antibiotics

Antibiotics are natural substances produced by microorganisms that inhibit or kill other microorganisms whereas antimicrobial agents are natural or synthetic drugs that inhibit growth of microorganisms. The discovery of antibiotics is described as the major medical milestone of the 20th century. The first antibiotic described was penicillin, discovered by Alexander Fleming in 1929 (Kraemer, Ramachandran, & Perron, 2019; Mohr, 2016). The successful therapeutic use of penicillin (a natural antibiotic) and sulfonamides (synthetic antimicrobial) in humans at the beginning of the 20th century marked the start of the modern antimicrobial revolution (Walsh 2013). After World War II, several antibiotics were discovered and developed for therapeutic use. The golden age of antibiotic discovery was during 1950–1960 when most of the antibiotics were discovered, including many used up to the present (Davies, 2006).

These new magical bullets changed medicine significantly, diminishing morbidity and mortality associated with bacterial infections and increased quality of life and life expectancy (Davies, 2006; Dhingra et al., 2020; Mohr, 2016; Xu, Davies, & Miao, 2007). Since 1962, only two new classes of antimicrobials have been developed. In the 21st century, the discovery of new antimicrobial drugs has slowed, and most newly introduced drugs have limited application (Dhingra et al., 2020).

Antibiotics are classified based on their action mechanism and spectrum, administration route, and chemical structure. These substances are classified, by structure, as β-lactams (including carbapenems abn monobactams) aminoglycosides, chloramphenicol, glycopeptides, lincomycin, macrolides, polyenes, polypeptides, quinolones and fluoroquinolones, rifamycin, sulfonamides, and tetracyclines (Gothwal & Shashidhar, 2015).

Antibiotics as pharmaceutical products are considered CECs for aquatic environments because they can penetrate these ecosystems by different routes, such as household, industry, and hospital wastewater (Fig. 5.1). These products are also not completely metabolized and are detected in sewage from excreted human and animal body fluids (Elessawy et al., 2020). For example, aminoglycosides and β-lactams are not entirely biodegradable, and their residues may induce antibiotic resistance in microorganisms present in the environment (Davies, 2006; Elessawy et al., 2020).

There has been an increased use and misuse of antibiotics in practically every field of human action for decades. These products are useful for human and veterinary medical purposes, agricultural production, animal husbandry, aquaculture, and the food industry (Kraemer et al., 2019). For example, antibiotic utilization is estimated to increase by 67% by 2030, with almost twice this increase in Brazil, China, India, Russia, and South Africa (Van, Yidana, Smooker, & Coloe, 2020). It is important to mention that antibiotics are used for non-therapeutic purposes more frequently than for therapeutic purposes.

The veterinary use of antibiotics for disease treatment is very helpful in promoting the welfare and health of animals and preventing disease propagation in animal lots (Van et al., 2020). The use of these substances is also increasing in aquaculture, one of the fastest growing food sectors, in livestock production, and for plant protection (Kirchhelle, 2018; Kraemer et al., 2019). Livestock excretes in urine and feces up to 80% of the parent compound or active antibiotic metabolite received by drinking water and feed (McKinney, Dungan, Moore, & Leytem, 2018; Schulz et al., 2019). The application of manure on land as fertilizer is a common route for introducing antibiotics to the environment. Depending on their hydrophobicity, sorption potential, and rate of degradation, excreted antibiotics can continue applying selection pressure in manure, soil, water/wastewater, and sediment/sludge (McKinney et al., 2018).

Antibiotics as micropollutants are commonly present in natural and human-made environments such as surface water, groundwater, wastewater and treated effluents at minimal concentrations (nanograms to milligrams per liter; Kraemer et al., 2019; Turolla, Cattaneo, Marazzi, Mezzanotte, & Antonelli, 2018). In general, wastewater treatment plants are not able to remove antibiotics and therefore they are constantly discharged into the sediments and water bodies. For this reason, antibiotics as micropollutants pose a major global threat (Kumar et al., 2019).

5.2.5 Antibiotic-resistant bacteria and antibiotic-resistant genes

Antibiotic resistance is considered a significant threat worldwide that directly impacts human, animal, and environmental health. This global crisis is predicted to cause 10 million deaths, a severe global economic impact with a cost of US$100 trillion by 2050-(Stanton, Bethel, Leonard, Gaze, and Garside 2020; Martins & Rabinowitz, 2020; World Health Organization, 2018; Roope et al., 2019).

