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Emerging Contaminants: Analysis, Aquatic Compartments and Water Pollution

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Abstract Over the past two decades, the presence of so-called emerging contaminants in various environmental compartments around the world, such as water, sediments, soils and atmosphere, and in a wide variety of consumer products has become a major concern for society, public health authorities, industry (namely food industry and water sector) and the agricultural sector. Some of these substances are endocrine disruptors and others are proven carcinogens and mutagens. In particular,

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there is a growing concern about the presence of emerging contaminants in water resources.

The list of substances and products is particularly long: pesticides, pharmaceuticals, drugs of abuse (including licit and illicit drugs), cosmetics, personal care products, surfactants, cleaning products, industrial formulations and chemicals, food additives, food packaging, metalloids, rare earth elements, nanomaterials, microplastics and pathogens. Most of these substances are found not only in domestic wastewater and industrial discharges, but also in surface and ground water, and consequently in drinking water and food sources. Therefore, emerging contaminants entering the aquatic compartment may cause known, unknown or suspected

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adverse effects on the ecosystems and/or human health. Many molecules have been classified in recent years as priority or priority hazardous substances, and thus, the industrial world and the municipal wastewater treatment plants are particularly concerned by the release of these substances by virtue of increasingly strict regulations. However, existing conventional municipal wastewater treatment plants and drinking water treatment plants were not designed for eliminating these new contaminants. In addition, most emerging contaminants are not yet routinely monitored either in industrial discharges or in the environment. From an academic point of view, emerging substances are also of great interest to the scientific community and receive special attention. The areas of research concern not only their effects on human health and their impact on environment, but also their sources, analysis and fate in the environment, as well as their remediation. Indeed, their behavior in the environment and their effects on all living organisms remain largely unknown. Many substances are difficult to remove by conventional water treatment processes. Thus, there is an intense research activity on all these topics.

The objective of this chapter is to present a recent state of knowledge on emerging substances and their presence in the aquatic environment. After general considerations on emerging contaminants, the first part is focused on chromatographic methods coupled to mass spectrometry for their analysis and detection, and on detection of microplastics in water and sediment. The presence of alkylphenols, rare earth elements and nanoparticles in the aquatic environment is then discussed. Finally, examples of contamination described from around the world, from China to Portugal, Mexico, Colombia and Brazil, are presented.

Keywords Emerging contaminants · Substances of global concern · Pharmaceuticals · Personal care products · Pesticides · Alkylphenols · Persistent organic pollutants · Microplastics · Rare earth elements · Nanoparticles · Biological agents · Analysis · Water pollution · Aquatic compartments

1.1 Introduction

Although water quality problems are largely associated with developing countries, they also persist in developed countries and include, for example, the loss of pristine water bodies, impacts related to changes in hydromorphology, the spread of invasive species, the loss of biodiversity, and the increasing occurrence of chemical substances (Morin-Crini and Crini 2017). The water quality problems are intimately linked to human activities, whether domestic, agricultural or industrial. Indeed, population growth, agricultural intensification, rapid urbanization, increased industrial production and climate change are beginning to impact on Nature's ability to provide safe and clean water for our essential uses and functions. One of the most important global environmental problems is water pollution by chemicals (Aristizabal-Ciro et al. 2017; Hernández-Padilla et al. 2017; Morin-Crini and Crini

2017; Botero-Coy et al. 2018; Crini and Lichtfouse 2018; Dong et al. 2018; Díaz-Casallas et al. 2019; Gallego-Schmid and Tarpani 2019; Kumar et al. 2019; Reichert et al. 2019; Deviller et al. 2020). We are all concerned about this problem and the anthropogenic sources are well-known, namely domestic discharges, hospital effluents, industrial wastewaters, runoff from agriculture, livestock and aquaculture, and landfill leachates. It is recognized that, due to insufficient chemical treatment abatement, the discharge of effluents from municipal wastewater treatment plants is an important route for the appearance of chemical substances such as pharmaceuticals in the aquatic environment (Hernández-Padilla et al. 2017; Botero-Coy et al. 2018; Crini and Lichtfouse 2018; Gallego-Schmid and Tarpani 2019; Inyinbor et al. 2019; Mohapatra and Kirpalani 2019; Patel et al. 2019).

Many chemical substances such as metals, dyes, phenols, pesticides, pharmaceuticals and other so-called emerging contaminants are indeed part of our daily lives as they are used in a wide variety of products and applications. For example, they are ubiquitously in every household: in food, energy drinks, medicines, household and cleaning products, personal care products, and cosmetics, paints, electronics and computers, furniture and even our clothes (Puzyn and Mostrag-Szlichtyng 2012; Mortimer 2013; Schrenk and Chopra 2013; Duedahl-Olesen 2013; Juliano and Magrini 2017). The vast majority of chemicals, called contaminants or pollutants depending on their toxicity and impact (Chapman 2007), end up in our discharges of wastewater treatment plants and ultimately in the aquatic compartments of the environment such as rivers, lakes, coastal and marine ecosystems, seawater and ice caps (Crini and Badot 2007, 2010; Kosma et al. 2014; Gee et al. 2015; Archer et al. 2017; Ebele et al. 2017; Peña-Guzmán et al. 2019; Xu et al. 2019). As a result, chemicals can be found not only in surface water and freshwater, but also in groundwater, which is the main source of drinking water in many countries (Dévier et al. 2013; Gee et al. 2015). The presence of chemicals in general, and particularly emerging substances, in water is a cause of concern and debate, as the risk they pose to human health and the environment is not yet fully understood. Biological agents are also widely found in the environment. They include bacteria, viruses, fungi (yeasts, molds) and parasites. The majority of these agents are harmless, but some may have potential to cause ill health. The bibliography on emerging chemical and biological contaminants is particularly abundant and many topics are of interest to the scientific community (Table 1.1). In particular, the presence, occurrence, transport of emerging contaminants in the water resources and their impact on water quality are documented in thousands of publications reported worldwide during the last two decades, demonstrating an increasing concern about them.

Due to their widespread use in our daily applications, chemicals are ubiquitous not only in water and sediments, but also in soils and the atmosphere, at concentrations between few ng/L and several µg/L (Salthammer 2014, 2020; Patel et al. 2019). In recent decades, thanks to significant advances in the analysis and detection of trace contaminants, emerging contaminants have also been detected in plants (due to soil and water pollution), food products, living organisms and protected species (*e.g.*, birds, polar bears), even in areas where there is no human activity (Datta et al. 2018; Routti et al. 2019). This demonstrates their uncontrolled

Table 1.1 Selected comprehensive reviews and papers on emerging contaminants published in the last five years

General topic	References
Alkylphenols	Careghini et al. 2015; Crini et al. 2016; Tuan Omar et al. 2016; Chokwe et al. 2017; Deshayes et al. 2017; Priac et al. 2017; Acir and Guenther 2018; Salgueiro-Gonzalez et al. 2017; Zaytseva and Medvedeva 2019; Olaniyan et al. 2020; Vargas-Berrones et al. 2020a, b
Aquatic toxicity	Harmon 2015; Priac et al. 2017; Acir and Guenther 2018; Koba et al. 2018; Lin et al. 2018a; Mearns et al. 2018; Mezzelani et al. 2018; Salgueiro-Gonzalez et al. 2018; de Marchi et al. 2019; Fekadu et al. 2019; Li et al. 2019b; Patel et al. 2019; Olaniyan et al. 2020
Aquifer	Moreau et al. 2019; Burri et al. 2019; Kurwadkar 2019; Daesslé et al. 2020; Sackaria and Elango 2020
Analysis	Lu and Gan 2014a; Gago-Ferrero et al. 2015; Löder and Gerdts 2015; Bijlsma et al. 2016; Jardak et al. 2016; Tuan Omar et al. 2016; Priac et al. 2017; Salgueiro-Gonzalez et al. 2017, 2018; Acir and Guenther 2018; Botero-Coy et al. 2018; Lorenzo et al. 2018; Patel et al. 2019; Sousa et al. 2019; de Oliveira et al. 2020; Kovalakova et al. 2020
Antibiotics	Botero-Coy et al. 2018; Dong et al. 2018; Gogoi et al. 2018; Mezzelani et al. 2018; Fekadu et al. 2019; Jurado et al. 2019; Kumar et al. 2019; Ng et al. 2019; Reichert et al. 2019; García et al. 2020; Khan et al. 2020; Patel et al. 2020; Wang and Zhuan 2020
Antibiotic resistance	Zad et al. 2018; Zhao et al. 2018; Kumar et al. 2019; Liu et al. 2019; Ng et al. 2019; Reichert et al. 2019; García et al. 2020
Behavior	Jardak et al. 2016; Ebele et al. 2017; Mearns et al. 2018; Li et al. 2019a; Houde et al. 2019; de Marchi et al. 2019; Patel et al. 2019; Starling et al. 2019; Yu et al. 2019
Bioaccumulation	Tuan Omar et al. 2016; Ebele et al. 2017; Damkjaer et al. 2018; Herrera-Melian et al. 2018; Jiang et al. 2018; Mauricio et al. 2018; Mearns et al. 2018; Mezzelani et al. 2018; Salgueiro-Gonzalez et al. 2018; Wang et al. 2018b; Houde et al. 2019; Patel et al. 2019; Xu et al. 2020
Biodegradation	Lu and Gan 2014a, b; Ebele et al. 2017; Couto et al. 2019; Cao et al. 2020; de Oliveira et al. 2020
Biomagnification	Mearns et al. 2018, 2019
Bisphenol A	Machado et al. 2016; Gogoi et al. 2018; Zhao et al. 2018; Xiao et al. 2020
Caffeine	Machado et al. 2016; Sodr�e et al. 2018; Montagner et al. 2019; Anastopoulos et al. 2020; Rigueto et al. 2020
Cosmetics	Juliano and Magrini 2017; Li et al. 2018a; Caldas et al. 2019
Disinfection by-products	Benitez et al. 2015; Nika et al. 2016; Zad et al. 2018; Gao et al. 2019; Ng et al. 2019; Khan et al. 2020
Drinking water	Gee et al. 2015; Hamza et al. 2016; Machado et al. 2016; Gwenzi et al. 2018; Sodr�e et al. 2018; Caldas et al. 2019; Gao et al. 2019; Patel et al. 2019; Starling et al. 2019; Iroegbu et al. 2020; Sousa et al. 2020
Ecotoxicology	Petrie et al. 2015; Cavalheiro et al. 2017; Kumar et al. 2019; Li et al. 2019b; Patel et al. 2019; Starling et al. 2019; Xu et al. 2019

(continued)

Table 1.1 (continued)

General topic	References
Ecological risk assessment	Gwenzi et al. 2018; Matich et al. 2019; Mezzelani et al. 2018; Pedrazzani et al. 2019; Xu et al. 2019
Endocrine disrupting compounds	Różalska et al. 2015; Ma et al. 2016; Murdoch and Sanin 2016; Tuan Omar et al. 2016; Archer et al. 2017; Acir and Guenther 2018; Dong et al. 2018; Gogoi et al. 2018; Liu et al. 2019; Ng et al. 2019; Olaniyan et al. 2020; Patel et al. 2020
Environmental fate	Cavalheiro et al. 2017; Monneret 2017; Priac et al. 2017; Archundia et al. 2018; Koumaki et al. 2018; Reichert et al. 2019; Yu et al. 2019
Exposure pathways	Chokwe et al. 2017; Koba et al. 2018; Mearns et al. 2018; Li et al. 2019b; Routti et al. 2019; Wu et al. 2020b; Xiao et al. 2020
Fate	Eggen and Vogelsang 2015; Katsigiannis et al. 2015; Noutsopoulos et al. 2015; Carr et al. 2016; Archer et al. 2017; Cavalheiro et al. 2017; Ebele et al. 2017; Datta et al. 2018; Gogoi et al. 2018; Zad et al. 2018; Zhao et al. 2018; Couto et al. 2019; de Marchi et al. 2019; Jurado et al. 2019; Mohapatra and Kirpalani 2019; Ng et al. 2019; Routti et al. 2019; Starling et al. 2019
Flame retardants	Hamza et al. 2016; Lin et al. 2018a; Zhao et al. 2018; Llompарт et al. 2019; Li et al. 2019a; Peña-Guzmán et al. 2019; Tongue et al. 2019; Wang et al. 2020; Wu et al. 2020b; Zhou et al. 2020; Zuiderveen et al. 2020
Food additives	Careghini et al. 2015; Moreau et al. 2019; Peña-Guzmán et al. 2019
Hormones	Barbosa et al. 2016; Gogoi et al. 2018; Mezzelani et al. 2018; Zad et al. 2018; Fekadu et al. 2019; Montagner et al. 2019; Ng et al. 2019; Peña-Guzmán et al. 2019; Sousa et al. 2019
Illicit drugs	Bijlsma et al. 2016; Archer et al. 2017; Ng et al. 2019; Peña-Guzmán et al. 2019
Indoor pollutants	Salthammer 2014, 2020; Cretescu et al. 2019
Industrial wastewater	Petrie et al. 2015; Jardak et al. 2016; Archer et al. 2017; Chokwe et al. 2017; Priac et al. 2017; Botero-Coy et al. 2018; Dong et al. 2018; Montagner et al. 2019; Moreau et al. 2019; Ng et al. 2019; Patel et al. 2019; Peña-Guzmán et al. 2019; Tolboom et al. 2019; Zhang et al. 2019; Daesslé et al. 2020
Life cycle assessment	Gallego-Schmid and Tarpani 2019
Marine organisms	Lin et al. 2018a; Mearns et al. 2018, 2019
Metabolites	Petrie et al. 2015; Acir and Guenther 2018; Koba et al. 2018; Patel et al. 2019
Metabolomics	Matich et al. 2019
Microplastics	Löder and Gerdts 2015; Oberbeckmann et al. 2015; Thompson 2015; Carr et al. 2016; Avio et al. 2017; Juliano and Magrini 2017; Barboza et al. 2018; Datta et al. 2018; Lambert and Wagner 2018; Li et al. 2018b; Lin et al. 2018a; Wagner and Lambert 2018; Zad et al. 2018; da Costa et al. 2019; Guo and Wang 2019; Mishra et al. 2019; Ng et al. 2019; Prata et al. 2019; Stock et al. 2019; Amato-Lourenço et al. 2020; Guo et al. 2020; Iroegbu et al. 2020; Kumar et al. 2020; Möller et al. 2020; Tiwari et al. 2020; Wong et al. 2020; Xu et al. 2020

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Table 1.1 (continued)

