Introduction on Emerging Contaminants in Rivers and Their Environmental Risk

Ladislav Mandaric, Mira Celic, Rafael Marcé, and Mira Petrovic

Abstract This chapter gives an introduction on emerging organic contaminants, defined as chemicals that occur in water resources and pose a potential environmental risk, although currently it cannot be clearly defined given the paucity of existing data. The main source of emerging contaminants are discussed, giving special attention to wastewater treatment plants (WWTP) and processes occurring therein that determine their fate and transformation. Fate and behavior in the aquatic environment is briefly outlined, discussing main biotic and abiotic transformations occurring in rivers. Finally, specific classes of emerging organic contaminants, such as pharmaceuticals, personal care products, perfluorinated compounds, polar pesticides, and nanoparticles, are discussed in more details, giving examples of the most relevant compounds and their characteristics and risk indicators.

Keywords Emerging contaminants, Environmental risk, Fate, Sources, Transformation

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L. Mandaric and R. Marcé
Catalan Institute for Water Research (ICRA), c/Emili Grahit 101, 17003 Girona, Spain

M. Celic
Catalan Institute for Water Research (ICRA), c/Emili Grahit 101, 17003 Girona, Spain

Faculty of Technology, University of Novi Sad, Bulevar Cara Lazara 1, 21000 Novi Sad, Serbia

M. Petrovic (✉)
Catalan Institute for Water Research (ICRA), c/Emili Grahit 101, 17003 Girona, Spain

Catalan Institution for Research and Advance Studies (ICREA), c/ Lluís Companys, 23, 08010 Barcelona, Italy
e-mail: mpetrovic@icra.cat

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1 Introduction and Definitions

The issue of environmental microcontaminants emerged in 1962 when Rachel Carson's "Silent Spring" described the detrimental effects of pesticides on the environment and on human health, making a call to consider unintended or unanticipated consequences of man-made chemicals released into the environment.

The amount of nonpolar hazardous compounds, i.e., persistent organic pollutants (POPs) and heavy metals, released by the industry started to decrease in the 1970s when the legislation forced reduction at source and implementation of efficient wastewater treatment plants (WWTP). The main concerns were related with the persistence of POPs in the environment, their bioaccumulation in human and animal tissues, and their biomagnification in food chains, which lead to significant impacts on both human health and the environment. Selected POPs were defined as priority pollutants, and intensive monitoring and control programs were implemented. To address the global concern, the United Nations signed a treaty in Stockholm, Sweden, in May 2001. Under the treaty, known as the Stockholm Convention, countries agreed to reduce or eliminate the production, use, and/or release of an initial twelve chemical groups, the so-called dirty dozen. Today, the emission of POPs has been reduced drastically by adopting appropriate measures and eliminating the dominant pollution sources.

In the European Union, water pollution is regulated under the Water Framework Directive [1], which established a framework for community action in the field of water policy. The most recent European regulation set Environmental Quality Standards (EQS) for 45 priority substances [2] and established a watch list with 10 additional substances (or groups of compounds) of possible concern that require targeted EU-wide monitoring in order to support the prioritization process in future reviews of the priority substance list.

However, our technological society is using a continuously growing number of chemicals, which currently can be estimated in some hundreds of thousands of compounds (most of them organics) in daily use. Consequently, a wide range of man-made chemicals, designed for use in industry, in agriculture, or as consumer goods, are emitted, as well as many other chemicals unintentionally formed as by-products of industrial processes or of combustion. There is a widespread consensus that this kind of contamination requires legislative intervention.

There are varying definitions for emerging contaminants, as well as discussion on the types of substances that should be included under this category. Norman network (http://www.norman-network.net/) defines “emerging substances” as substances that have been detected in the environment, which are not included in routine monitoring programs at the EU level, and whose fate, behavior, and (eco) toxicological effects are not well understood. On the other hand, “emerging pollutants” are defined as those pollutants not included in routine monitoring programs in the EU, but which may be candidates for future regulation, depending on research on their (eco)toxicity, on their potential health effects and public perception, or on their occurrence in the environment.

Currently the most frequently discussed emerging substances are:

- Algal toxins
- Biocides
- Disinfection by-products
- Drugs of abuse
- Flame retardants
- Industrial chemicals
- Nanomaterials (organic and inorganic)
- Perfluorinated substances
- Personal care products including fragrances, UV filters, antimicrobials, insect repellents, etc.
- Pharmaceuticals used in human and veterinary medicine, including hormones
- Plant protection products
- Plasticizers
- Surfactants
- Trace metals and their compounds
- Microplastics

Although most people make no differentiation between emerging contaminants and emerging pollutants, *contamination* and *pollution* should not be seen as the same, since all pollutants are contaminants, but only those contaminants that can result in adverse biological effects are pollutants. Therefore, to differentiate emerging pollutants from emerging contaminants, the chemical analyses and information on their presence in the environment must be complemented with information on their bioavailability and toxicity.

This chapter deals with emerging organic contaminants, defined as chemicals that occur in water resources and pose a potential environmental risk, although currently it cannot be clearly defined given the paucity of existing data.