Antimicrobial resistance was initially considered a clinical concern related to nosocomial infections confined to severely ill patients. However, during recent years, research into this global crisis indicates that it is a consequence of a large load of biocides (antimicrobials, pesticides, heavy metals, among others) that are dumped daily into the environment because of the overuse and misuse of biocides in practically every field of human action. The environment's role as a source and dissemination route for antibiotic resistance has recently been considered with scientific evidence (Karkman, Pärnänen, & Larsson, 2019; Martins & Rabinowitz, 2020; Ng & Gin, 2019). The release of antimicrobials originating from animals and humans to the environment induces a selective pressure that contributes to the rise and spread of antibiotic-resistant bacteria, and antibiotic-resistant genes (ARGs) (Fig. 5.1) (Martins & Rabinowitz, 2020).

Environmental bacteria can reach animals and humans in different ways, such as through vegetables being planted in soil treated with manure containing antibiotic residues or irrigated with wastewater. Aquatic environments play a significant role in spreading ARGs (Martins and Rabinowitz 2020). Treated effluents from wastewater treatment plants are among the most crucial point sources of resistant bacteria and resistant genes released to the environment. Wastewater treatment plants are considered hot spots for antibiotic resistance emergence and dissemination because untreated sewage contains animal, environmental, and human-originated bacteria in a mixture of antibiotic sub-therapeutic levels and other selective agents (Karkman et al., 2019). However, it is unclear if the rise of antibiotic-resistance genes in sewage and sewage-impacted environments results from fecal contamination with resistant bacteria or is a product of selection pressure by residual antibiotics (Karkman et al., 2019; Stanton et al., 2020).

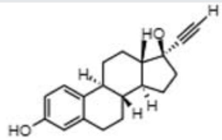
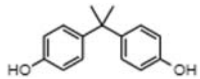
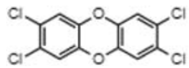
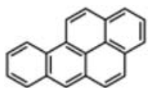
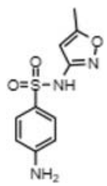
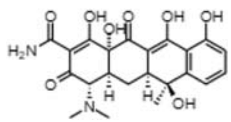
ARGs mobilize continuously according to the selective pressure of antibiotics. The spread and maintenance of these genes depend on their integration by integrons, transposons, plasmids, and genomic islands and the network interaction between ecologically connected bacterial populations and colonized human and animal hosts. The selection pressure for maintaining ARGs can lead to the establishment of new resistance factors in bacterial populations (Bengtsson-Palme, Kristiansson, & Larsson, 2018; Hernando-amado, Coque, Baquero, & Martínez, 2019).

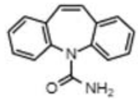
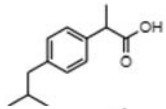
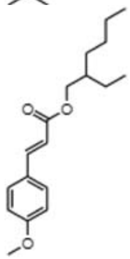
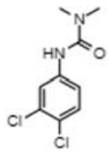
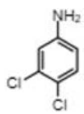
Measurable impacts on human health by ARGs exposition has been limited by empirical research (Stanton et al., 2020). Therefore, systematic surveillance of antibiotic use and antibiotic resistance prevalence in animals and humans is essential for managing bacterial infectious diseases with an integrated approach, which has been proposed by "One Health Perspective" (Huijbers, Flach, & Larsson, 2019; Mackenzie & Jeggo, 2019; What is One Health?). "One Health" recognizes that the health of people is closely connected to the health of animals and our shared environment; it focuses on the role of interconnected ecosystems the emergence and dissemination of the antimicrobial resistance challenge (Hernando-amado, Coque, Baquero, & Martínez, 2019; What is One Health?).

5.2.6 Others

Other categories of CECs include flame retardants (polybrominated diphenyl ethers), industrial additives and agents (EDTA), gasoline additives (dialkyl esthers and methyl-t-butyl ethers), perfluorinated compounds (perfluorotoctano sulfonates), artificial sweeteners (saccharin and aspartame), stimulants (caffeine), and nanomaterials (nanotubes, TiO_2; Salimi et al., 2017; Stefanakis & Becker, 2015). Table 5.1 summarizes some representative compounds for each group with their chemical structure, use, and environmental persistence.