General topic	References
Modeling	Wang et al. 2016c; Petrie et al. 2015; Peng et al. 2018; Li et al. 2019b; Moreau et al. 2019; Noutsopoulos et al. 2019; Sousa et al. 2019; Daesslé et al. 2020; Gibson 2020
Monitoring	Priac et al. 2017; Mearns et al. 2018; Sousa et al. 2018, 2019; Montagner et al. 2019; Moreau et al. 2019; Peña-Guzmán et al. 2019; Gibson 2020; Patel et al. 2020
Municipal wastewater	Bijlsma et al. 2016; Archer et al. 2017; Cavalheiro et al. 2017; Deshayes et al. 2017; Chokwe et al. 2017; Ebele et al. 2017; Hernández-Padilla et al. 2017; Priac et al. 2017; Dong et al. 2018; Gogoi et al. 2018; Gallego-Schmid and Tarpani 2019; Montagner et al. 2019; Peña-Guzmán et al. 2019; Starling et al. 2019
Nanoparticles/nanomaterials	Hamza et al. 2016; Mearns et al. 2018; Zhao et al. 2018; de Marchi et al. 2019; Matich et al. 2019; Sousa and Teixeira 2020
Occurrence	Kosma et al. 2014; Annamalai and Namasivayam 2015; Careghini et al. 2015; Eggen and Vogelsang 2015; Hao et al. 2015; Petrie et al. 2015; Barbosa et al. 2016; Jardak et al. 2016; Hamza et al. 2016; Liu et al. 2016; Xu et al. 2016; Cavalheiro et al. 2017; Chokwe et al. 2017; Ebele et al. 2017; Priac et al. 2017; Acir and Guenther 2018; Amin et al. 2018; Botero-Coy et al. 2018; Gogoi et al. 2018; Herrera-Melian et al. 2018; Mezzelani et al. 2018; Zhao et al. 2018; Couto et al. 2019; Fekadu et al. 2019; Gao et al. 2019; Jurado et al. 2019; Li et al. 2019b; Patel et al. 2019; Ng et al. 2019; Starling et al. 2019; Xu et al. 2019; Yu et al. 2019; Xu et al. 2020
Pathogens	Ng et al. 2019
Parabens	Juliano and Magrini 2017; Mearns et al. 2018; Caldas et al. 2019; Salthammer 2020
Pesticides	Barbosa et al. 2015; Hamza et al. 2016; Machado et al. 2016; Dong et al. 2018; Mearns et al. 2018; Sodr�e et al. 2018; Caldas et al. 2019; Houde et al. 2019; Montagner et al. 2019; Moreau et al. 2019; Ng et al. 2019; Xu et al. 2019; Patel et al. 2020
Persistence	Ebele et al. 2017; Priac et al. 2017; Mezzelani et al. 2018; Houde et al. 2019; Li et al. 2019a; Gibson 2020
Persistent organic pollutants	Eggen and Vogelsang 2015; Harmon 2015; Kallenborn et al. 2015; Zeng 2015; Hamza et al. 2016
Personal care products	Eggen and Vogelsang 2015; Archer et al. 2017; Aristizabal-Ciro et al. 2017; Ebele et al. 2017; Juliano and Magrini 2017; Dong et al. 2018; Gogoi et al. 2018; Li et al. 2018a; Caldas et al. 2019; Liu et al. 2019; Moreau et al. 2019; Ng et al. 2019; Peña-Guzmán et al. 2019; Xu et al. 2019; Patel et al. 2020
Pharmaceuticals	Eggen and Vogelsang 2015; Tuan Omar et al. 2016; Roberts et al. 2016; Archer et al. 2017; Aristizabal-Ciro et al. 2017; Ebele et al. 2017; Botero-Coy et al. 2018; Dong et al. 2018; Gogoi et al. 2018; Koba et al. 2018; Mezzelani et al. 2018; Couto et al. 2019; Fekadu et al. 2019; Li et al. 2019b; Liu et al. 2019; Moreau et al. 2019; Ng et al. 2019; Peña-Guzmán et al. 2019; Xu et al. 2019; Yu et al. 2019; Patel et al. 2019, 2020

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Table 1.1 (continued)

General topic	References
Plasticizers	Llompарт et al. 2019; Patel et al. 2020; Salthammer 2020; Wang et al. 2020
Perfluoroalkyl substances/ Polyfluoroalkyl compounds	DeWitt 2015; Xiao 2017; Dong et al. 2018; Lorenzo et al. 2018; Brusseau 2019; Klemes et al. 2019; Ng et al. 2019; Pan et al. 2020; Salthammer 2020
Radionuclides	Mearns et al. 2018; Zhang et al. 2019
Rare earth elements	Gwenzi et al. 2018; Mubashir 2018; Balarам 2019; Salthammer 2020
Reclaimed water	Gilabert-Alarcón et al. 2018; Sodré et al. 2018
Regulation	Barbosa et al. 2016; Acir and Guenther 2018; Dulio et al. 2018; Mearns et al. 2018; Jurado et al. 2019; Lapworth et al. 2019; Patel et al. 2019; Sousa et al. 2019
Remediation	Barbosa et al. 2016; Hamza et al. 2016; Jardak et al. 2016; Priac et al. 2017; Crini and Lichtfouse 2018; Ma et al. 2018; Couto et al. 2019; Crini et al. 2019; Kumar et al. 2019; Llompарт et al. 2019; Liu et al. 2019; Patel et al. 2019, 2020; Serna-Galvis et al. 2019; Tolboom et al. 2019; Zaytseva and Medvedeva 2019; Zhang et al. 2019; Dhangar and Kumar 2020; Godage and Gionfriddo 2020; Khan et al. 2020; Mautner 2020; Pesqueira et al. 2020; Rasheed et al. 2020; Vara and Karnena 2020; Wang and Zhuан 2020; Yadav et al. 2020; Zaied et al. 2020
Risk assessment	Thomaidi et al. 2015; Osorio et al. 2016; Archer et al. 2017; Tahar et al. 2017; Gwenzi et al. 2018; Mearns et al. 2018; Mezzelani et al. 2018; Sodré et al. 2018; Jurado et al. 2019; Montagner et al. 2019; Patel et al. 2019; Pedrazzani et al. 2019; Xu et al. 2019; Wang et al. 2020
Sediments	Careghini et al. 2015; Petrie et al. 2015; Yang et al. 2015; Bradley et al. 2016; Jin and Zhu 2016; Ebele et al. 2017; Koumaki et al. 2017; Koba et al. 2018; Mearns et al. 2018; Salgueiro-Gonzalez et al. 2018; Li et al. 2019a; Stock et al. 2019
Soils	Careghini et al. 2015; Guo et al. 2020
Sources	Thompson 2015; Jardak et al. 2016; Chokwe et al. 2017; Deshayes et al. 2017; Sodré et al. 2018; Gogoi et al. 2018; Mezzelani et al. 2018; Patel et al. 2019
Surfactants	Hamza et al. 2016; Jardak et al. 2016; Xiao 2017; Llompарт et al. 2019; Patel et al. 2020
Toxicity	Lu and Gan 2014a; Harmon 2015; Chokwe et al. 2017; Ebele et al. 2017; Priac et al. 2017; Acir and Guenther 2018; Guo et al. 2020; Olaniyan et al. 2020; Xiao et al. 2020
Tracers	Mearns et al. 2018; Moreau et al. 2019
Transport	Kallenborn et al. 2015; Ebele et al. 2017; Datta et al. 2018; Koba et al. 2018; Mearns et al. 2018; Zhao et al. 2018; Li et al. 2019b; Patel et al. 2019; Yu et al. 2019
Triclosan	Kosma et al. 2014; Juliano and Magrini 2017; Machado et al. 2016; Montagner et al. 2019
UV filters	Juliano and Magrini 2017; Mearns et al. 2018; Jurado et al. 2019; Peña-Guzmán et al. 2019; Sousa et al. 2019

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Table 1.1 (continued)

General topic	References
Wastewater treatment plants	Kosma et al. 2014; Hamza et al. 2016; Carr et al. 2016; Bijlsma et al. 2016; Archer et al. 2017; Hernández-Padilla et al. 2017; Botero-Coy et al. 2018; Gallego-Schmid and Tarpani 2019; Inyinbor et al. 2019; Mohapatra and Kirpalani 2019; Patel et al. 2019
Water compartment	Careghini et al. 2015; Koumaki et al. 2015; Machado et al. 2016; Archer et al. 2017; Aristizabal-Ciro et al. 2017; Ebele et al. 2017; Dong et al. 2018; Datta et al. 2018; Burri et al. 2019; Fekadu et al. 2019; Kurwadkar 2019; Li et al. 2019a; Montagner et al. 2019; Moreau et al. 2019; Peña-Guzmán et al. 2019; Starling et al. 2019; Stock et al. 2019; Xu et al. 2019; Daesslé et al. 2020; Kroon et al. 2020; Sackaria and Elango 2020; Wong et al. 2020
Water quality	Aristizabal-Ciro et al. 2017; Hernández-Padilla et al. 2017; Botero-Coy et al. 2018; Dong et al. 2018; Díaz-Casallas et al. 2019; Gallego-Schmid and Tarpani 2019; Kumar et al. 2019; Reichert et al. 2019; Deviller et al. 2020
Water management	Díaz-Casallas et al. 2019; Gilabert-Alarcón et al. 2018
Water reuse	Dulio et al. 2018; Ma et al. 2018; Sodré et al. 2018; Inyinbor et al. 2019; Deviller et al. 2020

movement in the global environment. Indeed, the issue of contaminants/pollutants and their impact on the environment (especially on water quality), society and human health is common to the entire World, making it a global concern at the present time. However, concentration levels are extremely variable from one continent to another, from one country to another and even from one region to another. Recently, Fekadu et al. (2019), comparing levels of contamination of pharmaceuticals such as carbamazepine and sulfamethoxazole in surface waters between Africa and Europe, observed that the maximum concentrations reported in Africa were 20,000 times higher than in Europe. The authors indicated that the variation in the consumption of pharmaceuticals, the partial removal of substances in wastewater treatment plants and the direct discharge of wastewater from livestock farms are among the reasons that may explain the observed differences (Fekadu et al. 2019). Other studies showed a correlation between the presence of emerging substances in the aquatic environment and discharges from wastewater treatment plants (Stackelberg et al. 2007; Kasprzyk-Hordern et al. 2008; Watkinson et al. 2009; Ort et al. 2010; Basile et al. 2011; Gonzalez et al. 2012; Machado et al. 2016; Priac et al. 2017; Gilabert-Alarcón et al. 2018; Mezzelani et al. 2018).

The vast majority of the anthropogenic substances are currently not regulated and some have been regulated only recently, namely certain pesticides and alkylphenols known as endocrine disruptors or endocrine-disrupting chemicals (Daughton 2004; Lu and Gan 2014a; Gee et al. 2015; Petrie et al. 2015; Barbosa et al. 2016; Morin-Crini and Crini 2017; Jurado et al. 2019; Sousa et al. 2019). For example, paraquat, an herbicide used worldwide since the 1960s that caused severe and fatal poisonings, was banned in the European Union in 2003 and withdrawn from the market in 2007. Another example is the organochlorine insecticide

chlordecone, introduced in 1958 and banned in 1978 in the US and in the early 1993 in the French West Indies (Rana et al. 2016). In 2000, a first list of 33 priority substances (several pesticides, the phthalate di(2-ethylhexyl)-phthalate, octylphenol, nonylphenol, solvents, among others) was established as a control measure for the next 15 years based on their significant risk to or *via* the aquatic environment (European Water Framework Directive 2000/60/EC; Decision 2455/2001/EC). In 2008, the Directive 2008/105/EC laid down the environmental quality standards (EQS) for the priority substances and certain other pollutants. Moreover, other groups of substances were also targeted to be reviewed for possible future prioritization (*e.g.*, bisphenol A, musk xylene, perfluorooctane sulphonic acid, dioxins, polychlorinated biphenyls), and in fact some of them were later included in the list of priority substances by Directive 2013/39/EU, which enlisted 45 priority substances or group of substances. Additionally, this Directive preconized the launch of the first Watch List and recommended to include diclofenac, 17- β -estradiol and 17- α -ethinylestradiol. The non-steroidal anti-inflammatory drug diclofenac is often detected in European municipal wastewater treatment plants influents and effluents, surface water and groundwater. The first complete European watch list of substances of emerging concern (European Decision 2015/495/EU of 20 March 2015) was launched in 2015 and included three hormones (17- α -ethinylestradiol, 17- β -estradiol and estrone), four pharmaceuticals (diclofenac, azithromycin, clarithromycin and erythromycin), eight pesticides (methiocarb, oxadiazon, imidacloprid, thiachloprid, thiamethoxam, clothianidin, acetamiprid and triallate), a UV filter (2-ethylhexyl-4-methoxycinnamate) and an antioxidant (2,6-di-*tert*-butyl-4-methylphenol) commonly used as food additive (Morin-Crini and Crini 2017). This list is dynamic and the latest update was published in 2018 (*e.g.*, with the European Decision 2018/840/EU), by removing tri-allate, oxadiazon, 2,6-di-*tert*-butyl-4-methylphenol and diclofenac (due to the sufficient high-quality monitoring data already available, according to the Decision), as well as 2-ethylhexyl-4-methoxycinnamate (since data is needed for sediment rather than water), and by adding 3 candidates: the insecticide metaflumizone, and the antibiotics amoxicillin and ciprofloxacin. Recently, the substances propiconazole and 4-nonylphenol were banned in Europe in November 2018 and July 2019, respectively. Indeed, from a regulatory point of view, the situation is constantly evolving (Barbosa et al. 2016; Jurado et al. 2019; Sousa et al. 2019). The chronicle of European science, policy and legislation to develop a groundwater monitoring list can be found in the review by Lapworth et al. (2019). Water contamination by pesticides, pharmaceuticals and industrial chemicals has become a global environmental and health crisis (Morin-Crini and Crini 2017; Crini and Lichtfouse 2018; Patel et al. 2019; Tolboom et al. 2019). There is also a mobilization of the global scientific community on all subjects concerning emerging substances, from their analysis to their removal, their behavior in the environment and their impact on health (Table 1.1).

The objective of this chapter is to present a recent state of knowledge on emerging substances, considering several aspects presented in three parts. After general considerations on emerging contaminants, the first part is devoted to analysis and detection of emerging substances with the presentation of chromatographic

methods coupled to mass spectrometry for their analysis and detection. The detection of microplastics in water and sediments is also discussed. The second part of this chapter presents the occurrence, fate and toxicity of alkylphenols, rare earth elements and nanoparticles in the aquatic environment. The third part presents selected examples of contamination described from around the world, from China to Portugal, and Latin America.