2 Main Sources and Routes of Entry of Emerging Contaminants to the Aquatic Environment

The main source of emerging contaminants found in waters is wastewater of urban, industrial, and agricultural origin (Fig. 1). Sewage generated in households includes waste liquid from toilets, baths, showers, kitchens, and sinks, which is disposed of via sewers and treated in wastewater treatment plants. However, municipal WWTPs are basically designed to remove pathogens and suspended or flocculated matter, but not other microcontaminants. Since 1980, health concerns related to microcontaminants have driven the development of new treatment technology (biotic and abiotic membranes, advanced oxidation and reduction, electrochemical treatments, combined processes, etc.). However, despite the range of advanced treatment options available, urban WWTPs typically use secondary biological

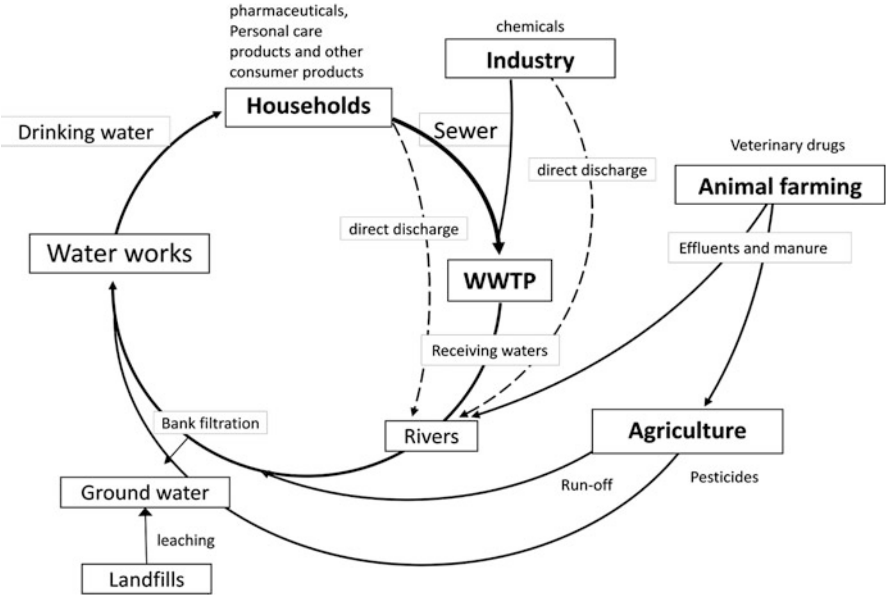

Fig. 1 Emerging contaminants within the water cycle

treatment such as conventional activated sludge, which removes only a fraction of the emerging contaminants. Therefore, WWTP effluents are currently the main route of entry of many emerging contaminants into the aquatic environment. The most concerning contaminants are persisting polar compounds of high solubility in water, which thus are able to penetrate through natural filtration and man-made treatments and present a potential risk in drinking water supply.

Other potential point sources of pollution by emerging contaminants include landfill sites, fish farms, power stations, and oil spillage from pipelines.

Emerging contaminants can also cause diffuse pollution as a result of activities such as farming and forestry. For instance, the leaching from manures applied as fertilizers, the runoff of pesticides used in agriculture and forestry, or the atmospheric deposition of industrial contaminants can all adversely affect the quality of surface and groundwater.

3 Elimination in WWTP and Sewer Systems

For polar microcontaminants like pharmaceuticals, physicochemical removal in WWTPs is of minor importance, and their elimination is largely dependent on microbial degradation in activated sludge tanks [3]. In there, the removal of emerging contaminants is related to four main processes (Fig. 2): photolysis, volatilization to air, sorption to sludge, and biodegradation [5]. Volatilization and sorption consist in a transfer of the contaminant between two phases (dissolved to gas and dissolved to solid, respectively), whereas the term biodegradation includes a myriad of catabolic processes that eventually lead to the partial or total breakdown of contaminant molecules.

Biodegradation is perhaps the most complex process occurring in biological treatments. It is a catabolic process, but the pathways leading to partial or total breakdown of contaminant molecules are not well known. Biodegradation can be achieved at stages of:

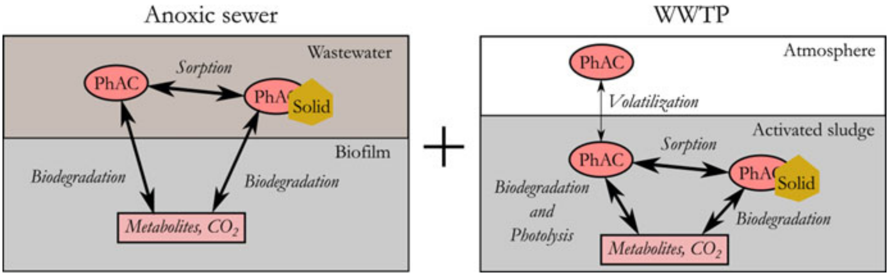

Fig. 2 The processes involved in the fate of pharmaceuticals in WWTPs and associated sewers. The role of anoxic sewers is *highlighted* in the figure because they are the most likely hot spots for removal of pharmaceuticals in sewer networks. The role of volatilization is minor in the plot, following the literature on pharmaceuticals. Modified and expanded from Pomiès et al. [4]

1. *Primary degradation*. Alteration of the chemical structure of a substance resulting in loss of a specific property of that substance.
2. *Environmentally acceptable*. Biodegradation to such an extent as to remove undesirable properties of the compound. This often corresponds to primary biodegradation, but it depends on the circumstances under which the products are discharged into the environment.
3. *Ultimate degradation*. Complete breakdown of a compound to either fully oxidized or reduced simple molecules (such as carbon dioxide/methane, nitrate/ammonium, and water).