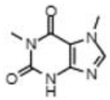
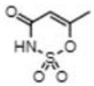
Table 5.1 Representative emerging contaminants, use, and environmental persistence.

Group	Subgroup	Example	Use	Persistence	Reference
Endocrine-disrupting chemicals	Synthetic estrogens	 17-α-ethynylestradiol	Treatment of menopause and birth control	Low persistence when treated with enzymatic methods.More persistence than other estrogens.	de Mes, Zeeman, and Lettinga (2005), Méndez et al. (2017)
	Bisphenols	 Bisphenol A	Plasticizer	Low persistence. Half-life is less than a week.	Staples, Dome, Klecka, Oblock, and Harris (1998); World Health Organization (2016)
	Dioxin-like compounds	 2,3,7,8-Tetrachlorodibenzo[*b,e*][1,4] dioxin	Currently not in use. By-products of combustion and industrial processes.	Highly persistent. It presents bioaccumulation and biomagnification.	WHO (2010), Martí et al. (2010)
	Aromatic polycyclic hydrocarbons	 Benzo[α]pyrene	By-products of industrial or combustion processes.	Medium to high persistence.	Abdel-Shafy and Mansour (2016)
Pharmaceuticals	Antibiotics	 Sulfamethoxazole	Clinical use.	Medium persistence.	Patrolecco et al. (2018)
		 Tetracycline	Animal use.	Significant persistence.	Daghrir and Drogui (2013)

	Antidepressants	 Carbamazepine	Clinical Use	High persistence	Yamamoto et al. (2009)
	Analgesics		Clinical use	Medium persistence	Yamamoto et al. (2009)
Personal care products	Organic UV Filters	 Ethylhexyl methoxycinnamate	Sun blockers	Has been found in different aquatic matrices.	Amine, Gomez, Halwani, Casellas, and Fenet (2012), Juliano and Magrini (2017)
	Microplastics	 Polyethylene		High persistence. Microplastics present bioaccumulation and biomagnification.	Juliano and Magrini (2017), Lusher, Burke, O'Connor, and Officer (2014), Wu et al. (2019)
Biocides	Herbicides	  Diuron and degradation product	Agricultural activities.	High persistence.	Durak et al. (2021), Giacomazzi and Cochet (2004)

(*Continued*)

Table 5.1 Representative emerging contaminants, use, and environmental persistence. ***Continued***

Group	Subgroup	Example	Use	Persistence	Reference
Antibiotic-resistance genes	β-lactamase	$bla_{OXA}bla_{TEM}bla_{SHV}$	-	High persistence	Dong, Wang, Fang, Wang, and Ye (2019), Knapp, Dolfing, Ehlert, and Graham (2010)
	Tetracyclines	*tet(A)tet(M)tet(O)*	-	High persistence	Knapp et al. (2010)
	Integrons	*Intl-1*	-	High persistence	Dong et al. (2019)
Others	Stimulants	1,7-dimethylxanthine 	Use in food preparations.	Low persistence, but continuous release.	Karkman et al. (2019), Korekar, Kumar, and Ugale (2020)
	Sweeteners	Acesulfame 	Use in food preparations.	Highly persistent.	Sang, Jiang, Tsoi, and Leung (2014)

5.3 DNA damage caused by synthetic environmental contaminant exposure

As mentioned in this chapter, CECs from industrial, agricultural, and domestic waste are continuously released into the environment contaminating soil, air, and water sources (Silveira, Lima, Reis, dos, Palmieri, & Andrade-Vieria, 2017). The World Health Organization had estimated that 12.6 million people died due to living or working in an unhealthy environment. Additionally, at least 4.9 million deaths (86 million of disability-adjusted life years, DALYs) per year are attributable to environmental exposure and management of specific chemicals. In this respect, low- and middle-income countries bear the most significant environmental burden in all types of diseases and injuries (Prüss-Ustün, Vickers, Haefliger, & Bertollini, 2011; World Health Organization, 2016).

Regarding emerging pollutant exposure, pesticides pose a severe threat to the surrounding and non-target species, including humans. Mixing and loading pesticides during agriculture activities are the main exposure routes. Long-term exposure could harm human health, resulting in disruption of various organ systems, such as the nervous, reproductive, respiratory, immune, and cardiovascular systems (Kaur & Kaur, 2018).