1.2 General Considerations on Emerging Contaminants

1.2.1 Contamination and Pollution

Contamination/Pollution arises from all sectors of human activity, and is due to natural (petroleum, minerals, etc.) and anthropogenic causes (*e.g.*, sewage treatment sludge or persistent organic pollutants produced by waste incineration) and especially to synthetic substances produced by chemical industries (*e.g.*, dyes, fertilizers, pesticides, and so on). The terms contamination/pollution and contaminant/pollutant are often used in relation to subjects like environment, food and medicine (Crini and Badot 2007, 2010; Morin-Crini and Crini 2017). Both contaminant and pollutant refer to undesirable or unwanted substances. Pollutant refers to a harmful substance but contaminant is not necessarily harmful since contamination refers simply to the presence of a chemical substance where it should not be. This means that all pollutants are contaminants, but not all contaminants are pollutants. In this chapter, both these terms were used.

1.2.2 What Is an Emerging Contaminant?

A chemical pollutant is a substance toxic for flora, fauna and for humans, and present at concentrations such that, in Nature, has repercussions for the environment and/or on health in general (Crini and Badot 2007, 2010; Sauvé and Desrosiers 2014; Harmon 2015). Examples of pollutants/micropollutants known to the public are various, including nitrates, phosphates, pesticides such as glyphosate or atrazine, detergents (cleaning products), metals, dyes, pharmaceuticals such as diclofenac or ibuprofen, licit drugs (caffeine 1,3,7-trimethyl-3-7-dihydro-1H-purine-2,6-dione), illicit drugs (cocaine, amphetamines), synthetic (17- α -ethinylestradiol) and natural (17- β -estradiol) hormones, cosmetics and personal care products (parabens, triclosan, sunscreens and UV filters, domestic biocides, disinfectants), food derivatives and additives (nitrites, caffeine, artificial sweeteners), food packaging and containers (phthalates, other plasticizers), industrial substances (bisphenol A, surfactants, chlorinated solvents such as trichloroethylene, disinfection products, biocides, lubricants, silicones,

substances used in nonstick materials, ingredients used in paints), microbial pathogens, indoor pollutants, etc. Other substances, that are less known by the public, are considered substances of concern: estrogens (estriol), pesticides less known by the public but widely used such as methiocarb, triallate and oxadiazon, neonicotinoids (insecticides), 2,6-di-*tert*-butyl-4-methylphenol (anti-oxidant), UV filter (2-ethylhexyl-4-methoxycinnamate), macrolide antibiotics used in veterinary medicine and aquaculture, volatile organic compounds, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, bromine-containing flame-retardants, perfluorinated compounds and perfluorinated alkyl substances, polybrominated diphenyl ethers, alkylphenols and alkylphenol polyethoxylates, rare earth elements, radionuclides, metalloids such as selenium, and many more (Kolpin et al. 2002; Daughton 2004; Tijani et al. 2016). The public is also increasingly aware of so-called emerging substances: antibiotics, analgesics, hormones and other drugs (anti-inflammatory, anti-diabetic, antiepileptic), nanoparticles, bioterrorism and sabotage agents, and pathogens (cyanotoxins or algal toxins, mycotoxins, antibiotic-resistant organisms, etc.). The list of emerging substances and products is therefore particularly long (Tijani et al. 2016) and is also of great interest to the scientific community (Table 1.1).

The term “emerging contaminants/pollutants” refers primarily to those for which there are currently no regulations requiring monitoring or public reporting of their presence in our water supply or wastewaters. The US Environmental Protection Agency (EPA) defines an emerging pollutant as “a chemical or material which because of a recent source that it originates, or because of a new pathway that has developed, and for which a lack of published health standards exist poses a perceived, potential, or real threat to the human health or the environment” (source: US EPA 2012, Washington, DC). Their occurrence results from point (urban and industry) or diffuse (agriculture) contamination/pollution sources. Various other terms and definitions can be found in the literature. Indeed, there is no generally accepted definition, each definition and interpretation depending on the respective perspective and/or objective (Morin-Crini and Crini 2017; Salthammer 2020). In Europe, the term contaminant of emerging concern is a common term for chemicals that are currently not regulated (not submitted to a routine monitoring and/or emission control regime) but may be under scrutiny for future regulation (Dulio et al. 2018).

In the bibliography, there are several terms to denote emerging contaminants almost interchangeably such as emerging organic contaminants, emerging substances, substances of emerging concern, contaminants of emerging concern, emerging pollutants, emerging micropollutants and other similar terminologies (trace organic contaminants, micropollutants, trace organic compounds, trace pollutants, constituents of emerging concern, xenobiotic organic compounds, etc.). However, it is important to point out that all emerging pollutants are emerging contaminants, but not all emerging contaminants are emerging pollutants. This is often confused in the literature. There are also terms that refer to subsets of emerging substances. All of these terms refer to many different types of chemicals, such as pharmaceuticals and drugs (medicines, non-prescription drugs, endocrine disrupting compounds), personal care products and cosmetics (soaps, fragrances, bisphenols, parabens, triclosan, endocrine disrupting compounds), household cleaning

products, industrial compounds (surfactants, flame/fire retardants, monomers and polymers, solvents), pesticides (new formulations), and other agricultural products (fertilizers, lawn care products) and biocides (Tijani et al. 2016; Morin-Crini and Crini 2017; Patel et al. 2019). Endocrine disruptors can be found in the pharmaceutical and/or cosmetic category. They also include a range of other compounds, including pesticides and phytochemicals, as well as industrial chemicals. Many researchers consider endocrine disruptors to be a narrower subclass of emerging substances. This term refers to specific substances that have been shown to have an effect on the endocrine system of aquatic organisms or that have been designed to act on the human hormone system. Other substances, products and new technologies of concern include UV filters, corrosion inhibitors (benzothiazoles), 3D-printing (thermoplastics, additives), E-cigarettes and E-shishas, nanomaterials and nanoparticles (new products of new anthropogenic processes, nanosprays), microplastics and nanoplastics (considered as truly “new” to the environment). Biological agents and other pathogens (pathogenic bacteria, multi-drug resistant microbes) can also be defined as emerging (Morin-Crini and Crini 2017; Crini and Lichtfouse 2018; García et al. 2020). Indeed, the literature also includes discussion of antibiotic-resistant microorganisms and antibiotic-resistance genes under the broad category of emerging contaminants. More recently, nanoparticles have also been included in the class of emerging substances (Mearns et al. 2018; Zhao et al. 2018; de Marchi et al. 2019; Matich et al. 2019).

Luo et al. (2014) proposed to classify emerging contaminants in five categories, namely personal care products (fragrances, disinfectants, UV filters and insect repellents), pharmaceuticals (non-steroidal anti-inflammatory drugs, antibiotics, lipid regulator, anticonvulsants, β -blockers), steroid hormones, industrial chemicals (plasticizers, fire retardants, bisphenol A, phthalates) and surfactants (cleaning products, alkylphenols), excluding pesticides. According to Norman network (2016), over 1000 emerging chemicals are recognized and classified in four main groups, *i.e.*, drugs, personal care products, endocrine disruptors and pesticides (Norman network 2016; Dulio et al. 2018). Another simplified classification for pharmaceuticals and personal care products proposed by Ebele et al. (2017) considers only one main family of endocrine disruptors, which is subdivided into three categories: (1) personal care products including cosmetics, disinfectants, conservation agents, fragrances and UV screens; (2) nonsteroidal drugs, including antibiotics, analgesics, and other pharmaceuticals (human and veterinary drugs); and (3) steroids (estrogens, etc.). Patel et al. (2020) recently proposed four groups of emerging contaminants (excluding pesticides), *i.e.*, pharmaceuticals, endocrine disruptors (including cosmetics, hormones, xenobiotics, plastics), personal care products (including cosmetics, UV filters, disinfectants, insect repellents such as triclosan, synthetic hormones, lipid regulators and steroids), and perfluorinated compounds. Other researchers and organizations have classified emerging substances into three broad categories: pharmaceuticals, personal care products and endocrine disrupting compounds, excluding pesticides. However, these classifications can be confusing because some personal care products are also endocrine-disrupting chemicals while other drugs are not (Darbre 2015; Gee et al. 2015). In reality, there is not yet an

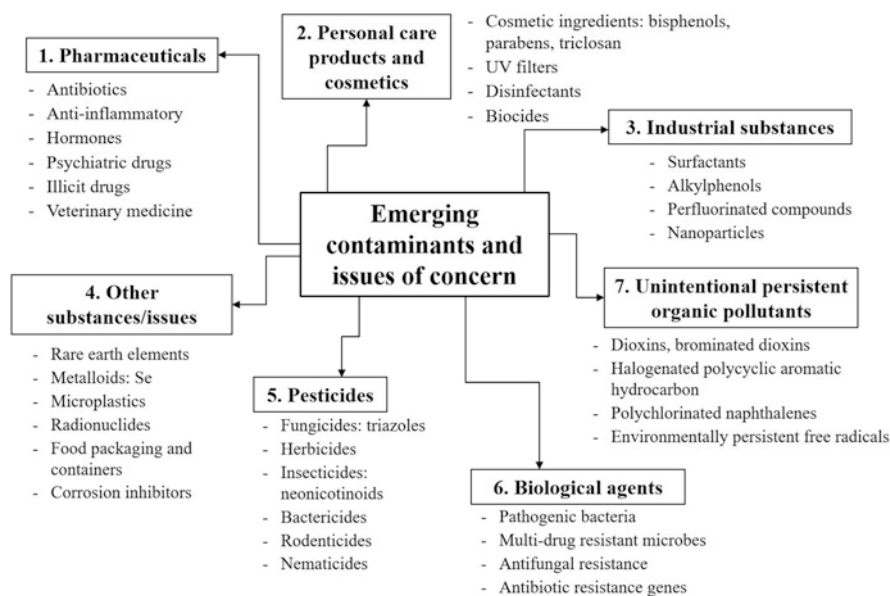


Fig. 1.1 Classification of emerging contaminants and issues of concern in water compartments

internationally recognized general classification for emerging substances. Nevertheless, many researchers agree with the definition given by the US EPA (Gogoi et al. 2018). Figure 1.1 provides a general classification of emerging contaminants and issues of concern in water compartments into seven categories, regardless of their risk to health or the environment.

1.2.3 Examples of Emerging Contaminants of Recent Concern

Polyfluoroalkyl or perfluoroalkyl, known by the abbreviation PFASs, are a family of emerging contaminants that have recently become a concern (Melzer et al. 2010; Gallo et al. 2012; Barry et al. 2013; Vestergren and Cousins 2013; DeWitt 2015; Xiao 2017; Dong et al. 2018; Lorenzo et al. 2018; Brusseau 2019; Ng et al. 2019; Klemes et al. 2019; Pan et al. 2020; Salthammer 2020). Perfluoroalkyl substances is a term used for a family of highly fluorinated chemicals (the term perfluorinated compounds can also be found in the literature). These substances contain fluorinated molecular chains that degrade very slowly in the environment and have a high bioaccumulation potential. They include subclasses such as perfluoroalkyl sulphonic acids (PFASs) and perfluoroalkyl carboxylic acids (PFCAs). The list is particularly long as the Chemical Abstracts Service registers more than 4000 compounds.

These synthetic substances have been produced and widely used since the 1950s before their harmful health effects and persistence came to light. Today, they are still widely used in consumer products and for industrial uses, finding targeted applications in a wide variety of fields. For example, perfluoroalkyl substances (perfluoroalkyl sulfonates and perfluoroalkyl carboxylates) are widely used as polymer constituents in food containers and packaging (fast-food packaging, pizza boxes), processing aids in non-stick cookware (Teflon®), surface-active agents in waterproof clothing and stain-resistant carpet (stain-resistant textiles, water-resistant textiles), and cleaning products. They are also used as individual ingredients in firefighting foams used in many military installations and airports, and in painting materials (Xiao et al. 2013; DeWitt 2015; Brusseau 2019; Pan et al. 2020). Other applications include coatings and metal plating, hydraulic fluids, medical devices, cosmetics (shampoos), pesticides, and photo imaging. The best known are perfluorooctanoic acid (PFOA) used as a repellent coating for textiles, paper products and cookware and perfluorooctanesulfonic acid (PFOS) used in fire fighting foams, carpet treatments, and mist suppressants in metal plating operations.

In 2009, perfluoroalkyl substances were listed in Annex B of the Stockholm Convention on Persistent Organic Pollutants (Stockholm Convention 2009: CN524-TREATIES 4, UNEP, Geneva) as substances of concern, restricted but not completely banned. Many substances are currently being considered for restriction under the 2015 Rome Directive (Stockholm Convention 2015: Decision POPRC-11/4, UNEP, Rome) and will be banned under the EU Chemicals Regulation from 2020. Indeed, perfluoroalkyl substances are chemicals considered to be persistent organic pollutants and long-range transported anthropic contaminants found at high concentrations in human and wildlife populations around the World, including in Arctic marine mammals. Their ubiquitous persistence in the environment and their toxicity in animal models raise concerns about the effects on human health of chronic low-level exposure (Melzer et al. 2010; DeWitt 2015; Pan et al. 2020). Perfluoroalkyl substances have been linked to cancer, liver damage and thyroid disease (Melzer et al. 2010; Gallo et al. 2012; Barry et al. 2013; Vestergren and Cousins 2013). Klemes et al. (2019) recently reported that more than 16 million people in the United States were exposed to drinking water with perfluorinated alkyl substances concentrations exceeding 10 ng/L. Melzer et al. (2010) previously reported that higher concentrations of serum perfluorooctanoate and perfluorooctane sulfonate are associated with current thyroid disease in the general adult population in the United States. Gallo et al. (2012) demonstrated an association between concentrations of perfluorooctanoate and perfluorooctane sulfonate and serum levels of alanine of transaminase, a marker of hepatocellular damage. In another study, Barry et al. (2013) reported that exposure to perfluorooctanoic acid is associated with renal, pancreatic and testicular cancer in rats. Other examples can be found in the review by Vestergren and Cousins (2013).

The presence of perfluoroalkyl substances in tap water has become a priority. However, due to their chemical stability and composition, these substances are poorly or even not eliminated by conventional water treatment methods. Because they have no carbon-carbon double bonds and no functional groups, they are also

resistant to advanced oxidation processes. Innovation is therefore required to find removal solutions.