Two main mechanisms have been suggested: direct metabolization (i.e., the use of the microcontaminant as a source of carbon and/or energy by the biological community) and co-metabolism. Co-metabolism refers to the fortuitous degradation of a nongrowth substrate (i.e., the pharmaceutical) in the obligate presence of a growth substrate or another transformable compound (e.g., dissolved or particulate organic carbon). Since the amounts of microcontaminant are usually too low to be used as a growth substrate, co-metabolism is supposed to be the main biodegradation pathway in activated sludge. However, given the complexity of the matrix and of the biological communities present, most likely direct metabolism and co-metabolism coexist in biological treatments, at different rates depending on the operational parameters of the facility and the overall quality of the raw water arriving into the WWTP.

Sorption the aqueous compartment and the solid phase of the sludge or mixed liquor in a biological reactor continuously exchange pollutants in both directions (sorption and desorption). The mechanisms that sustain the process of sorption are complex and still not fully understood, and recently the colloidal fraction has been suggested to also play a significant role [6]. Sorption appears to be influenced by the characteristics of both the matrix and the pollutant. This complexity is frequently lumped in a linear formulation that uses a single sorption coefficient [7], also referred as partition coefficient (K_d). Substantial effort has been devoted to the empirical quantification of K_d values for different compounds in particular WWTPs (see [4] for a good compilation of K_d values in activated sludge, including pharmaceuticals), although the generation of K_d values from octanol–water partition coefficient (K_{ow}) values is common practice as well [8]. However, because the K_d of pharmaceuticals depends on sludge characteristics (including pH), using K_{ow} to derive K_d can lead to severe bias. In fact, sorption is known to depend on several mechanisms beyond the hydrophobic interactions summarized by K_{ow}: electrostatic interactions, cationic exchanges, cationic bridges, surface complexation, and hydrogen bridges [9]. However, because sorption depends also on sludge characteristics, K_d values can vary widely among WWTPs, in a way that is nowadays difficult to predict.

Photolysis in WWTP may occur by direct absorption of light by the microcontaminants or through the absorption of light by intermediary compounds [10]. Photolysis is dependent on the intrinsic absorbance properties of the pollutant and the light conditions in the WWTP tanks, basically governed by the presence of suspended solids.

Volatilization of contaminants in WWTPs depends strongly on the physicochemical properties of the pollutant and the operational features of the WWTP. Aeration of activated sludge dramatically affects volatilization that can also take place by atmosphere-biological reactor equilibration following Henry's law. As such, volatilization is only relevant for volatile substances, but we still lack clear guidelines to define volatile and nonvolatile contaminants, mainly because the interactions between the properties of the molecules and the operation of the WWTPs.

3.1 Sewers: From Unreactive Pipes to Hot-Spot Reactors?

The major source of many emerging microcontaminants such as pharmaceuticals or personal care products reaching WWTP facilities is households, where products are consumed by population and eventually released to the sewer networks. Sewers are infrastructures composed by drains, pipes, and pumping stations that transport wastewater to the treatment facilities. There are two main types of sewer networks: gravity networks where water flows unimpeded following elevation gradients and pressure networks composed of completely filled tubes that transport wastewater with the aid of pumping stations [11]. Sewers have been traditionally considered as unreactive transport networks, but recent findings suggest that they are in fact active chemical and biological reactors [12]. There is still few information on the occurrence of microcontaminants in sewers, and in-sewer transformation of contaminants is usually neglected. However, sorption and biodegradation mechanisms are possible in sewers (Fig. 2), although the available information to parameterize those processes is extremely scarce [13,14]. It seems that pressure pipes, which increase the residence time and facilitate the development of anoxic conditions and the establishment of biofilms in pipe walls, are the most biologically active sections of sewer networks.

As far as we know, there is only one study reporting in situ changes in pharmaceutical concentrations along sewers [13]. This study showed that the concentration of most compounds suffered changes below 10% along the sewers, whereas diltiazem, citalopram, clarithromycin, bezafibrate, and amlodipine suffered decreases up to 60%. Even negative removal was observed for sulfamethoxazole and irbesartan, probably due to the conversion of conjugates back to their parent compounds in the sewer. All in all, recent findings show that the transformation of pharmaceuticals begins in sewers, and we anticipate that this topic will be a focus of future research, because the estimates of apparent consumption using inflow loads to WWTPs can be deeply flawed by neglecting transformation in sewers.

4 Fate and Behavior in the Aquatic Environment: Biotic and Abiotic Transformations in Rivers

Once released to the environment, a number of processes govern the fate and transport of contaminants and control their concentrations. Most important are the physical processes of dispersion and dilution and chemical and biological processes such as biodegradation, abiotic oxidation and hydrolysis, photolysis, adsorption/desorption, and volatilization (Fig. 3). Since the basic concepts of these processes are already defined and discussed in Sect. 3, here we mention only some specificity when occurring in natural aquatic environment.

4.1 *Biodegradation*

Biodegradability is generally regarded as the most important property for environmental hazard assessment of organic microcontaminants. It is strongly dependent on environmental conditions, such as temperature, redox potential, and the microbial communities present. Also, the degree of bioavailability of a microcontaminant is important, i.e., accessibility of the compound to microorganisms and its uptake