Several pesticides are included as EDCs and related to the risk of breast cancer. To this respect, pesticides can act as a xenoestrogen, interact with estrogen receptors and disrupt them, inducing malignancy or/and catalyzing existing DNA mutations in susceptible individuals in laboratory animals models. Other endocrine disruptors are plasticizers, such as BPA, DDT, pesticides, and polychlorinated biphenyls. These compounds are commonly used in agriculture, industry, and consumer products, and are also related to breast cancer (Calaf, Ponce-Cusi, Aguayo, Muñoz, & Bleak, 2020; Ferro, Parvathaneni, Patel, & Cheriyath, 2012; Santamaría-Ulloa, 2009). Santamaría-Ulloa (2009) reported an association between pesticide environmental exposure and breast cancer for women older than 45 years old in Costa Rica in Central America. The exposure was statistically significant in some rural and agricultural areas of the country, where these activities are more prevalent (Santamaría-Ulloa, 2009).

Pesticides affect the tubulin and microtubules that separate chromosomes during cell division, potencially generating aneuploidies and also interfere with other molecular and biochemical processes. For example, the activity of DNA repair enzymes is obstructed and that reduces cellular DNA repair capacity. Another effect of these biocides is the overproduction of reactive oxygen species (ROS), resulting in cell membrane damage, DNA and RNA damage, enzyme inactivation, lipid peroxidation, and protein oxidation. Thus, reactive oxidative species (ROS) cause oxidative stress that interferes with DNA integrity and its repair mechanisms, leading to mutations and diseases (Kaur & Kaur, 2018; Srivastava & Singh, 2020).

Methyl paraoxon from malathion (organochloride pesticide) is another pesticide commonly used on plants that produces toxic effects. This compound deactivates the acetylcholinesterase's active site by phosphorylation, leading to its deactivation and further inhibition of acetylcholine hydrolysis, leading to nervous system damage (Srivastava & Singh, 2020).

Lan et al. (2018) evaluated the genotoxicity of 20 disinfection by-products in drinking water using a toxicogenomics approach. The study identified the genotoxicity potential of all 20 products and associated them with oxidative DNA damage and base alkylation as the major molecular mechanisms of genotoxicity (Lan et al., 2018).

A better understanding of DNA damage caused by ECs could help prevent the consequences of their exposure. Although some efforts have been made in this respect, more comprehensive studies are required to find a preventive measures to the harmful consequences of these heterogeneous group of compounds (Kaur & Kaur, 2018).

5.4 Emerging contaminants in soil, in sediments, and transportation

The emerging contaminants (ECs) can arrive at the soil and sediments in two ways: (1) point source pollution and (2) diffuse pollution. The first one is a single identifiable source, such as industrial effluent or septic tanks. Diffuse pollution is difficult to identify as coming from a discrete location; for instance, runoff (Lapworth, Baran, Stuart, & Ward, 2012). Some direct entry pathways to soil include extensive cattle breeding operations, irrigation with treated or untreated wastewater, intentional disposal, landfill leachates, sewage leaks, and phosphogypsum amendments. Indirect pathways include atmospheric air masses traveling long distances and depositing over plants, animals, and soil (Gomes et al., 2017). Fig. 5.1 represents the main entry pathways of ECs to the environment.

Land use can impact EC's presence in water, sediments, and soil. The residential and industrial zones (urban land uses) are identified as hotspots and large-scale EC sources of pyrethroid bifenthrin, poly-fluoroalkyl substances, polybrominated biphenyls, and polybrominated diphenyl ethers and phthalates. ECs were found in different soil proportions, sediments, and water from all types of land use studied (Sardiña, Leahy, Metzeling, Stevenson, & Hinwood, 2019).

Reuse of untreated wastewater reuse is a common practice around the world as a consequence of scarcity of water resources. China, Mexico, and India use untreated wastewater for irrigation of 460 thousand hectares of crops, followed by Colombia, Chile, Ghana, Pakistan, South Africa, Syria, and Turkey (each with less than 50 ha of irrigation surface). The top countries that use treated wastewater for irrigation purposes are Chile, Mexico, Israel, Egypt, Cyprus, Italy, and Argentina (Ungureanu, Vlăduț, & Voicu, 2020).