Another topical issue concerns plastics/microplastics (Wagner et al. 2014; Avio et al. 2017; Lambert and Wagner 2018; Peeken et al. 2018). Plastics are synthetic polymers composed of different materials that range from cellulose to crude oil and are used in a broad ever-growing spectrum of applications. They are separated into thermoplastics and thermosets and consist of different synthetic polymers of which polypropylene, polyethylene, polyvinyl-chloride, polyurethane, polyethylene terephthalate and polystyrene were the most commercially demanded in 2017 (Plastics Europe 2017). Moreover, tire wear may be included in a larger definition of microplastics (Wagner et al. 2018) (although ISO does not cover it; ISO 2013). Plastics are important materials that are abundant in our economy (because they are lighter and cheaper than other materials) and are part of our daily lives, making our lives easier in many ways. Since the 1950s, the plastic production rose exponentially to 359 million tons in 2018 (Plastics Europe 2019). However, if they are not properly disposed of or recycled after use, they are often released into the environment where they can persist for long periods of time and break down into smaller and smaller pieces, called microplastics, which are of concern (Lambert and Wagner 2018). Figure 1.2 shows accumulation of plastic debris on a shoreline in France.

Microplastics are indeed widespread contaminants worldwide, from the Arctic to the Antarctic (Peeken et al. 2018) *via* tropical islands (Imhof et al. 2017), present not only in all the aquatic compartments (rivers, sediments, marine environment), but also in soils and in the atmosphere (Avio et al. 2017; Prata et al. 2019; Möller et al. 2020; Xu et al. 2020). In fact, plastics have also been detected in remote mountain lakes and deep-sea sediments (Cauwenberghe et al. 2013; Free et al. 2014), and



Fig. 1.2 Accumulation of plastic debris on a shoreline in France. (Source: Florence Carreras, INRA, France)

even in the air we breathe (Gasperi et al. 2018; Allen et al. 2019). They are considered as emerging contaminants. However, the first studies on the description of polystyrene spherules and pieces in the environment and their effects date back to the 1970s with the works of Carpenter and co-workers (Carpenter et al. 1972; Carpenter and Smith 1972). Microplastics were already identified as persistent in the environment and as potentially to accumulate in different marine ecosystems.

Special attention is paid to plastic pollution of the marine environment. Indeed, this issue is a growing environmental concern worldwide, as shown by the recent explosion of literature on their identification, quantification and behavior (*e.g.*, Avio et al. 2017; Juliano and Magrini 2017; Barboza et al. 2018; Lin et al. 2018b; da Costa et al. 2019; Mishra et al. 2019; Ng et al. 2019; Prata et al. 2019; Stock et al. 2019; Guo et al. 2020; Iroegbu et al. 2020; Wong et al. 2020). The first studies have been conducted in the marine environment, mainly about macroplastics, (*e.g.*, UNEP 2009; Hidalgo-Ruz et al. 2012), and started only some years ago in freshwater environments (*e.g.*, Li et al. 2018b; Wagner and Lambert 2018). Plastics have also been investigated in rivers (Lin et al. 2018b; Rodrigues et al. 2018b), lakes (*e.g.*, Eriksen et al. 2013; Turner et al. 2019), beaches (Turra et al. 2014) and in the deep sea (Kanhai et al. 2019).

The majority of plastic debris or microplastics (particles <5 mm) in the seas comes from the fragmentation of larger products (*e.g.*, fishing net, household practices, bottles). There is growing evidence that microplastics also enters the water compartment directly from other sources, including cosmetics (nanoplastics used as ingredients), clothing and industrial processes (Juliano and Magrini 2017). Microfibers present in aquatic systems may also be released from the textile industries and from wastewater treatment plants (baths and washing clothes). Plastic microbeads are indeed present as abrasive scrubbers in personal care and cosmetic products (hand cleansers, toothpastes, facial scrubs, shampoos, etc.). Several studies have demonstrated the negative impacts of plastics and plastic debris on wildlife and the evidence of seafood contamination by microplastics, and therefore their potential effects on human health (Avio et al. 2017; Juliano and Magrini 2017; Barboza et al. 2018; da Costa et al. 2019; Mishra et al. 2019; Prata et al. 2019; Stock et al. 2019; Guo et al. 2020). From a scientific point of view, there is an urgent need for knowledge on the sources, fate and environmental concentrations over time (Wong et al. 2020).

The review by Barboza et al. (2018) showed the negative effects of plastics and plastic debris on marine fauna, and thus a potential effect on human health, due to the evidence of contamination of marine species (*e.g.*, seafood) by microplastics, for example through the ingestion of microplastics as they are confounded with prey. However, data on the presence and occurrence of microplastics in marine species (and seafood in general) used for human consumption are scarce. This information is necessary for providing a basis for a sound risk assessment. Another important challenge is to understand the processes and mechanisms involved in the entry and assimilation of plastic debris into human tissues and their potential effects on human health. From a water engineering point of view, plastic-based debris are too small to be trapped in wastewater treatment plants. Therefore, they enter into water sources

through domestic drainage systems and are transported to seas and oceans. Wastewater treatment plants should adopt innovative ideas to deal with this contamination.

A third example of substances of recent concern are nanoparticles, which are organic or inorganic particles that are smaller than 100 nm, widely used in consumer products (cosmetics, sunscreens, electronics, food), pharmacy, medicine, and chemical industry (nano-plasticizers, coatings, textiles, catalysis). Other sectors are also concerned, such as automotive parts, building materials, sports equipment, and energy (Mearns et al. 2018; Zhao et al. 2018; de Marchi et al. 2019; Matich et al. 2019; Sousa and Teixeira 2020). Indeed, research and development in nanotechnology (including nanoscience, nanomaterials, and nanoparticles) is booming. However, the development of a regulatory framework and environmental impact assessment tools concerning the potential toxicity of nanoparticles for the environment and/or health has not yet been completed. Unfortunately, this lack of regulatory control means that the increasing environmental exposure to nanoparticles is occurring without awareness of the general public about the exposure and potential environmental toxicity of these emerging contaminants. In recent years, the term nanotoxicity has been coined. Likewise, the terms nanopollution and nanopollutants are also increasingly being used, but there is still very little research on the presence and behavior of nanoparticles and nanoproducts in aquatic compartments, as well as on their impact on wastewater and waste treatment systems, and on the production of drinking water. These are important areas for future research by local scientific institutions. Like other emerging substances, existing wastewater treatment and water purification technologies are not primarily designed to deal with nanopollution/nanocontamination (Sousa and Teixeira 2020). Nanoparticles have already been detected in wastewater, surface water, and treated drinking water, with concentrations ranging from ng/L to µg/L.

The scientific community is also increasingly concerned about the global contamination of water by other pollutants (Table 1.1), such as cosmetic ingredients (parabens, triclosan, bisphenol A) and UV filters (organic filters such as 2-ethylhexyl-methoxycinnamate, inorganic filters such as TiO₂ and ZnO), alkylphenols (detergents), rare earth elements (*e.g.*, used in the production of electronic devices, mobile phones, super-capacitors, or as contrast agents in medical imaging), radioactive elements or radionuclides (some such as radium-226, radium-228 and uranium are natural groundwater contaminants; and thus contamination of drinking water is a significant, emerging issue), anti-retroviral drugs (used for human immunodeficiency virus), psychiatric drugs (antiepileptics such as carbamazepine used for the treatment of epilepsy and bipolar disorder, antidepressants such as selective serotonin reuptake inhibitors, anxiolytics such as benzodiazepines), cardiovascular drugs (beta-blockers such as atenolol), hypocholesterolaemic drugs, and biological agents such as pathogenic bacteria and antibiotic-resistance genes (Table 1.1). These substances are problematic because most of them: (1) are currently not regulated in humans and the environment; (2) are not systematically monitored as part of environmental and public health programs; and (3) have their mechanism of environmental and human toxicity poorly understood. There is an urgent need for

scientific knowledge from a chemical, biological, toxicological and ecotoxicological point of view (Gwenzi et al. 2018; Pedrazzani et al. 2019; Xu et al. 2019; Zhang et al. 2019; Olaniyan et al. 2020).

Another recent area of concern, not only for the public but also for the scientific community, is indoor pollutants (Slezakova et al. 2012; Salthammer 2014, 2020; Cretescu et al. 2019). It is recognized that indoor air is highly polluted: 5–10 times more polluted than outdoor air. There are many sources of indoor air pollution (at home as well as in offices), such as combustion and tobacco products (gas appliances, tobacco smoke, candles), cooking processes, building materials and furnishings, cleaning and personal care products (perfumes), paints, central heating and cooling systems, humidity, and other sources (indoor and outdoor particulate matter, biological agents, etc.). Chemical (volatile organic compounds, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, polybrominated biphenyl ethers, particulate matter, radioelements such as radon, pesticides, etc.) and biological (pollens, bacteria, and mold) pollutants can accumulate to levels that can cause health, nuisance and comfort problems (Slezakova et al. 2012). The comprehensive review recently published by Salthammer (2020) can be consulted on emerging indoor pollutants.

1.2.4 Biological Agents

In recent years, cases of fatal emerging/re-emerging viral infections have significantly affected human health despite extraordinary advances in biomedical knowledge. The recurrent epidemics of dengue and chikungunya in tropical and subtropical regions, the Zika epidemic in the Americas and the Caribbean, and the global SARS epidemics and Covid-19 pandemics are dramatic examples.

Like chemical hazards, biological threats are part of our societies. Indeed, biological agents are ubiquitous in the environment and in our daily lives. Since they are invisible, it is difficult to assess the risks they present. According to the European Directive 2000/54/EC, the four main groups of biological agents are: bacteria, viruses, parasites, and fungi. In this Directive, biological agents are also defined as “the micro-organisms, including those which have been genetically modified, cell cultures and human endoparasites, which may be able to provoke any infection, allergy or toxicity” (European Directive 2000/54/EC). A microorganism is defined as a microbiological entity, cellular or non-cellular, which is capable of replication or of transferring genetic material. A cell culture is defined as the *in-vitro* growth of cells derived from multicellular organisms. Like any other organism, a biological agent simply tries to live and procreate (Parvez and Parveen 2017). Pathogenic microorganisms are present in the secretions, feces, urines of patients or asymptomatic carriers, subsequently retrieved in the wastewater, the wastewater treatment plants, and the receiving surface water. Hence, pathogenic biological agents can be considered as emerging pollutants.

Pathogens are organisms/microorganisms able to cause diseases. A minor part of organisms/microorganisms are pathogens. They include viruses, bacteria, fungi, and parasites, which can be found anywhere in the environment, including water, air, food, soil, and surfaces we are in contact with at home. Every pathogen needs a host to grow and survive. Once the pathogen has settled in a host, it must avoid the host immune responses, and thrive before being transmitted to a new host. Pathogens can be transmitted in several ways depending on their type: through skin contact, body fluids, airborne particles, water and food, contact with feces, and contact with a contaminated surface.

Viruses are responsible for a number of infections, many of which are contagious. Examples of viruses causing viral diseases include human immunodeficiency virus (HIV), dengue virus, rotavirus, and coronavirus. They are made up of a piece of genetic code (DNA or RNA) and protected by a coating or protein. Depending on the type of virus, they can cause a wide range of acute or chronic respiratory, gastrointestinal, or genital infections. However, viruses are unable to thrive and reproduce independently. Hence, viruses use the components of the host cell to replicate, damage or destroy the infected cells, before being released. There are efficient vaccines and antiviral treatments for some, but not for all, viral diseases.

Bacteria are microorganisms made of a single cell that can live almost everywhere on Earth. They are more complex organisms than viruses that can thrive independently of a host. Only a few bacterial species cause infections. Indeed, some species are beneficial (*e.g.*, those present in dairy products or in human gut), others are harmful (*e.g.*, those causing infections such as tuberculosis are called pathogenic bacteria). Examples of bacterial infections are gastroenteritis, meningitis, tuberculosis, and Lyme disease. Some bacterial diseases can be prevented by vaccination. Bacterial infections are treated by antibiotics.

Fungi can be found naturally in the environment, and also on the human skin. Some of them cause infections and the structure of their cell walls can make them resistant to antifungal agents. Some new species of fungi, such as *Candida auris*, are especially pathogenic. Parasites are organisms that behave like tiny animals, living in or on a host and feeding from or at the expense of the host. Three main types of parasites (*i.e.*, protozoa, helminths and ectoparasites) can cause diseases (*e.g.* malaria) in humans. They can be spread after an insect bite or contamination by soil, water, or air.

Antibiotic-resistant bacteria and antibiotic resistance genes have recently been identified as the greatest threats to public health by the World Health Organization. They are a potential hazard to public safety and water quality. The contamination of wastewater systems by antibiotic-resistance genes and the global spread of antibiotic-resistant superbugs is of great concern. Indeed, an area of great interest to the scientific community is the phenomenon of bacterial resistance (Zad et al. 2018; Zhao et al. 2018; Kumar et al. 2019; Liu et al. 2019; Ng et al. 2019; Reichert et al. 2019; García et al. 2020). Some bacterial clones have become resistant to most of the antibiotics, even to the last-resort compounds carbapenems or colistin, making the associated infections difficult to treat. This is due to the overuse of antibiotics by humans and animals. However, studies have also linked the use of antibiotic in

agriculture with infections in humans caused by antibiotic-resistant microbes. The great majority of pharmaceuticals consumed by humans and animals end up in feces and urine, which reach sewage treatment plants and/or soil. In addition, the gut of animals and human is the major reservoir of antibiotic-resistant bacteria. Since wastewater treatment plants are not designed to eliminate pharmaceuticals or antibiotic-resistant bacteria, treated effluents still contain pharmaceuticals (*e.g.*, antibiotics, hormones) and antibiotic-resistant microorganisms. In addition, the manure produced by animals receiving antibiotics that is commonly used as fertilizer, can become a source of antibiotics and antibiotic-resistance determinants for soils and crops. Besides, in areas affected by water scarcity, wastewater reuse is becoming a common practice in agriculture, potentially introducing these emerging pollutants into the food chain. In fact, there is still very little information on antibiotic resistant organisms in water sources, drinking water treatment plants and drinking water distribution systems, and the impact of their presence on human health. There is also an urgent need to improve understanding of the mechanisms associated with the spread and development of these organisms, not only in treatment plants and the environment (water, sediment, and soil), but also in the human body and in clinical and veterinary settings (see the two chapters devoted to these topics in this book).

1.3 Analysis and Detection of Emerging Contaminants

The proliferation of chemical substances, both known and unknown, that can have adverse effects on human health and the environment has increased the need for early detection for the safe identification of these contaminants. High-performance analytical tools and validated protocols now exist to identify and quantify contaminants in various environmental matrices. All water stakeholders concerned with water pollution issues, whether they are university researchers, government agencies, regulatory bodies or environmental interest groups, have tools at their disposal that allow them to collect and evaluate data from a variety of sources. These data are important for advancing knowledge about emerging substances and for preparing future regulatory or monitoring requirements.