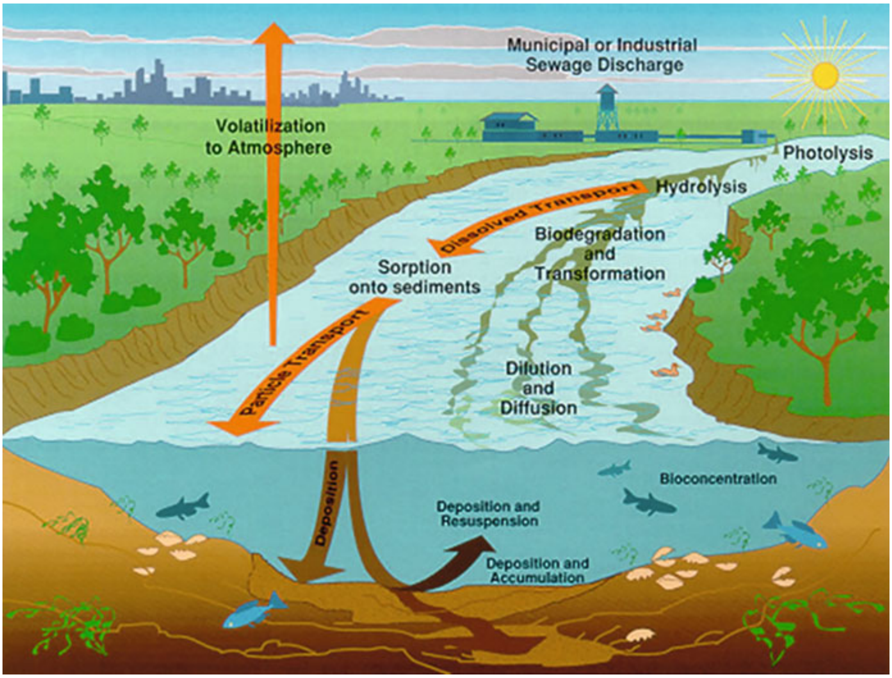

Fig. 3 Fate of contaminants in the aquatic environment

by microbial cells. Dissolved compounds generally are more bioavailable. Other important factors influencing the biodegradation are exposure time to biomass, availability of co-substrates (for compounds degraded co-metabolically), and the fraction of inert matter.

4.2 Photolysis

Direct photolysis in natural water involves the transformation of contaminants resulting from the direct absorption of a photon and should be distinguished from indirect photolysis, a second important abiotic degradation pathway in the environment. Indirect photolysis in natural water involves the transformation of contaminants due to energy transfer from naturally occurring photosensitizers or the transformation of a chemical due to reactions with transient oxidants such as hydroxyl radicals, singlet oxygen, and peroxy radicals.

4.3 Sorption

The interface between water and natural solids (e.g., suspended particulate matter and sediments in rivers) plays an important role in the transport of microcontaminants in river systems. Adsorption depends on both the surface characteristics and the properties of the contaminant. Neutral compounds tend to sorb onto solid organic matter, and cations and anions tend to sorb onto negatively (e.g., clay) and positively (e.g., iron oxide) charged surfaces, respectively. A number of other reactions like complex formations with metal ions, ion exchange, and hydrogen bindings also affect the partition of the organic compound between the solid and the liquid phase. Once the contaminants are sorbed, they can be deposited and eventually become buried in the sediments. However, the buried contaminants can be remobilized, by resuspension of the sediments during flood events.

The relative importance of the abovementioned processes depends on the rates at which they occur under environmental conditions. These rates are, in turn, dependent on the chemical structure and properties of the substance and its distribution in the various compartments of the environment. The most important physical properties of contaminants are water solubility, acidity (pK_a), vapor pressure, Henry's law constant (H), hydrophobicity expressed as the octanol/water partition coefficient (K_{ow}), and the organic carbon/water partition coefficient (K_{oc}).

The degree of ionization of ionizable and polar contaminants (many pharmaceuticals and pesticides), which depends on pH, affects their solubility, transport, sorption, and bioavailability. For an ionizable compound, acidic or basic, which can exist as neutral or dissociated form, the partitioning depends on pH and pK_a of the compound. In addition, the charged groups within the molecules can lead to ionic, ion paring and complexation reactions with the particulate matter and microorganisms, thus contributing to partitioning the contaminants to the solids. For example, microcontaminants having carboxylic acid functionalities with pK_a values much less than 7 (such as some nonsteroidal anti-inflammatory drugs or polar pesticides) are likely to remain in the solution phase, and removal by sorption to settling particles may be limited. For contaminants having functional groups that are prone to photolysis (e.g., conjugated aromatics, nitro-compounds, furans, phenols), a diverse set of photochemical processes are expected, and oxidative losses via reaction with mineral and humic substances also occur in sediments or soils. Photolytic reactions are often complex, involving various competing or parallel pathways and leading to multiple reaction products that may either be more toxic than the parent compound, retain the properties of the parent compound, or lose toxicity [15].

Some of the above physical properties are strongly dependent on environmental conditions. For example, temperature strongly affects vapor pressure, water solubility, and, therefore, Henry's law constant. Temperature may also affect deposition. For example, the distribution of POPs is inversely related to vapor pressure and thus to temperature. Lower temperatures favor greater partitioning from the vapor phase to particles suspended in the atmosphere. The pH is also important in evaluating environmental processing of the compounds, even though they are not subject to hydrolytic reactions. The speciation of the compound will influence its partitioning behavior, as well as its light-absorbing properties. Some compounds have multiple pH-sensitive functional groups (e.g., tetracycline antibiotics have three or four pK_a values), which results in the possibility of protonated/positive, neutral (or zwitterionic), and deprotonated/negative forms of a drug being present depending on the pH of the specific water body.