In 2006 Kinney et al. demonstrated the presence of 19 ECs in wastewater effluents and their accumulation in the irrigated soil. After three months of monitoring, the accumulation of sulfamethoxazole was 12,710%, and fluoxetine was 14,400%. Additionally, the study showed that some ECs could be mobile enough to leach to the top 30 cm of soil (Chad, Edward, Stephen, & Jeffery, 2006). This situation extends worldwide. In 2009, Kasprzyk-Hordern, Dinsdale, and Guwy (2009) found concentrations up to 3 kg day^{-1} of ECs (as endocrine disruptors, illicit drugs, and PPCPs) in treated wastewater discharged into rivers in south Wales, United Kingdom. In Germany,(Ternes, Bonerz, Herrmann, Teiser, and Andersen 2007) reported 52 ECs in irrigation water from the wastewater effluent. They also found six compounds in groundwater, the most resistant of which were carbamazepine and sulfamethoxazole. In Mexico, a study conducted in Mezquital Valley found 65 active pharmaceutical compounds in wastewater, 10 were found in irrigation channels, and 26 were found in groundwater related to the aquatic ecosystem. It is important to mention that some sectors of the studied zone have been irrigated with wastewater for more than 100 years (Lesser et al., 2018). Another example of irrigation with contaminated wastewater is the Al Hayer area in Saudi Arabia. Sixty-four ECs were detected in wastewater, and six pharmaceuticals and seven pesticides were detected in plants, showing the accumulation of these substances in soil and crops (Picó et al., 2019).

Antibiotic resistance in soil is less understood; some microbial communities present a basal antibiotic profile. However, irrigation with contaminated wastewater can boost the propagation of antibiotic resistance genes in a field (Cerqueira et al., 2019). A recent study, which combined microcosmos experiments with field observations, demonstrated that the irrigation with treated wastewater significantly increased the abundance of five ARG [*intI1*, *sul1*, *qnrS*, *bla*$_{OXA-58}$, *tet*(M)] in irrigated soil in comparison with non-irrigated fields. The relative abundance of *intI1*, *bla*$_{OXA-58}$, *qnrS*, *sul1*, and *tet*(M) correlated with the irrigation intensity and decreased during irrigation brakes. The studied genes remained constantly higher in irrigated in comparison with non-irrigated soil, indicating their persistence upon its entrance to the environment (Kampouris et al., 2021).

Recently, a quantitative risk analysis assessment model was proposed by Delli Compagni et al. (2020) to predict the associated risk of contaminated effluent irrigation and bioaccumulation of EC in crops (maize, rice, wheat, and ryegrass). The model sensitivity analysis showed that the fraction of EC sorbed onto total suspended solids is the most sensitive studied parameter. Furthermore, some pollutants, like ammonium, nitrate, and nitrite, impacted microbial growth parameters. In general, there is a measurable public health risk related to the intake of crops contaminated with EC due to its bioaccumulation in vegetable products (Delli Compagni et al., 2020). Additionally, some biosolids, which resulted from wastewater treatment, can be used as sources of essential nutrients and organic matter in agricultural soils (Clarke & Smith, 2011). The Norwegian Scientific Committee for Food Safety recommends measuring the concentration of the 14 drugs (mesalazine, ranitidine, dipyridamole, sotalol, metoprolol, losartan, atorvastatin, tetracycline, ciprofloxacin, carisoprodol, gabapentin, levetiracetam, chlorprothixene, fexofenadine), which are identified as hazardous after a risk assessment analysis (Eriksen et al., 2009).

To improve soil quality in agriculture, manure is commonly used as organic fertilizer (Das, Jeong, Das, & Kim, 2017). However, manure can influence the soil microbiome and spread antimicrobial resistance. A study conducted in Italy analyzed the impact of manure from dairy cattle, chickens, and swine on the soil microbiome, antimicrobial substances, and antibiotic resistance genes. The main conclusions were that the microbiome was not affected by manure, but the antibiotic resistance genes showed different patterns, some genes as *bla*$_{OXA-1}$, *ermA*, *ermB*, *qnrS*, and *oqxA* were enriched while *bla*$_{CTX-M-1LIKE}$, *bla*$_{TEM}$, and *bla*$_{SHV}$ disappeared. Additionally, flumequine (a veterinary antibiotic) exerts a selective pressure for *qnrS* and *oqxA* accumulation in soil (Laconi et al., 2021). Further studies are needed to understand the antibiotic resistance genes behavior in soil and other ecosystems.