1.3.1 Chromatographic Methods Coupled to Mass Spectrometry for the Analysis of Emerging Contaminants

The increase of the production, as well as consumption, of compounds designed to improve health, leads to their increased release into the environment. The governments try to regulate this impact into the environment with emission limits for different chemicals and the societies try to minimize, with the available technology, the amount of these pollutants that end up in aquatic ecosystems (IOM 2014). The

complexity of the chemical mixtures that are present in the environment demands that the scientific community works on increasingly sensitive methods for the analysis of these compounds, as shown in Table 1.1.

When planning to study contaminants in environmental matrices, it is necessary to develop an entire study design. Within this study design, the following points need to be considered: (1) sampling, (2) sample preparation, (3) chemical analysis, as well as (4) data visualization and analysis.

The collection of samples requires a previous study to make them representative. The previous study should depend on a great extension of the target chemicals or the expected concentrations, as well as on the information to be extracted from the results (García-Córcoles et al. 2019). For example, for a study involving pesticide analysis, the areas to be selected should be those where the major economic activity is agriculture, or in the case of a study of pharmaceuticals, it should be based on population density and age.

Sample Collection and Preparation For the study of contamination/pollution, water is usually the most often investigated environmental matrix due to its physicochemical characteristic and since it is relatively easy to analyse and is in nature an important reservoir of pollutants in Nature. These samples are usually collected from surface water, wastewater treatment plants, groundwater or even drinking water. There are two predominant methods of sample collection: grab samples or composite samples. When performing grab sampling, a certain volume of water is collected at a specific time and place. The sampled amount of water is usually relatively small. This type of sampling is usually performed only when contaminant concentrations can be expected to be high and hence easy to detect with analytical methods. The second method is more complex since the sampling is performed with a time window that can last from hours to days. It is often used to observe a wider range of contaminants or when relatively low concentrations are expected and are more difficult to detect with simple techniques. An example is the so-called large volume solid phase extraction in which the selected site is sampled for a certain time and the sample is filtered into solid phase extraction cartridges. The contaminants are accumulated and can subsequently be extracted in the laboratory (Schulze et al. 2017).

Not many methods perform direct analysis of samples. Most of the studies in water perform pre-concentration techniques using solid phase extraction (Carmona and Picó 2018; López de Alda et al. 2003; Dimpe and Nomngongo 2016) since they are considered relatively cheap, fast, reliable and reproducible methods (Tang et al. 2019).

Solid phase extraction is the most widely used extraction technique for environmental samples (Dimpe and Nomngongo 2016; Carmona and Picó 2018; Lorenzo et al. 2018; García-Córcoles et al. 2019) and is an effective tool for isolating and purifying compounds. The retention of emerging contaminants was improved thanks to the development of new polymeric sorbents, which are mainly made by hydrophilic-hydrophilic material (Wille et al. 2012). Nowadays, most of the studies with solid phase extraction techniques use Oasis® HLB cartridges (divinyl benzene

and vinylpyrrolidone copolymer) followed by StrataX[®] cartridges (polymeric reversed phase that provides a strong retention of neutral, acidic and basic compounds). Another widely used method for the extraction of emerging pollutants is the liquid-liquid extraction, although this can be time consuming (due to its complex automation), difficult and expensive, since a large volume of organic solvents is needed. Furthermore, this procedure requires a subsequent clean-up and a pre-concentration phase prior to the chromatographic analysis (Wang et al. 2013; García-Córcoles et al. 2019).

In the case of solid matrices, such as sediments, soils or biota, the Quick, Easy, Cheap, Effective, Rugged and Safe (known as QuEChERS) method developed by Anastassiades et al. (2003) is frequently used for the extraction of emerging contaminants (Calatayud-Vernich et al. 2016). This method was optimized for the extraction of pesticides from fruits and consists mainly of two phases: extraction and clean-up. The extraction phase uses salts, such as MgSO₄, to reduce the water content, and others such as NaCl, sodium acetate or citrate salts for all other applications. For the clean-up step, the use of primary/secondary amine stands out for the elimination of, among others, organic acids, fatty acids, sugars and atrazine pigments, or the sorbent C18 that eliminates fats, sterols and other non-polar interferences. Other methods have been optimized over the years for the extraction of a greater number of compounds, such as solid-liquid extraction. A method using solid-liquid extraction with a McIlvaine-EDTA buffer (pH = 5.5) accompanied by solid phase extraction was described by Carmona et al. (2017) as an improvement of the traditional QuEChERS. The method using McIlvaine-EDTA buffer reduces matrix effects to less than 20% and provides recoveries above 50%. In addition, more extracted compounds have been detected in studies with screening analysis. Other methods for the extraction of organic contaminants in solid matrices are based on the technique of pressurized liquid extraction which requires solvents at high temperatures and pressures that may transform some analytes into different transformation products.

Instrumental Analysis In recent years, the number of scientific publications that focused on the study of emerging contaminants in aquatic ecosystems has increased exponentially. Most of these publications base their analyses on a multitude of chromatographic techniques coupled with mass spectrometry as shown in recent reviews (Fig. 1.3) (Carmona and Picó 2018; Lorenzo et al. 2018; García-Córcoles et al. 2019; Tang et al. 2019; Álvarez-Ruiz and Picó 2020). Chromatography is a physical method of separation in which the components are separated and distributed between two phases, a stationary and a mobile phase. The Russian botanical Mikhail Tsvett thus conceived it in 1903 based on the ability of a column of finely powdered solid materials such as Al₂O₃, to adsorb substances from a solution that drips through it. Tsvett used this method to separate coloured components of plant pigments. The column developed its colour bands, and this technique was called chromatography separation. The Tsvett method remained unknown for a long time until switched back to biochemists in the 1930s.

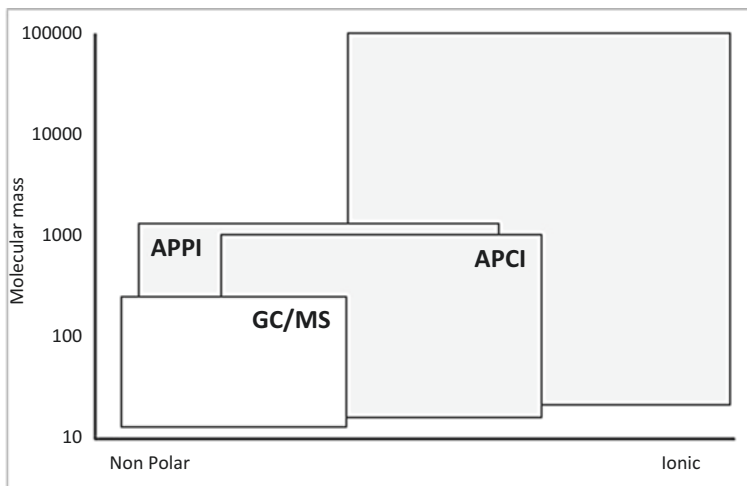


Fig. 1.3 Relationship between gas chromatography/mass spectrometry (GC/MS) and different interfaces of liquid chromatography/mass spectrometry (LC/MS) (*APPI* atmospheric pressure photoionization, *APCI* atmospheric pressure chemical ionization, source: Eric Carmona, Leipzig, Germany)

The first type of chromatography is known as adsorption chromatography. In 1942, Archer Martin and Richard Synge co-developed the partition chromatography by using a liquid absorbed on a solid as the stationary phase and the other immiscible liquid stationary phase as mobile phase. In this method, called liquid-liquid chromatography, the compounds are distributed into two liquid phases. This achievement inspired the development of other separation methods, namely gas chromatography. The effectiveness of liquid-liquid chromatography was increased in the 1970s by the use of small particles for support and by pumping fluid, in order to enhance the mobile phase through the stationary phase under pressure. This method is known as high Pressure liquid chromatography. With the various chromatography techniques, it is possible to separate and detect compounds quantities of components (parts per billion and even parts per trillion). Chromatography effectiveness is even higher when combined with other instruments such as with mass spectrometry for analysis.

One of the main reasons for the delay in the application of liquid chromatography-mass spectrometry was the difficulty involved with the coupling liquid chromatography and mass spectrometry. From the 70s several liquid chromatography-mass spectrometry interfaces have been developed, but it was only after commissioning of atmospheric pressure interfaces (electrospray ionization and atmospheric pressure chemical ionization) when liquid chromatography-mass spectrometry began to be a robust alternative to the methods of gas chromatography-mass spectrometry.

Advances in chromatographic techniques have led to increased detection of analysis of emerging contaminants (in the order of ng/L or µg/L). The most used techniques for the separation of these compounds are the gas chromatography and the

liquid chromatography. The selection of one of them depends on the physical-chemical properties of the compounds to be detected. Volatile and semi volatile compounds are analysed in the gas chromatograph, such as phenols or phtalates and non-volatile ones in the liquid chromatograph (Tousova et al. 2017; Lebedev et al. 2018). According to most of the literature reviews consulted, an average of 80% of the studies use liquid chromatograph versus gas chromatograph.

Both techniques require the use of columns for the compounds separation. In Liquid Chromatography, the most common mode is reverse phase separation which is characterized by a stationary phase that is less polar than the mobile phase (Rennie 2016). Columns that are characterized by this type of separation have stationary phases with long chains of aliphatic carbons attached to silica with pores of the micrometric order. The silica columns most used in liquid chromatography are those with 8 or 18 hydrocarbon chains (C8 and C18), being the C18 column the most used due to the robustness offered through the retention of both polar and non-polar analytes. In the case of gas chromatography, the most used columns are capillary ones between 30 and 60 m, due to their efficiency, high resolution and speed (Zhang et al. 2016b). These types of columns usually have a diameter between 0.1 μ m and 0.5 μ m. These columns can be classified into three different types: support coated open tubular, porous layer open tubular and wall coated open tubular column, being the last one the most used (Dettmer-Wilde and Engewald 2014; Baduel et al. 2015).

When designing a method for analysis and depending on both the equipment available and the compounds to be identified, a robust and stable mobile phase selection is important. The mobile phase is used to transport the analytes to the stationary phase. It can also play an important role in the separation of compounds in the case of liquid chromatography. The mobile phase in liquid chromatography analysis generally consists of two solvents. One is an aqueous type (A) and the other is an organic solvent (B) and generally includes an acid or salt to improve separation. The mixture ratio of both constituents usually changes over time of analysis to allow a better elution of the compounds in the column. The most common organic solvents used are methanol or acetonitrile. These are supplemented by a salt, in the case of the negative ionization mode for further mass spectrometry detection, such as ammonium acetate, ammonium formate or ammonium fluoride. The latter has been demonstrated to improve chromatographic signals, compared to other salts and also to improve the capacity and efficiency of electrospray (Carmona et al. 2014) for the study of some emerging pollutants such as pharmaceuticals, illicit drugs and personal care products. For the positive ionization mode, the most commonly used acids are acetic acid and formic acid (Carmona et al. 2017; Sadutto et al. 2020; Álvarez-Ruiz and Picó 2020). In gas chromatography the mobile phase is usually an inert gas such as helium or another non-reactive gas such as nitrogen. Helium is usually the most used gas (about 90%) (Li et al. 2019b) for the transport of analytes. Chromatographs have been evolving, including increasing their pressure or increasing their capacity for the use of more than two mobile phases at the same time. Chromatography is a technique that is usually coupled to tandem with mass spectrometry for environmental analysis.

Mass spectrometry is a universal and specific instrumental technique, highly sensitive, which enables the unequivocal identification of a substance. The principle of the mass spectrometry is the production of ions from neutral compounds and observing the subsequent decomposition of these ions in “product ions”. These ions decomposed (fragments also possess charge) move quickly and are classified according to their ratio m/z (ratio between mass and charge number of the ion). The mass spectrometer not only classifies the fragments, but also measures the amount that is formed. When a molecule is supplied with a given energy, the molecule is decomposed in a certain pattern, which fragments are always obtained at the same intensity ratio. This particular pattern is plotted in the mass spectrum, which, for this reason, is called the fingerprint of the substance. Thus, the mass spectrum allows the unequivocal identification of the molecules.

Mass spectrometers are generally sophisticated instruments, which comprise: (A) sample introduction system, that may be, in this case, a liquid chromatograph; (B) an ionization source, where the molecular fragmentation characteristic of each compound occurs; (C) a mass analyser or filter which separates the ion fragments generated according to their mass/charge ratio and (D) a detector, which collects and characterizes the fragment ions leaving the analyser. This instrumental technique is the most used for the determination and identification of emerging contaminants. This is a method with many different uses, ranging from forensics to health research, as well as for the study of the environment, since it is highly sensitive and reliable. There are different types of mass spectrometers depending on the objective of the study. Among them, for the study of emerging contaminants, the triple quadrupole (QqQ), the time of flight (TOF) and the orbitrap stand out. The most common mode for the study of emerging contaminants is electrospray ionization.

In studies on emerging pollution, the most widely used technique with mass spectrometry is the so-called target analysis or target screening, i.e., studies to identify and quantify a series of known compounds in complex matrices (Krauss et al. 2010; Ccanccapa-Cartagena et al. 2019). This technique requires a series of reference standards for the quantification and confirmation of the compound. The triple quadrupole consists of three quadrupoles connected in series. Quadrupole 1 (Q1) and the quadrupole 3 (Q3) operate as two quadrupole analysers connected in series. The quadrupole 2 (q2) or collision cell is placed in between Q1 and Q3. It is a special quadrupole in which energy is applied. The collision energy, that allows fragment ions, is obtained in the ionization source. This energy can take different values, which allows different fragments and/or different intensity relationships between them in mass spectra. This instrumental technique is highly sensitive and selective.

Another widely used technique is suspect screening. The suspect screening method implements an identification of expected compounds using databases (libraries) for their identification. This method, which has the so-called known unknowns approach, starts with a list of expected substances. Unlike the target analysis, it is not based on reference standards for confirmation and quantification, but on the specific information available for the compound, such as the molecular formula (which allows the calculation of the m/z of the expected ion). In contrast to this technique, *non-target screening* starts without any information about the

compounds to be detected. The number of chemically significant structures that can be assigned to a particular peak is limited to those structures that show a close relationship with the original compound (Krauss et al. 2010). The most common mass spectrometers for this type of analysis are the QToF (time-of-flight mass spectrometry) or the orbitrap (ion trap), the latter being the least used (Andrés-Costa et al. 2016). In the QToF, which is the most used for the realization of these techniques, after the ions have crossed the quadrupole, they reach an ion button in which a high voltage pulse is applied that accelerates the ions in the so-called flight tube. An ion mirror at the end of the tube reflects the ions which sends them to the detector and records their time of arrival. The time of flight for each mass is unique and is determined by the energy at which the ion is accelerated, the distance and the m/z .

For the analysis of the obtained data, although each device has its specific software, nowadays there are new open-source softwares, such as MZmine. This can identify the compounds as well as integrate them for their later quantification. This type of software can be used for target, suspect and non-target screening.