For the majority of emerging contaminants covered by this chapter (polar compounds such as pharmaceuticals, polar pesticides, personal care products, etc.), the attenuation in the aquatic environment is governed by three main processes: biodegradation, sunlight photolysis, and sorption to bed sediment. Table 1

Table 1 Environmental persistence and partitioning of selected emerging contaminants with relatively high potential ecological risk and high consumption

Compounds	Photolysis	Biodegradation	Sorption
Ciprofloxacin	++	–	+++
Sulfamethoxazole	++	+++	–
Naproxen	+++	+	++
Ibuprofen	+	+++	–
Diclofenac	+++	++	–
Mefenamic acid	+	+	–
Acetaminophen	+	+++	–
Carbamazepine	–	–	–
Propranolol	+++	+	+++
Gemfibrozil	–	–	–
Triclosan	++	++	+++
Methylparaben	–	+++	+

+++ rapid, ++ medium, + slow, – very poor or nonexisting gives an overview of relative contribution of biodegradation, photolysis, and sorption to the attenuation for selected emerging contaminants with high potential to enter the aquatic environment.

5 Main Classes of Emerging Contaminants: Characteristic and Risk Indicators

5.1 Pharmaceuticals and Hormones

Pharmaceuticals are a group of chemical substances that have medicinal properties and encompass all prescription, nonprescription, and over-the-counter therapeutic drugs, in addition to veterinary drugs. They are produced worldwide on a 100,000 t scale, and in a vast array of contaminants of anthropogenic origin reaching our water supplies, pharmaceuticals are among the ones with the most continuous input into the environment. Most modern drugs are small organic compounds with a molecular weight below 500 Da, which are moderately water soluble as well as lipophilic, in order to be bioavailable and biologically active. They are designed to have specific pharmacologic and physiologic effects at low doses, and thus, are inherently potent, and can produce unintended outcomes in wildlife [16]. Their consumption will continue to increase due to the expanding population, inverting age structure, increase of per capita consumption, expanding potential markets, patent expirations, new target age-groups, etc. After the oral, parenteral, or topical administration, pharmaceuticals are excreted via the liver and kidneys as a mixture of parent compounds and metabolites that are usually more polar and hydrophilic than the original drug. After their usage for the intended purpose, a large fraction of these substances is discharged into the wastewater unchanged or in the form of degradation products that are often hardly eliminable in conventional WWTPs. Depending on the efficiency of the treatment and chemical nature of a compound, pharmaceuticals can reach surface and groundwaters.

Pharmaceuticals have been found in treated sewage effluents, surface waters, soil, and tap water. Although the levels are generally low, there is rising concern about potential long-term impacts to both humans and aquatic organisms as a result of the continuous environmental exposure to these compounds. These levels are unable to induce acute effects in humans, i.e., they are far below the recommended prescription dose, but have been found to affect aquatic ecosystems.

Some examples of common pharmaceuticals found in the aquatic environment are shown in Table 2.

Table 2 Pharmaceuticals frequently found in the aquatic environment

Therapeutic class	Representative compounds
Analgesic/anti-inflammatory	Ibuprofen
	Ketoprofen
	Naproxen
	Diclofenac
	Salicylic acid (aspirin metabolite)
	Acetaminophen (Paracetamol)
	Codein
Antibiotics	Sulfamethoxazole
	Ofloxacin
	Ciprofloxacin
	Norfloxacin
	Trimethoprim
	Erythromycin
	Azithromycin
	Clarithromycin
Beta-blockers	Atenolol
	Metoprolol
	Sotalol
	Propanolol
Lipid regulators	Gemfibrozil
	Bezafibrat
	Clofibric acid (metabolite)
Antidepressants	Diazepam
	Citalopram
	Paroxetine
	Fluoxetine
Antiepileptic	Carbamazepine
Gastric protectors	Ranitidine
Diuretics	Hydroclorotiazida
	Furosemide
X-ray contrast media	Iopromida
	Diatrizoate
	Iopamidol
Antidiabetic	Glibenclamide

5.1.1 Natural and Synthetic Hormones

Natural and synthetic steroid hormones are considered as the most potent endocrine-disrupting compounds. The three major naturally occurring estrogens in women are estrone (E1), 17β-estradiol (E2), and estriol (E3); synthetic estrogens, such as 17α-ethinyl estradiol (EE2); and progestogens, such as norethindrone, norgestrel, and levonorgestrel which are widespread in contraceptive formulations and for treatment of certain hormonal disorders and cancers. Both natural and synthetic steroids, in either a conjugated (as glucuronides and sulfates, principally) or an unconjugated form, are excreted in the urine of mammals and enter the aquatic environment via WWTP effluents or untreated discharges. These potent estrogenic compounds have been shown to induce estrogenic responses in fish at low concentrations in water (0.1–1 ng/L) [17–19], and such concentrations are sometimes found at sites downstream of discharges of WWTP effluents and have been associated to impaired reproduction and developmental processes, such as feminization, decreased fertility, or hermaphroditism [20–22].

5.2 Personal Care Products (PCP)

Personal care products include all consumer chemicals typically found in fragrances, lotions, shampoos, cosmetics, sunscreens, soaps, etc.

5.2.1 Fragrances

Synthetic musk fragrances are a group of bioaccumulative and persistent xenobiotics. They are used in a wide range of consumer products such as detergents, cosmetics, and other personal care products. There are four different musk families according to their physicochemical properties: nitro musks (musk ketone, musk ambrette, musk xylene, musk tibetan, and musk moskene), polycyclic musks (galaxolide, tonalide, celestolide, phantolide, cashmeran, and traseolide), macrocyclic musks (ambrettolide, muscone, ethylene brassilate, globalide), and alicyclic musks (romandolide and helvetolide). Polycyclic and nitro musks are not structurally or chemically similar to the natural ones and have a lipophilic nature, causing them to bioaccumulate in sediments, sludge, and biota and biomagnify throughout the food chain [23].