5.5 Emerging contaminants in soil and sediments are bioavailable

Once the contaminant is introduced to the soil, its fate depends on different factors. Soil type is one of the most important. The chemical composition of soil can influence the efficiency of compound removal. For example, carbamazepine is more efficiently removed in volcanic soil than sandy soil (Gielen, Heuvel, van den, Clinton, & Greenfield, 2009). The temperature is another relevant factor; ECs concentration in cooler months is higher than in the hottest months (Biel-Maeso, Corada-Fernández, & Lara-Martín, 2018). Some chemicals can undergo different processes in the environment such as volatilization and photodegradation, or can be transported by soil runoff and or erosion to surface water. Some chemicals can be leached into groundwater and/or undergo adsorption/desorption onto/from soil organic/inorganic solid and colloidal components. Other compounds undergo a partial or total chemical decomposition and/or biodegradation (Wuana, Okieimen, & Vesuwe, 2014) and in some cases can be absorbed by plants, where roots accumulate the ECs. The contaminants' chemical characteristics are also relevant; lipophilicity (the capacity to be absorbed by lipids) is one of the most important (Miller, Nason, Karthikeyan, & Pedersen, 2016).

The environmental conditions can affect the chemical pathways by which ECs are metabolized in soil. It is common to observe quick changes between aerobic and anaerobic conditions in the soil environment. For this reason, another aspect to consider is the electron-accepting processes (TEAPs). This is the last step in overall decomposition of organic material and microbial respiration process (Sutton-Grier, Keller, Koch, Gilmour, & Megonigal, 2011). A recent study analyzed TEAPs to remove EC from the soil and concluded that some chemicals could be degraded under aerobic conditions, while other chemicals required sulfate-reducing conditions (anaerobic state). Moreover, some compounds such as carbamazepine are difficult to degrade in natural conditions (Fang, Vanzin, Cupples, & Strathmann, 2020).

The sorption and percolation capacity of the soil impacts the EC fate. An experiment with different soil composition columns demonstrated that soils with low clay content present more EC migration. Some pharmaceutical compounds such as carbamazepine and hydrochlorothiazide are less mobile (the soil pH does not change its behavior). When the soil columns were washed for one week, the majority of the compounds could be detected, indicating the persistence potential and the possibility of contaminating groundwater (Biel-Maeso et al., 2021).

In 2009 an exhaustive report about biosolids from wastewater conducted in Norway found that soil density, infiltration, distribution coefficient, degradation rate, and plant uptake are key factors to predict the stability and bioavailability of some ECs in the soil. For example, the increase of soil density correlates with a decrease in heavy metal concentration; each EC's degradation rate is related to its half-life and is directly influenced by temperature. Precipitation can also influence the soil infiltration of each pollutant (Eriksen et al., 2009). As mentioned before, manure is one of the entry sources of antibiotic resistance genes to soil. In 2020 Radu et al. (Radu et al. 2021) published a study about the natural resilience of agriculture soil to manure practices. They measured the antibiotic resistance genes before manuring (baseline), during a crop-manuring campaign, and during a crop-manuring-free campaign. As a result, they found that manure can raise antibiotic resistance gene relative abundance, but, after manure amendment, the studied genes' concentration returned to baseline levels within a crop-growing season. Moreover, the pesticide application raised the relative abundance of some genes [*aph(3')-IIa*, *ermB*, and *tet*(W)] in non-manured soil.

It is possible to detect antibiotic resistance patterns in sediments. A study conducted in Costa Rica by Arias et al. (2014) found an increase in antibiotic resistance in microbial communities exposed continuously to antibiotics. According to their results, basal levels of antibiotics were found in pristine environments (Palo Verde National Forest). The concentration of antibiotics correlated to different agricultural/farming activities. The resistance pattern of microbial communities was lower in sediments from agriculture fields, intermediate in aquaculture, and the highest levels were found in swine farming sediments (Arias-Andres, Ruepert, García Santamaría, & Rodrígez, 2014).