1.3.2 Detection of Microplastics in Water and Sediment

Plastics in environmental samples are usually size categorized in macroplastics (>25 mm; MSFD Technical Subgroup on Marine Litter, MSFD 2013), mesoplastics (5–25 mm) and microplastics (<5 mm). Microplastics may further be differentiated in size classes of 1–5 mm (large microplastics) and <1 mm (small microplastics; Galgani et al. 2013) or different size fractions (1–5 mm, 0.5–1 mm, 100–500 μ m, 50–100 μ m, 10–50 μ m, 5–10 μ m and 1–5 μ m; Braun et al. 2018). Furthermore, different forms of microplastics are distinguished (e.g. fragments, fibers, films, spheres). Figure 1.4 shows different microplastic forms from the Elbe River, Germany. Primary microplastics mostly consist of small-sized industrially manufactured pellets (microbeads) which are used in personal care products (Fendall and Sewell 2009) or for further processing (Thompson 2015). Secondary microplastics refer to a fragmentation of larger pieces of plastics during use or because of weathering in the environment (Barnes et al. 2009; Thompson 2015). It includes fragments of plastic litter in aquatic environments and on land (Ryan et al. 2009), films from agricultural use (Astner et al. 2019) or fibers from textiles (Carr et al. 2016). Although many researchers intensively studied microplastics in the water and sediment, the results are difficult to compare. A first suggestion for standardized sampling has been published by Frias et al. (2018) for sediments. ISO TC 61/SC 14 (ISO/CD 23187; ISO 2020) is currently also working on a standardization for microplastic preparation and analytics.

Studying environmental samples for microplastic analysis is complex as the polymers are not only influenced by their manifold characteristics (Hartmann et al. 2019), but may also be altered by the development of biofilms (Oberbeckmann et al. 2015), hetero-aggregates or sorbed pollutants (Guo and Wang 2019). For identifying microplastics in water and sediment, the samples most often have to be treated

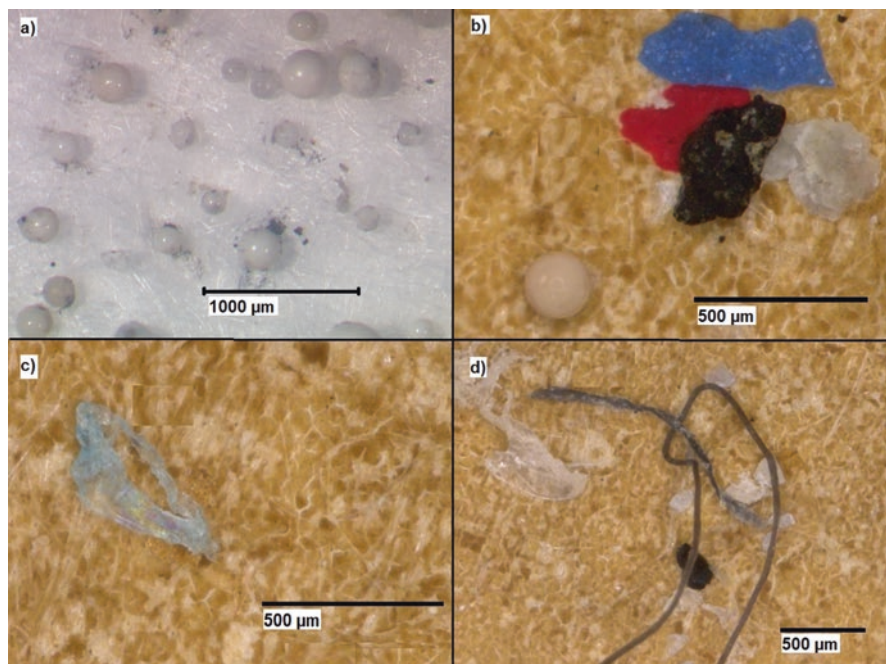


Fig. 1.4 Different microplastic forms from the Elber River, Germany: (a) white spheres; (b) blue, red, white and black fragments and one white sphere; (c) light blue film; and (d) brown and black fibers. (Source: Friederike Stock, Koblenz, Germany)

beforehand. Microplastics are relatively small and difficult to detect in environmental samples. Sediment and soil usually contain a high content of organic matter which hampers the identification by means of e.g. Raman spectroscopy or Fourier transform infrared (FTIR) spectroscopy. Therefore, the sample volume has to be reduced (for sediments *e.g.*, by means of sieving and a size fractionation; water and sediment samples: digestion of organics, density separation). The most common procedure for water and sediment samples is organic digestion with acids, bases, oxidizers or enzymes before measuring the samples (Stock et al. 2019). These solutions may however affect synthetic polymers, *e.g.*, degrade, discolorate or dissolve them (Cole et al. 2011). Therefore, samples only have to be treated when a high amount of suspended matter is present.

Before measuring the samples, most researchers separate minerals (*e.g.*, $>2.5 \text{ g/cm}^3$ for quartz, feldspar and calcite) from organics and polymers (<0.01 and $>1.4 \text{ g/cm}^3$, *e.g.*, foamed polystyrene and polyvinyl-chloride; Hidalgo-Ruz et al. 2012). Microplastics will generally float and minerals sink to the ground. Different density solutions are usually used: sodium chloride, zinc chloride, sodium iodide, sodium bromide, sodium polytungstate or potassium formate (Stock et al. 2019). Depending on the density of the solution ($>1.2 \text{ g/cm}^3$), only parts or all polymers are recovered from environmental samples. The same holds true as for organic digestion; density separation is only necessary when the sample contains a larger part of inorganic

material. Contamination of samples also has to be taken into account. During preparation and analysis, especially air-borne fibers may contaminate the samples (Dris et al. 2017). Therefore, a blank sample for checking the contamination during preparation and measuring is absolutely needed in order to detect external contamination.

For identifying polymers, different analytical methods have been developed. Depending on the specific research question, one of these methods is chosen rendering information about quantity, quality or mass. Visual identification of plastic particles allows a first preliminary evaluation, description, photograph and measurement of larger plastic particles (Löder and Gerdts 2015). Digital, visual or light microscopes are usually used to identify particles. Visual identification is based on polymer-specific characteristics such as color, form, absence of organic structures or equal thickness of fibers (Norén 2007). Hidalgo-Ruz et al. (2012) recommends a size of $>500\mu\text{m}$ or $>1\text{ mm}$ as smaller particles may be confounded with inorganic or organic material. However, as this method is subjective and only larger particles are taken into account, all particles have to be verified later by means of FTIR, Raman or pyrolysis.

The most common methods for identifying microplastics are FTIR spectroscopy, Raman spectroscopy and pyrolysis gas chromatography-mass spectrometry (GC-MS). Furthermore, research is conducted with thermal extraction and desorption-gas chromatography mass spectrometry (Dümichen et al. 2017), scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (Gniadek and Dąbrowska 2019) or quantitative nuclear magnetic resonance spectroscopy (Peez et al. 2019).

FTIR spectroscopy allows identifying single particles of a sample by absorbing IR radiation in reflection or transmission mode. Each infrared spectrum of a sample is compared to a reference spectrum and can thus be identified (Löder and Gerdts 2015). Selected particles $>500\mu\text{m}$ can be measured with an ATR-FTIR (attenuated total reflectance), smaller ones ($>10\mu\text{m}$) with a μFTIR which is very time-consuming. μFTIR measurements in transmission mode are feasible with transparent filters (e.g. aluminum oxide) and thin samples. If water is present, particles are black or too thick ($50\text{--}100\mu\text{m}$), the IR radiation is totally absorbed and thus no identification is possible. In order to measure an entire filter, a focal plane array may be coupled to the FTIR which identifies automatically all particles present.

Raman spectroscopy detects the molecular composition by investigating its vibrational and rotational frequencies with lasers and wavelengths from 500 nm to 1064 nm. The spectral fingerprint of a chemical structure allows the determination of the specific polymer. The basis of a Raman is the Raman shift which is the difference of Rayleigh photons and inelastically scattered photons (McNesby and Pesce-Rodriguez 2006; Kuhar et al. 2018). Such as the μFTIR , μRaman is used for measuring small particles ($>1\mu\text{m}$) and is also time-consuming when analyzing single particles. Raman and FTIR are complementary methods as the signals are stronger in Raman and weaker in IR. The advantage of Raman spectroscopy is that water does not influence the measurement and that a higher depth can be reached, i.e. more particles can be measured and identified. However, samples need to be

well prepared as organic/inorganic particles may lead to fluorescence influencing the spectra and Raman measurements are still time-consuming (Dris et al. 2015).

Pyrolysis gas chromatography mass spectrometry renders qualitative information about one single particle or quantitative information by calculating the mass of selected plastic polymers in environmental matrices. Moreover, plastic additives might be measured. Molecules are thermally degraded to determine their chemical composition by using a gas chromatograph for separation and a mass spectrometer for identification (Käppler et al. 2018; Dierkes et al. 2019). The measured pyrograms are compared to a library with the most common polymer types. The disadvantage of pyrolysis gas chromatography mass spectrometry is that particles can only be used once, as they are destroyed during the measurement.

In summary, microplastics are small plastic/polymer fragments in debris of various sizes that have accumulated in the global environment, particularly in all major marine habitats from the poles to the equator, from the sea surface and coastline to the depths. Techniques and methodologies for evaluating the detection of microplastics in aqueous environments are available. However, the detection and quantification of plastics in environmental matrices is currently an analytical challenge due to the laborious and varied analytical procedures currently used (Barboza et al. 2018). Indeed, the comparability of data on microplastics is currently hampered by a wide variety of different methodologies, resulting in the production of data of widely differing quality and resolution. Recently, da Costa et al. (2019) and Prata et al. (2019) also highlighted the difficulty comparison of data obtained in different studies due to the lack of standardized sampling protocols, methodologies and techniques for their identification and quantification, because of the many different characteristics of polymers. A critical evaluation of the methodologies used for the detection and identification of microplastics is necessary. Environmental research on these materials is also not consensual and definitions are unclear (Barboza et al. 2018). The classification of plastics is not a trivial issue. Recently, the term nanoplastics (<100 nm) has been introduced but there is no universally agreed definition. In addition, there are no established standard methods yet to accurately establish their ecotoxicological effects. This aspect is also of interest to the scientific community.

1.4 Emerging Contaminants in the Environment

1.4.1 Occurrence, Fate and Toxicity of Alkylphenols in the Aquatic Environment

Alkylphenols are a group of chemicals used in the production of surfactants, resins, antioxidants, pesticides, construction materials and automobile supplies (Ying et al. 2002; Lamprea et al. 2018). Nonylphenol ethoxylates and octylphenol ethoxylates are the most common non-ionic surfactants. When nonylphenol ethoxylates and octylphenol ethoxylates are released to wastewater treatment plants and

environmental matrices, they are subjected to incomplete biodegradation, leading to the formation of nonylphenol and octylphenol (Fairbairn et al. 2016; Xu et al. 2016). Nonylphenol and octylphenol can also be leached from concrete, elastomeric bitumen, and tires in runoff (Lamprea et al. 2018). Short-chain alkylphenols, such as 4-*tert*-butylphenol and 4-*tert*-pentylphenol, are often present in building materials such as paints, coating, and adhesives (Janousek et al. 2020). Some alkylphenols, e.g., 6-di-*tert*-butyl-4-methylphenol, are also used as antioxidants in food and cosmetics (Lu et al. 2019). Produced water discharges from offshore oil and gas production can be an important source for some alkylphenols (C1-C3) in the marine environment (Lofthus et al. 2016). Alkylphenols are known as environmental endocrine disruptors, and their levels in some areas may exceed water quality criteria (Zhang et al. 2017). Alkylphenols are therefore recognized as emerging contaminants of concern and, in the European Water Framework Directive (2013/39/EU), nonylphenols (in particular 4-*para*-nonylphenol) and octylphenols (4-*tert*-octylphenol) are classified as priority substances.

Occurrence Nonylphenol and octylphenol are frequently detected in the aquatic environment worldwide due to their widespread use (Table 1.2). It should be noted that nonylphenol or technical nonylphenol is a mixture of alkylphenols with different carbon chain lengths, branching, and substitution positions. Technical nonylphenol consists mostly of 4-nonylphenol, which is theoretically composed of 211 isomers, and 4-*n*-nonylphenol is the linear isomer. Similarly, 4-*tert*-octylphenol is one of the isomers of octylphenol. Most of the recent reports on nonylphenol and octylphenol are from China (Table 1.2). The highest levels have been reported from Guangzhou, the largest city in Pearl River Delta, where maximum concentrations of nonylphenol in river water and sediment were 5050 ng/L and 14,400 ng/g, respectively (Xu et al. 2018). Levels of nonylphenol and octylphenol in other Asian countries are also high, with nonylphenol as high as 1100 ng/L in seawater in Tokyo Bay, Japan (Song et al. 2020). Levels of nonylphenol and octylphenol in European countries are much lower, with the highest concentration reported in pond sediments in Greece being 323 ng/g for nonylphenol (Bokony et al. 2018). Limited data are available for countries in Africa and North and South America (Table 1.2). The presence of other alkylphenols has hardly been reported. Liu et al. (2016) reported levels of 4-*tert*-butylphenol, 2,4-di-*tert*-pentylphenol, 4-*n*-heptylphenol, 4-butylphenol, and 4-*n*-hexylphenol in surface waters, suspended particulates, and sediment in Lake Taihu and its tributaries in China, and their concentrations were lower than those of nonylphenol and octylphenol. Saeed et al. (2017) reported C4-C9 alkylphenols in coastal waters and sediments in Kuwait, with concentrations of ng/L and subng/L in water and ng/g and subng/g in sediments, respectively.