5.2.2 UV Filters

Organic UV filters are found in sunscreen cosmetics and other personal care products as protection against UV radiation. The organic UV filters most commonly found in the aquatic environment are:

- Benzophenones (BP-1, BP-3, BP-4)
- 2-Phenylbenzimidazole-5-sulfonic acid (PBSA)
- 4-Methyl-benzylidene camphor (4-MBC)
- Ethylhexyl methoxycinnamate (EHMC)
- Isoamyl methoxycinnamate (IAMC)
- Octocrylene (OC)

- Octyl dimethyl-*p*-aminobenzoate (OD-PABA)

Most of these compounds are lipophilic (log K_{ow} 4–8) with conjugated aromatic rings and are relatively stable against biotic degradation [24]. It has been reported that the estrogenic activity of most of the commonly used organic UV filters is in the range of other well-characterized estrogenic chemicals such as estradiol [25].

5.2.3 Antimicrobials and Preservatives

Antimicrobials and preservatives are chemicals that kill or prevent the growth of microbes (bacteria, viruses, fungi, or protozoa), and as such, they are commonly added to many consumer products to reduce or prevent microbial contamination. The most commonly used antimicrobials are triclosan and triclocarban, frequently added to soaps and body washes, toothpastes, and other cosmetics. They have received increasing attention because of their pronounced microbial and algal toxicity, suspect estrogenicity, and their potential for fostering antimicrobial resistance [26]. Triclosan is also known to undergo phototransformation in aqueous solution to form toxic 2,8-dichlorodibenzo-*p*-dioxin (2,8-DCDD).

Parabens are another group of compounds with bactericidal and fungicidal properties. They are widely used preservatives in cosmetic and pharmaceutical products, such as shampoos, commercial moisturizers, shaving gels, spray tanning solution, makeup, personal lubricants, topical pharmaceuticals, and toothpaste. There are seven different types of parabens with bactericidal and fungicidal properties currently in use (benzyl, butyl, ethyl, isobutyl, isopropyl, methyl, and propyl). They are also used as food additives. They are becoming increasingly controversial, because in vitro and in vivo tests have shown that parabens have weak estrogenic activity [27]. Preliminary data on environmental concentrations, however, suggest only minimal risk to aquatic organisms, as effect concentrations are generally 1000× higher than what has been observed in surface water.

5.3 Perfluorinated Compounds (PFCs)

PFCs comprise a large group of compounds characterized by a fully fluorinated hydrophobic linear carbon chain attached to one or more hydrophilic heads.

The examples of same PFCs are:

- PFOA or perfluorooctanoic acid, used to make fluoropolymers such as Teflon, among other applications
- PFOS or perfluorooctanesulfonic acid, used in the semiconductor industry and fire-fighting foam mixture
- PFNA or perfluorononanoic acid, used as surfactant in the emulsion polymerization of fluoropolymers, like PFOA
- PFBS or perfluorobutanesulfonic acid, used as a replacement for PFOS

- POSF or perfluorooctanesulfonyl fluoride, used to make PFOS-based compounds
- PFOSA or perfluorooctanesulfonamide

PFCs repel both water and oil and are therefore ideal chemicals for surface treatments. These compounds have been used for many industrial applications including stain repellents (such as Teflon), textile, paints, waxes, polishes, electronics, adhesives, and food packaging [28]. PFCs have been found in the aquatic environment in different compartments, including water at levels of pg/L in lakes, ng/L in rivers, soils and sediments (at levels of ng/g), and biota samples (at levels of μg/kg in fish samples) [29]. They are resistant to breakdown and may be accumulated attached to proteins and biomagnified through the food chain. Among PFCs, PFOA and PFOS are regarded as being the terminal degradation end-products, and these are the chemicals that have frequently been detected in environmental samples and often occur at high concentrations. Studies have shown that PFOA and PFOS have potential to cause liver cancer, affect the lipid metabolism, disturb the immune system, and reduce human fertility. PFCs enter the environment through direct (directly from manufacture wastes or direct application) and indirect sources (due to their decomposition or disposal through the life cycle of products). WWTPs have been also identified as relevant pathway of PFCs releases into the environment.

5.4 Plasticizers

Phthalate acid esters (*PAEs*) are chemical compounds widely used in different industrial applications, mainly as plasticizers for polyvinyl chloride (PVC) resins, adhesives, and cellulose film coatings. They comprise a large group of compounds, being main representatives dimethyl (DMP), diethyl (DEP), dibutyl (DBP), butylbenzyl (BBP), di(2-ethylhexyl) (DEHP), and di-*n*-octyl phthalate(DnOP). DEHP is included on the list of priority pollutants under the EU Water Framework Directive (WFD). Considerable direct (production of plastic materials) and indirect emission, via leaching and volatilization from plastic products after their usage, disposal, and incineration, explains their ubiquity in the environment. Because of this, urban and industrial wastewater treatment plants, landfill areas, and municipal incinerators are the major sources of these contaminants. In all reported studies, DEHP was found to be the predominant PAE, due to its high production (nearly 90% of European plasticizer use) and its physicochemical properties (low solubility and relatively high K_{ow}). PAEs are substances of low acute and chronic toxicity, which generally decreases with increasing alkyl chain length. They are also characterized by their limited bioaccumulation through the aquatic food chain because of their biotransformation that progressively increases with trophic level [30]. However, phthalates are categorized as suspected endocrine disrupters [31]. Endocrine disruptive effects were observed in vivo for DBP, DEHP, BBP, DEP, and DHP with relative potency ranged from 10^{-4} to 10^{-7} (relative to 17β-estradiol) [32].