5.5.1 Emerging contaminants removal: remediation strategies

In 2012 a study was conducted that focused on identifying the best way to remove ECs from biosolids from wastewater treatment; they found that composting followed by thermal drying is the best method for stabilizing the organic matter and anaerobic treatment is better than aerobic for removing ECs

(Roig et al., 2012). A laboratory study with soil focused on the adsorption and degradation of nine different pharmaceuticals and four artificial sweeteners using anaerobic and aerobic conditions. The EC sorption constants (calculated using a Freundlich isotherm model) were relatively low and depended on each physicochemical contaminants' properties and the soil. The ECs were susceptible to microbial degradation under aerobic conditions; nevertheless, the ECs were less persistent under anaerobic conditions than aerobic conditions. The most resistant ECs in this study were sucralose and carbamazepine, and both were suggested as potential markers for assessing the impact of soil and groundwater pollution (Biel-Maeso, González-González, Lara-Martín, & Corada-Fernández, 2019).

Some efforts are currently underway in remediation strategies for contaminated soil; one of the most promising is electrochemical technologies because this technology does not require reagents nor does it produce secondary waste/sludge after treatment (Wen, Fu, & Li, 2021). Electrokinetic remediation consists in applying a low-intensity direct current between two electrodes; the electrolysis reaction at the inert electrodes produces protons (anode) and hydroxyl ions (cathode) that cause a pH gradient (Acar & Alshawabkeh, 1993). This principle was applied using soil and effluent irrigation water from a rice field in Portugal; before remediation, the EC persists in soil at a level of 20%−100% after six days, in vitro electrokinetic remediation improves ECs removal from soil by 30% (compared with natural attenuation) and avoids its dispersion in soil. These results support electrokinetic remediation as a promising strategy to remove and avoid dispersion of ECs in soil (Ferreira, Guedes, Mateus, Ribeiro, & Couto, 2020).

Another strategy for remediation is the Fenton oxidation reaction, useful in water matrices. The principle of the process is to generate a chain reaction by ferrous salt and H_2O_2 into degraded target pollutants; the reaction can occur in an acidic aqueous medium ($pH = 3$) or in a solid matrix (carbon material, clay, polymers, and zeolite). (Scaria, Gopinath, & Nidheesh 2021) published an exhaustive review of the Fenton reaction demonstrating that it is reliable, reusable, sustainable, and versatile in removing ECs such as artificial sweeteners, flame retardants, PPCPs, and steroid estrogens from water and wastewater. However, more studies are needed to validate the efficiency of the process and its implementation in real conditions (Scaria et al., 2021).

The conventional remediation strategies for antibiotic removal showed partially effective results (Kumar et al., 2019). Furthermore, bioremediation, based on microorganisms that can naturally degrade and utilize these compounds, provides a new prospect for removing antibiotics from the environment (Koch et al. 2021). Yang et al. (2019) reported the degradation of tetracyclines, β-lactams, and sulphamethoxazole antibiotics in sludge, using *Pseudomonas* sp., *Bacillus* sp., and *Clostridium* sp. strains. It was observed that the efficiency of the biodegradation of antibiotics could be maintained for three degradation cycles using the isolated bacterial strains. Two groups of potential microbial communities associated with the anaerobic and aerobic degradation in sludge were revealed. Twenty-four antibiotic-degrading bacterial genera were identified as significant in sludge (Yang, Liu, & Chang, 2020).

5.6 Conclusion

Literature reports on CECs and their fate in water, wastewater, and soil are abundant. However, different matrices, properties, contaminants, and experiments make it difficult to summarize the state of the art. Wastewater treatment plant effluents are the major source of CECs to the environment and can enter into the food chain through plants from irrigated crops; therefore, they are a crucial control point that should be improved using advanced technologies so that trace contaminants be removed at the source. It is also important to establish standard protocols to measure key contaminants, like carbamazepine, sulfamethoxazole, and sucralose, to compare data across studies. Quantitative risk assessment analyses are needed to determine the relationship between ECs and their metabolites concentrations with human exposure and disease to establish a safe benchmark concentration in wastewater, soil, and sediments. Additionally, the fate of ARGs needs to be studied more to understand their consequences in the environment. Finally, remediation efforts are necessary to reduce the presence of CECs and the associated risk in nature.

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