Environmental Fate Adsorption of alkylphenol to solid particles (sediment and suspended solids) and organic matter is a critical process that dominates their fate, transport, bioavailability and toxicity in the aquatic environment. Hu et al. (2019) reported that log K_{OC} values of nonylphenol and octylphenol calculated under field conditions were 4.63–4.78 and 4.74–4.84, respectively, indicating their high affinity

Table 1.2 Occurrence of nonylphenol and octylphenol in aquatic environment (concentration in water in ng/L; concentration in sediment in ng/g dry weight; detection frequency in %)

Region, Country	Matrix	Compound	Concentration range (mean)	Sample number	Detection frequency	References
Yinma River Basin, China	River water	4-Nonylphenol	14.13–392.41 (71.77)	51	100%	Sun et al. (2019)
Yinma River Basin, China	River sediment	4-Nonylphenol	1.33–98.44 (30.68)	51	100%	Sun et al. (2019)
Bahe River, China	River water	4- <i>tert</i> -Octylphenol	<1.2–126.0 (47.43)	10	100%	Wang et al. (2018b)
Bahe River, China	River water	Nonylphenol	108.1–634.8 (252.57)	10	100%	Wang et al. (2018b)
Three Gorges Reservoir Region, China	River water	Nonylphenol	<1.7–33.3 (10.8)	14	71.4%	Wang et al. (2016c)
Three Gorges Reservoir Region, China	River water	Octylphenol	<0.3–120 (32.3)	14	71.4%	Wang et al. (2016c)
Three Gorges Reservoir Region, China	River sediment	Nonylphenol	<1.5–8.5 (5.0)	14	85.7%	Wang et al. (2016c)
Three Gorges Reservoir Region, China	River sediment	Octylphenol	<0.5–12.4 (5.30)	14	92.9%	Wang et al. (2016c)
Xiangjiang River, China	River water	4- <i>tert</i> -Octylphenol	<0.27–156.1 (16.28)	160	72.2%	Luo et al. (2019)
Xiangjiang River, China	River water	4-Octylphenol	<0.67–40.8 (7.3)	160	69.5%	Luo et al. (2019)
Xiangjiang River, China	River water	4-Nonylphenol	<0.79–12.9 (2.65)	160	74%	Luo et al. (2019)
Zunyi, Guizhou province, China	River water	Nonylphenol	174–3411 (1730)	6	100%	Yu et al. (2017)
Pearl River networks, China	River water	4-Nonylphenol	27.20–824.18 (219.33)	31	100%	Xie et al. (2020)

(continued)

Table 1.2 (continued)

Region, Country	Matrix	Compound	Concentration range (mean)	Sample number	Detection frequency	References
Pearl River networks, China	River water	Octylphenols	1.11–57.19 (13.64)	31	100%	Xie et al. (2020)
Pearl River networks, China	River sediment	4-Nonylphenol	128.59–3831.95 (1248.39)	19	100%	Xie et al. (2020)
Pearl River networks, China	River sediment	Octylphenol	4.59–79.71 (32.17)	19	100%	Xie et al. (2020)
Hong Kong, China	Sea water	Nonylphenol	76.5–1353.6 (342.3)	24	100%	Xu et al. (2018)
Hong Kong, China	Suspended particles	Nonylphenol	97.7–1492.5 (365.1)	24	100%	Xu et al. (2018)
Hong Kong, China	Marine sediment	Nonylphenol	114.6–2665 (579.0)	24	100%	Xu et al. (2018)
Guangzhou, China	River water	4-Nonylphenol	22.5–5050 (1300)	22	100%	Peng et al. (2017)
Guangzhou, China	River water	4- <i>tert</i> -Octylphenol	<0.42–165 (50.3)	22	92%	Peng et al. (2017)
Guangzhou, China	River sediment	4-Nonylphenol	10.9–14,400 (4100)	22	100%	Peng et al. (2017)
Guangzhou, China	River sediment	4- <i>tert</i> -Octylphenol	<0.3–261 (64.3)	22	79%	Peng et al. (2017)
Tainan Canal, China	Marine sediment	Nonylphenol	1.16–324 (20.34)	69	93.9%	Shiu et al. (2019)
Tainan Canal, China	Marine sediment	Octylphenol	0.36–55.81 (3.99)	10	22.5%	Shiu et al. (2019)
Kenting National Park, Taiwan	Sea water	Nonylphenol	0.04–26.5 (7.69)	10	100%	
Kenting National Park, Taiwan	Sea water	Octylphenol	<0.0024–113 (15.4)	125	20%	Kung et al. (2018)
The Yellow and Bohai seas, South Korea and China	Marine sediment	4- <i>tert</i> -Octylphenol	<0.10–2.33 (0.30)	125	56.8%	Yoon et al. (2020)

(continued)

Table 1.2 (continued)

Region, Country	Matrix	Compound	Concentration range (mean)	Sample number	Detection frequency	References
The Yellow and Bohai seas, South Korea and China	Marine sediment	Nonylphenol	<0.91–111.15 (4.55)	125	38.4%	Yoon et al. (2020)
Tokyo Bay and Nagasaki Bay, Japan	Sea water	4- <i>tert</i> -Octylphenol	4.2–290.0 (61.3)	6	100%	Song et al. (2020)
Tokyo Bay and Nagasaki Bay, Japan	Sea water	4-Nonylphenol	37–1100 (410)	42	100%	Song et al. (2020)
Nationwide, Vietnam	River water	4- <i>tert</i> -Octylphenol	<10–850	42	47.6%	Chau et al. (2018)
Sai Gon and Dong Nai river basin, Vietnam	River water	Octylphenol	<2.0–35 (12.26)	14	N/A	Minh et al. (2016)
Villages in Delta and Anambra state, Nigeria	Groundwater	NP	100–90,300 (34479.8)	5	100%	Onyekwere et al. (2019)
Vojvodina Province, Serbia	Surface water	4- <i>tert</i> -Octylphenol	6–15 (9)	18	72%	Skrbic et al. (2018)
Nationwide, Hungary	Pond sediment	Nonylphenol	70–323 (165)	12	100%	Bokony et al. (2018)
Strymonas River, Greece	Surface water	Nonylphenol	<10–119 (17)	18	78%	Tousova et al. (2017)
Strymonas River, Greece	Surface water	Octylphenol	<3–28	18	22%	Tousova et al. (2017)
Marina del Este beach, Spain	Marine sediment	Nonylphenol	146–340 (237)	9	100%	Martin et al. (2017)
Malopolska, Poland	River sediment	4- <i>tert</i> -Octylphenol	2.9–8.9 (3.87)	25	100%	Czech et al. (2016)
Po River delta, Italy	Lake sediment	Octylphenol	0.44–3.97 (1.73)	6	100%	Casatta et al. (2016)

(continued)

Table 1.2 (continued)

Region, Country	Matrix	Compound	Concentration range (mean)	Sample number	Detection frequency	References
Po River delta, Italy	Lake sediment	4-Octylphenol	0.13–1.43 (0.68)	6	100%	Casatta et al. (2016)
Po River delta, Italy	Lake sediment	Nonylphenol	19.44–202.27 (82.19)	6	100%	Casatta et al. (2016)
Po River delta, Italy	Lake sediment	4-Nonylphenol	<0.12–1.24 (0.62)	6	50%	Casatta et al. (2016)
Nationwide, Mexico	Recreational water	4-Nonylphenol	0.83–12.61 (3.61)	10	83%	Vargas-Berrones et al. (2020a)
Cuautla River, Mexico	Surface water	4-Nonylphenol	1.23–44.77 (7.53)	9	44%	Calderon-Moreno et al. (2019)
Cuautla River, Mexico	Surface water	4- <i>tert</i> -Octylphenol	0.30–28.10 (11.24)	9	100%	Calderon-Moreno et al. (2019)
São Paulo State, Brazil	Surface water	4- <i>n</i> -Nonylphenol	1–2018 (429)	205	2%	Montagner et al. (2019)
São Paulo State, Brazil	Surface water	4- <i>n</i> -Octylphenol	2–1029 (266)	205	2%	Montagner et al. (2019)
Santos Bay, Brazil	Marine sediment	4-Nonylphenol	<10–72.5 (32.2)	28	100%	Dos Santos et al. (2018)

for organic matter. Gong et al. (2016) found that in the Pearl River system in South China, log K_{OC} values for nonylphenol in suspended particulate matter and sediment were 5.05 ± 0.33 and 4.59 ± 0.26 , respectively. The corresponding values for octylphenol were 4.89 ± 0.41 and 4.32 ± 0.49 , respectively. Biodegradation is another major factor in the fate of alkylphenols in the aquatic environment. Fate modeling in the Yong River in China indicated that the contribution of adsorption was greater than that of biodegradation, while the opposite was true for 4-*t*-octylphenol (Cheng et al. 2018). The half-lives for nonylphenol in estuarine waters alone and estuarine waters with sediment would be 2.36 ± 1.76 and 1.31 ± 0.51 d (Yang et al. 2016). Another study showed that the half-lives of nonylphenol in the water/sediment system under several redox conditions, ranging from aerobic to sulfate reduction, ranged from 3.2 to 6.2 d (Koumaki et al. 2018). A variety of bacteria, fungi and microalgae have been found to degrade alkylphenols. The consortium of cyanobacteria *Arthrospira Maxima* and the green microalgae *Chlorella vulgaris* can remove

96% of 4-nonylphenol from water in 96 h (Zaytseva and Medvedeva 2019). Other microalgae can also remove nonylphenol to varying degrees (He et al. 2016). Fungi of the genera *Aspergillus* and *Penicillium* have been found to effectively degrade 4-*n*-nonylphenol within a few days (Zhang et al. 2016a; Yang et al. 2018). It should be noted that the biodegradation of nonylphenol is isomer-specific and affected greatly by the redox potential; for example, the half-lives of 19 nonylphenol isomers in oxic river sediments ranged from 0.9 to 13.2 d (Lu and Gan 2014a). Biodegradation pathways of 4-nonylphenol include *ipso*-hydroxylation in the *para* position, nitrification at the *ortho*-position, and oxidation of the alkyl-chain, in particular ω -oxidation and then β -oxidation of the nonyl chain when fungi are involved. However, the routes of action of 4-*n*-nonylphenol are different. One pathway is initiated by hydroxylation at the terminal β -carbon atom, followed by oxidation and decarboxylation. Another pathway is initiated by hydroxylation at the *ortho*-positions and followed by ring-opening reactions (Zhang et al. 2016a; Yang et al. 2018).

Toxicity The estrogenicity of nonylphenol and octylphenol has been known for decades and has been confirmed in fish (Ahmadpanah et al. 2019; Sayed et al. 2019), aquatic invertebrates (Hart et al. 2016; Guo et al. 2019) and plants (Cahyanurani et al. 2017; Cheng et al. 2019). Nonylphenol is hepatotoxic (Abd-Elkareem et al. 2018), hemotoxic (Ahmadpanah et al. 2019), histopathological (Shirdel and Kalbassi 2016), genotoxic (Sharma and Chadha 2017a, b; Sayed et al. 2018), immunotoxic (Sayed et al. 2019), and reproductive toxic (Watanabe et al. 2017; Saravanan et al. 2019) to fish. In an extended one-generation medaka test, when 3 generations of Japanese medaka (*Oryzias latipes*) were exposed to 1.27–89.4 $\mu\text{g/L}$ of 4-nonylphenol, the parental generation was not affected while the fecundity, fertile egg and the fertility of the first generation decreased. However, 4-nonylphenol did not affect the survival and hatching of the second generation (Watanabe et al. 2017). Vazquez et al. (2016) also reported that the reproductive capacity of *Cichlasoma dimerus* caused by 4-*t*-octylphenol could be recovered when transferred to octylphenol-free water. Exposure to nonylphenol may increase vitellogenin and vitellogenin receptor expression in the shrimp *Macrobrachium rosenbergii* (Guo et al. 2019), weaken the immune system of the Pacific oyster *Crassostrea gigas* (Hart et al. 2016), reduce the biomass of mussels (*Lampsilis siliquoidea* and *Villosa iris*) (Ivey et al. 2018), and disrupt lipid storage (Jordao et al. 2016), moulting, and reproduction of the water flea *Daphnia magna* (Kim et al. 2019). Nonylphenol and octylphenol can also induce oxidative responses in algae such as *Gracilaria lemaneiformis* (Zhong et al. 2017) and *Dictyosphaerium sp.* (Cheng et al. 2019) and the submersed macrophyte *Ceratophyllum demersum* (Cahyanurani et al. 2017). The Yeast Estrogen Screen Test, the Two Hybrid Yeast Test, the MVLN Cell Test and the E-Screen Test all showed that the estrogenicity of nonylphenol was isomer-specific (Lu and Gan 2014a). However, no studies were conducted in aquatic species. The co-existence of other pollutants may increase or decrease the toxicity of alkylphenols to aquatic species. The equitoxic mixture of copper and nonylphenol was antagonistic to the embryos and larvae of *Rhinella*

arenarum toad at LC50 (Aronzon et al. 2020). Carnevali et al. (2017) demonstrated that dietary intake of bisphenol A, octylphenol, and nonylphenol by juvenile sea bream was antagonistic to its lipid metabolism. However, Cd(II) enhanced growth inhibition and superoxide induction in the alga *Chlorella sorokiniana* (Wang et al. 2018a). All these results suggest that further research is needed on the co-toxicity of nonylphenol and other pollutants.

1.4.2 Environmental Impact of Rare Earth Elements

Rare earth elements (REEs) are a group of 17 elements (fifteen lanthanides as well as yttrium and scandium) that tend to occur in the same ore deposits in Nature and exhibit similar physical and chemical properties. One of the members of the lanthanide series, promethium (Pm) which has only radioactive isotopes is usually recovered from the leftovers of uranium fission. Rare earth elements occur at trace concentration levels in the upper continental crust with total content ranging from <1 to 65µg/g (Table 1.3). These are highly electropositive and normally exists predominantly in trivalent stage (M^{3+}), with the exception of cerium which exists in quadrivalent valent state (Ce^{4+}) and europium which exists in divalent state (Eu^{2+}) under oxidizing and reducing environments respectively (Balaram 1996). Their unique electronic, optical, magnetic, and catalytic properties give them the ability to donate and accept electrons, making them suitable for integral components of many hi-tech products such as mobile phones, computers, home entertainment, medical devices, military defense systems, autocatalytic converters, petroleum refining and for polishing of optical-quality glass, and emerging clean energies. Thus, their industrial applications can be divided mainly into catalysts, ceramics, metallurgy, polishing and other applications (Fig. 1.5). A number of reviews has been published in recent times on all aspects of rare earth elements including their applications, occurrence, exploration, and their chemical analysis (*e.g.*, Mubashir 2018; Balaram 2019). The extensive applications of these elements have led to their wide distribution in all environmental compartments, raising concerns over their potential effects on human health. Because of well-known toxic effects of elements such as As, Cd, Pb, Hg and U, most of the environmental toxicity studies so far have been confined to this set of elements only (*e.g.*, Sparks 2005; Reddy et al. 2012; Duggal et al. 2017). Even platinum group elements have received considerable attention in recent years for their impact on human health due to their extensive utilization in autocatalysts (Balaram 2020). But in recent times, technological innovations coupled to modern living conditions have been contributing to the enhancing intake of significant quantities of rare earth elements by humans. Several studies demonstrated that these elements have toxic effects on human health and therefore are considered as emerging pollutants (*e.g.*, Pagano et al. 2015; Rim 2016). These elements can accumulate in the different environmental compartments and also in the biota, by many different routes such as mining, mineral processing, e-waste, agriculture practices, medicines and rudimentary recycling and disposal practices.