Bisphenol-A (BPA) is used to make polycarbonate polymers and epoxy resins that are used in the production of various types of food and drink containers, compact disks, electronics, and automobile parts. BPA is released into the environment through WWTP effluents, landfill leachates, via hydrolysis of BPA from plastics, or natural degradation of polycarbonate plastics due to moderate water solubility and low vapor pressure. The potential risks of BPA include reproduction and development effects and neurochemical and behavioral effects [33]. Endocrine disruptive effects were observed in vivo with relative potency from 1.0×10^{-5} to 8.1×10^{-5} (relative to 17β-estradiol) [34].

5.5 Anticorrosive Agents

Benzotriazole (BT) and tolyltriazole (TT) are high production volume chemicals that have been extensively used as corrosion inhibitors. Additionally, they are used as silver polishing agents in dishwasher tablets and powders, as antifreezes, in heating and cooling systems, hydraulic fluids, and vapor phase inhibitors. They are water soluble, are not readily degradable, and have a limited sorption tendency. In WWTP they are only partially removed, and a substantial fraction reaches surface water. Several studies showed that the BT and TT are widely distributed in surface waters. Loos et al. [35] detected BT and TT in 94% and 81% of 122 river water samples distributed over the EU, with mean concentrations of 493 ng/L and 617 ng/L for BT and TT, respectively. Harris et al. [36] showed in vitro that BT possessed clear antiestrogenic properties. This chemical was approximately 100-fold less potent than tamoxifen, which was used as a positive control. Later in vivo studies confirmed that BT had adverse potential on the endocrine system of fish, which may lead to adverse effects, including compromised growth and reproduction, altered development, abnormal behavior, and alterations in hormone biosynthesis [37].

5.6 Surfactants

Surfactants are organic chemicals that reduce surface tension in water and other liquids and exhibit a tendency to form micelles in solvents. Surfactants, used in industrial processes as well as in households, are among the most produced of all organic chemicals. The most familiar uses for surfactants are soaps, laundry detergents, dishwashing liquids, and shampoos. Other important uses are in textile and leather processing, mining flocculates, petroleum recovery (also after oil spills), pesticide adjuvants, additives in lubricants, and additives for emulsion polymerization. There are hundreds of compounds that can be used as surfactants and are usually classified by their ionic behavior in solutions: anionic, cationic, nonionic, or amphoteric. Surfactants are among the most relevant organic pollutants of anthropogenic origin and have very high potential to enter the environment, since their widespread use, primarily in aqueous solutions, leads to later introduction into the environment via wastewater discharges.

The awareness of potential environmental problems has led to a series of legislation measures resulting in a ban and replacement of nonbiodegradable and toxic surfactants. Examples are the replacement of ABS with LAS in the mid-1960s, voluntary replacement of DTDMAC in some European countries, and more recent restriction of use of alkylphenol ethoxylates (APEOs) in household detergents, which resulted in a substantial drop in the levels observed. APEOs are a class of nonionic surfactants that raised great attention and concern. Although parent APEOs are not highly toxic, their environmental acceptability is strongly disputed because of persistent metabolic products (alkylphenols (APs) and carboxylic derivatives (APECs)) generated during wastewater treatment. The estrogenic potential of these compounds is four to six orders of magnitude lower than that of the endogenous 17β-estradiol [38]; however, it has been reported that concentrations found in certain sewage effluents and in receiving rivers are sufficient to induce hormonal response in some fish species [33]. Moreover, NP and short-chain NPEOs are lipophilic compounds with a log K_{ow} of 4,48 (NP) and around 4.2 (NP_1EO, NP_2EO, and NP_3EO), so they partition preferentially to the organic fraction of sediments and show considerable potential to bioaccumulate in freshwater organisms [39]. Because of these findings, APEOs are banned or restricted in the EU.

Additionally, due to their unique surface-active properties, surfactants have the capacity to remobilize nonpolar contaminants, such as polycyclic aromatic hydrocarbons or heavy metals that have accumulated in sediments or WWTP sludges. This ability can be positively exploited, e.g., in the remediation of contaminated soils, but it is undesirable in cases where the surfactants are present in digested sewage sludge used to amend soil.

5.7 Nanomaterials (NMs)

Nanomaterials are small-scale substances and materials that have structural components smaller than 1 μm or (usually less than 100 nm) in at least one dimension [40]. Nanomaterials are divided simply into organic (carbon-based) nanomaterials, such as fullerenes, graphene, single-walled and multiwalled carbon nanotubes, and inorganic nanomaterials, such as titanium dioxide, zinc oxide, and silver. Due to their size, nanomaterials possess unique physical, chemical, and biological properties. In addition, they settle very slowly and, as they remain suspended for long periods in water and air, can be transported over greater distances than larger particles of the same material [41].

The specific properties of nanomaterials raise concerns about adverse effects on biological systems, which, at the cellular level, include structural arrangements that resemble nanomaterials [42, 43]. However, the toxic effects and environmental impact of nanomaterials are not fully understood, and the study of nanomaterials in the aquatic environment is currently a “hot topic.” A number of carefully designed studies have been conducted to understand the fate, transport, stability, and toxicity of nanoparticles in the aquatic environment [44]. Current results suggest that the main risk for the environment is associated to metals and metal oxides, both in particles and as ions, but further investigation of ecotoxicity, including long-term studies, especially of algae and aquatic invertebrates, are needed, together with studies of their action mechanisms at the cellular and the genetic level [45].

5.8 Plant Protection Products (Emerging Pesticides)

Pesticides represent a wide range of chemical compounds used to limit, inhibit, and prevent the growth of harmful animals, insects, invasive plants, weeds, bacteria, and fungi. Despite their recognized importance, pesticides are among the most important types of environmental pollutants, produced and released into the environment in huge quantities. Nearly 20,000 pesticide products have entered the market since registration began in 1947 [46], with an estimated 1–2.5 million tons of active ingredients used each year, predominantly in agriculture [47].

Although pesticides are applied mostly on soils, they have a high potential to reach the aquatic environment, via runoff, agricultural storm-water discharges, and return flows from irrigated fields. Consequently, numerous monitoring studies have documented the occurrence of pesticide residues at trace concentrations (on the order of μg/L and lower) in water around the world. As reported by several authors [48–50], many pesticides have the potential to cause adverse effects on human health and the environment, even at low concentrations, since they are persistent and bioaccumulate in biota. Although various pesticides are currently included in the list of priority substances in the EU regulations (1/3 of priority substances listed in EU WFD are pesticides), many others are still unregulated.

6 Monitoring of Emerging Contaminants in the Aquatic Environment: Chemical Analysis, General Trends, Main Challenges

In the last two decades, numerous analytical methods have been developed for the determination of different classes of emerging contaminants in environmental samples (water, sediment, soil, biota). Generally, the identification and quantification of emerging contaminants at low concentrations in complex environmental matrices requires analytical methods of high sensitivity and selectivity, which typically rely on liquid or gas chromatography (LC or GC) coupled to mass spectrometry (MS). The application of advanced low- or high-resolution MS instruments in environmental analysis has allowed the determination of a broader range of compounds and, thus, a more comprehensive assessment of environmental contaminants.

The preferred analytical approach is based on target analysis of preselected compounds of interest, using tandem MS instruments. Over the years, a gradual shift from class-specific methods to multi-residue methods for simultaneous analysis of a large number of target compounds, belonging to different classes, has occurred. For example, Robles-Molina et al. [51] developed a multi-residue method based on solid-phase extraction and liquid chromatography-time-of-flight mass spectrometry for the simultaneous determination of over 400 priority and emerging pollutants in water and wastewater. On the other hand, Pintado-Herrera et al. [52] used atmospheric pressure gas chromatography-time-of-flight-mass spectrometry (APGC-ToF-MS) for the simultaneous determination of 102 regulated and emerging contaminants in aqueous samples after stir bar sorptive extraction (SBSE). A number of multi-residue methods have been developed for the analysis of multiclass pharmaceuticals, illicit drugs, pesticides, PFC. Just to mention a few, Gros et al. [53] developed a method to determine 81 pharmaceutical residues, covering various therapeutic groups, and some of their main metabolites, in surface and treated waters (influent and effluent wastewaters, river, reservoirs, sea, and drinking water); Baker and Kasprzyk-Hordern [54] defined a multi-residue method for the environmental monitoring of 65 stimulants, opioid and morphine derivatives, benzodiazepines, antidepressants, dissociative anesthetics, drug precursors, human urine indicators, and their metabolites in wastewater and surface water. Masiá et al. [55] developed a method for the analysis of 43 polar pesticides in environmental waters.

However, the advances in analytical instrumentation and analytical capabilities do not provide the answer for many important questions such as the following ones: Which compounds should be monitored? Is it worthy to monitor hundreds of emerging contaminants that analytical chemists are capable of analyzing today? Is chemical analysis of specific compounds sufficient to assess contaminants present in the environment?

The current analytical approach has another drawback. The majority of analytical methods only focus on parent target compounds and rarely include metabolites and transformation products, which sometimes can be more toxic and persistent than the original compounds. One reason for that trend is that the majority of transformation products are not known and many of those that are known are not commercially available or are too expensive. But the main reason is that all relevant contaminants, metabolites, and transformation products that may be encountered in the aquatic environment are impossible to be included in any targeted multi-residue method, making therefore a strong case for the application of nontarget screening protocols using high-resolution mass spectrometry (HR-MS) [56, 57]. In comparison to triple quadrupole mass spectrometers, which operate at unit resolution for specific target analytes, HR-MS instruments such as time of flight (TOF), quadrupole time of flight (QqTOF), and Orbitrap mass spectrometers are capable of acquiring full-scan mass spectra at high resolution for all analytes having, therefore, the unique potential of retrospective data analysis for compounds not included in the first data processing. Accurate mass full-scan MS permits analysis of a large number of compounds and their degradation products that fall outside the scope of target methods. However, general screening for unknown substances is time-consuming and expensive and is often shattered by problems, such as lack of mass spectral libraries. Therefore, the main challenge is to prioritize contaminants and decide on the significance of the chemical data. Effect-related analysis, focused on relevant compounds, nowadays seems to be the most appropriate way to assess and study environmental contamination.

7 Future Challenges

Today, the major challenge is to evaluate the potential ecological effects associated with the presence of emerging contaminants in the aquatic environment and to establish causal links between pollution by emerging contaminants and the quality of ecological systems. Nevertheless, the direct estimation of effects caused by environmental pollutants on ecosystems is not straightforward, since we lack data on the occurrence of many emerging contaminants, on their fate and behavior in the environment, and on their long-term effects on aquatic ecosystems. In addition, the ecotoxicological significance of many emerging contaminants and effects of "chemical cocktails" remains largely unknown, and novel tools are needed to evaluate the risk of emerging contaminants in the environment.

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