Table 1.3 Rare earth element (REE) concentrations (in $\mu\text{g/g}$) in different environmental compartments in comparison to the average concentrations of the upper continental crust

Rare earth element	Soils of ex-mining area ^a	Plant species ^b – <i>Dicranopteris dichotoma</i>			Fertilizer enriched with REE ^c	Runoff water from traffic area ^d , Beijing, China (ng/mL)	Background concentrations in surface water ^e (ng/mL)	Background concentrations in ground water ^e (ng/mL)	Maximum permissible concentrations (ng/mL)	UCC ^f
		Leaves	Shoot	Root						
La	94.69	1568.00	59.39	1305.07	15,400	5.56	<0.08	<0.08	10.1	31
Ce	420.5	2290.33	738.63	1482.60	24,100	10.4	<0.13	0.956	22.1	63
Pr	33.79	149.77	48.53	566.70	11,800	1.40	<0.08	0.125	9.1	7.1
Nd	112.3	1499.00	112.23	687.40	1100	4.04	<0.39	<0.39	1.8	27
Sm	–	–	–	–	2000	0.97	<0.56	<0.56	8.2	4.7
Eu	59.84	29.32	12.53	161.55	200	0.25	<0.17	<0.17	–	1.0
Gd	42.26	75.08	47.49	157.63	1100	0.91	<0.33	0.198	7.1	4.0
Tb	42.26	85.37	45.85	98.40	25.8	0.12	<0.10	<0.10	–	0.7
Dy	18.66	47.78	17.11	166.30	91.6	0.57	<0.22	0.069	9.3	3.9
Ho	12.12	13.24	6.39	59.39	4.3	0.13	<0.09	<0.09	–	0.83
Er	43.5	13.24	6.56	34.58	26.9	0.011	<0.14	0.072	–	2.3
Tm	10.15	8.37	13.50	17.57	1.4	0.07	<0.07	0.175	–	0.30
Yb	38.23	18.49	15.45	151.56	5.3	0.43	<0.13	<0.13	–	1.96
Lu	9.33	7.48	6.18	16.10	0.5	0.10	<0.05	<0.05	–	0.31
Sc	39.89	33.16	33.40	177.83	–	–	<2.80	0.001	–	14.0
Y	79.2	219.07	57.70	111.65	–	3.12	<0.22	0.416	6.4	21

^aSoils of ex-mining area (representative) (Khan et al. 2017)

^bPlant species, *Dicranopteris dichotoma* (Khan et al. 2017)

^cFertilizer enriched with rare earth elements (Hu et al. 2006)

^dRunoff water from traffic area, Beijing, China (Shajib et al. 2020)

^eBackground concentrations in surface/ground water and maximum permissible concentrations (Sneller et al. 2000)

^fUCC – recommended average concentrations of rare earth elements in the upper continental crust (Rudnick and Gao 2003)

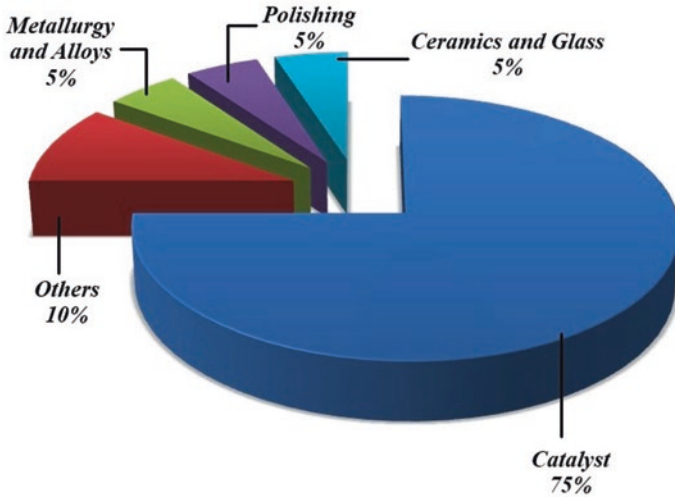


Fig. 1.5 The estimated current end use of rare earth elements. (Adapted from U.S. Geological Survey, USGS 2020, Reston, Virginia)

Impact of Rare Earth Elements Mining Though its more than a century since commercial mining of rare earth elements started, their global production and consumption have seen a significant increase during last half century, thus currently posing mounting environmental risk. Intense rare earth elements mining and production activities have led to significant environmental and health impacts already in countries such as China, US, India, Malaysia and Brazil. There are a number of potential environmental implications to mining of rare earth elements if not done properly. Mining activities such as cutting, drilling, blasting, transportation, stockpiling, and processing can release dust containing rare earth elements, other toxic metals and chemicals into air and surrounding water bodies that can impact local soil, vegetation, wildlife, and humans. Some of the rare earth element minerals contain significant amounts of radioactive elements such as uranium and thorium, which can contaminate air, soil, surface water and groundwater (Balaram 2019). According to Hurst (2010), approximately one ton of calcined rare earth ore generates 9600–12,000 cubic meters of waste gas containing dust concentrate, hydrofluoric acid, sulfur dioxide, and sulfuric acid, approximately 75 cubic meters of acidic wastewater, and about one ton of radioactive waste residue containing water. Most of that wastewater is normally discharged without being effectively treated, which can not only contaminate potable water for daily living of the neighboring communities, but also contaminates the surrounding water environment and irrigated farmlands. For example, an urban street dust of an industrial city, Zhuzhou in central China recorded very significant concentrations of rare earth elements (Σ REEs ranged from 66.1 to 237.4 μ g/g with an average of 115.9 μ g/g) which reveals the gravity of the rare earth elements pollution, particularly in industrial cities (Sun et al. 2017). More mining of rare earth elements, however, will mean more environmental degradation and human health hazards as waste disposal areas can be

exposed to weathering conditions and have the potential to pollute the air, soil and water if adequate monitoring and protection measures are not applied (Barakos et al. 2018). These problems are due to insufficient environmental regulations and controls in the mining and processing areas in different countries.

Rare Earth Elements in e-Waste Toxic metals are increasingly present in water systems around the World due to human activities, such as unregulated mining and more recently, the inadequate disposal of electronic waste. Dumping of huge amounts of e-waste that facilitate the release of significant quantities of rare earth elements along with several other toxic elements is leading to severe contamination of the subsoils and ground water (Haxel et al. 2002). Each year, the electronics industry generates up to 50 million tons of e-waste, but as the number of consumers rises, and the lifespan of devices shrinks in response to demand for the updated equipment, this figure could cross 50 million tons in the coming years. Rare earth elements are known to be more mobile in solutions rich in F^- , Cl^- , HCO_3^- , CO_3^{2-} , HPO_4^{2-} , PO_4^{3-} ions (Xiong and Yusheng 1991). In addition, large quantities of rare earth elements are also getting into the agricultural soils through the phosphate-based fertilizers (Table 1.3). Under natural conditions, rare earth elements may become available only in small amounts via the groundwater and the atmosphere; however, their increased use and enhanced amounts have created several new routes for bioaccumulation (in plants, animals, and human beings). Background level of rare earth elements content in waters, both surface and subsoil, varies significantly and depends mostly on the local geology.

Recycling of Rare Earth Elements Recycling and recovering activities of the valuable rare earth elements found in advanced electronic gadgets such as mobile phones, smart television sets, magnets, computers, batteries and catalysts, have been a challenge for both manufacturers and environmental groups. Several research groups are involved in the developments of technologies that could recover these materials for reuse (Hasegawa et al. 2018; Jowitt et al. 2018). The intensity of this activity is driven by the demand for these elements and its future potential and sustainability requires a significant amount of research on these aspects. One of the biggest electronic companies, Apple has already started expanding the company's global recycling programs (Balaram 2019). Increasing the amount of rare earth elements recycling may contribute to overcoming some of the criticality issues related to the supply of these elements. However, recycling activities such as the treatment of raw materials, beneficiation, separation of rare earth elements as oxides and their purification can also contribute to the release of substantial amounts of these metals into the environment.

Adverse Effects of the Use of Rare Earth Elements in Agriculture Rare earth elements containing micro fertilizers are extensively utilized in agriculture because of the striking positive effects in terms of crop yield and quality (Hu et al. 2006), therefore leading to further increase in the concentrations of these elements in soils (Guo et al. 1988; Diatloff et al. 1995). Although several findings reported positive

effects of rare earth elements on plant growth, many questions about their biological role remain unclear. Their concentrations in vegetables produced from mining area are higher and can have health implications especially in children (Zhuang et al. 2017). In general, the mineral fertilizers (*i.e.*, phosphate fertilizers) and soil conditioners contain macronutrients (Ca, Mg, N, P, and S), micronutrients (such as Fe and Si) and rare earth elements. In soils, the rare earth elements can also originate from local geological parent materials (Liu 1988). Although the accumulated concentrations of rare earth elements have been reported to be very low, the accumulation capacity of a particular plant depends upon several factors such as plant species, their growing conditions and the rare earth elements content in the substrate soil or rock (Fu et al. 2001). Table 1.3 presents the concentrations of rare earth element in different parts of plants such as roots, stem and leaves of a particular plant species, which can give an idea on how these elements can reach biota. Following excessive application of rare earth elements in agriculture, there is a raising environmental concern that these elements may enter the food chain in greater quantities though plant uptake, which might be deleterious to human health. For instance, the studies conducted by Redling (2006) confirmed very low concentrations of rare earth elements in cereal grains and no significant accumulation due to rare earth elements fertilization. Thus, grains and products made of them such as wheat flour are considered to be safe. Thomas et al. (2014) have indicated that countries like Russia and Nigeria where the natural abundance levels of rare earth elements are high in their soils will have more environmental threats arising from the increased input of these elements. However, close monitoring may be needed in countries where phosphate-based fertilizers (mined from monazite deposits) are applied in large scale.

Rare Earth Elements in Medicine Their unique properties, such as radiation emission and magnetism, allow these elements to be used in many health and medical applications, such as in anti-tumor agent, kidney dialysis medicine and surgical equipment (Giese 2018). Though, there are currently a few major applications of rare earth elements in medicine and many others are on the horizon (Lu et al. 2017). Lanthanide compounds with outstanding stability (photo- and redox-stability) and luminescent properties have found wider applications in cancer therapy and imaging (Teo et al. 2016). For example, Gadolinium has been used in a chelated form as a contrast agent in magnetic resonance imaging measurements (Raju et al. 2010). Even the pharmaceutical samples analyzed for inorganic impurities are found to contain appreciable amounts of rare earth elements when analyzed by inductively coupled plasma mass spectrometry (ICP-MS) (Balaram 2016). The implications of the presence of this range of rare earth elements concentrations in pharmaceuticals, are not clear at present. On one hand, rare earth elements have been found to disease-causing and occupational poisoning of local residents in mining areas, water pollution, and farmland destruction, etc. A body of evidence; has shown that rare earth elements are associated with antioxidant properties that are used in the treatment of many diseases (Rim 2016). Several studies (Zhang et al. 2000; Wakabayashi et al. 2016) confirmed the antibacterial and antifungal activities of rare earth elements

that are comparable to those of copper ions, and thus these elements are starting to be used for several pharmaceutical applications. Rare earth elements can also be used as nematocide as they can also inhibit the formation and germination of fungal spores and thus influence large number of organisms (Zhang et al. 2000). Recently, the medical and biological properties of rare earth elements have been reviewed by Panichev (2015). New medical applications for these elements are being found at an increasing rate and emerging advancements such as nanotechnology might be used to enhance their use in medicine in the future.

Health Effects to Humans Extensive mining activities and dumping of huge amounts of e-waste are facilitating release of significant quantities rare earth elements along with several other toxic elements and radionuclides into the subsoils and ground water. In addition, the largescale application of rare earth elements in various modern technologies is continually growing despite the knowledge about the environmental concerns of these elements. In addition, there is also a widespread use of these elements in agriculture and medicine sectors (Xiong and Yusheng 1991). As a result, large quantities of rare earth elements are also getting migrated into the agricultural soils, groundwater and thereby food products. Unfortunately, there is no sufficient data available about the toxicity of rare earth elements to human health and thus, their maximum acceptable limits in drinking water were not provided yet by any international health organization. Sneller et al. (2000) have reported maximum permissible concentrations for different rare earth elements in drinking water and the validity of these values is not known (Table 1.3). Currently, there are substantial gaps in our understanding of the adverse effects of rare earth elements to human health, their anthropogenic levels and fate, their biogeochemical or anthropogenic cycling, and their individual and additive toxicological effects. Most of the harmful effects resulting from human exposure to rare earth elements exposure are reported in occupational studies of mine workers and others who regularly deal with rare earth elements or their products, where exposure is typically much higher than that which the general population would experience. There are also several reports of occupational exposure to rare earth elements that resulted in bioaccumulation and adverse effects to human health (McDonald et al. 2015; Yoon et al. 2005; Giovanni 2016; Rim 2016). More studies are required to identify various anthropogenic sources, transfer mechanisms, bioaccumulation and their environmental behavior to minimize human health risks in future.

Despite substantial increase in the number of studies, many questions about the environmental and biological effects of rare earth elements remain unanswered. As the use of rare earth elements in industrial, agricultural and health applications is expected to increase to a great extent in the future, risk assessment studies on the daily intake of rare earth elements through dust, air, water and food, and on the subsequent long-term health effects on humans including pregnant women, children, and other vulnerable populations, have to be speeded up. In order to fill in the current gaps in our understanding of the roles of different rare earth elements, multifaceted studies focusing on different organisms and exposure routes are needed. As the mining, processing and recycling of rare earth elements will be imperative in the

future in order to meet the demand for these elements, it is necessary to formulate verified guidelines and monitoring systems to guarantee the welfare of workers, but also to protect the environment in general.

1.4.3 Engineered Nanoparticles in Drinking Waters Sources

In the last decade, nanotechnology has brought a large number of nanoparticles, engineered nanoparticles and nanomaterials to applications in multiple daily products and for many industrial products, due to their specific physicochemical properties (Mueller and Nowack 2008; Gottschalk and Nowack 2011). For example, titanium dioxide and zinc oxide nanoparticles can be found in sunscreens and cosmetics (Lu et al. 2015); titanium dioxide, silver, and silicon dioxide in paints and coatings (Hanus and Harris 2013); silver nanoparticles in textiles due to their antimicrobial properties (Hardin and Kim 2016); cerium oxide nanoparticles as fuel additives (Dale et al. 2017); C60-fullerenes in dermatological and skin care products (Mousavi et al. 2017); or carbon nanotubes as nanofertilizers (Iavicoli et al. 2017). This increase in use of engineered nanoparticles ends up in waste streams, and consequently in the environment and drinking water resources. The potential human risks from engineered nanoparticles in drinking water are still unknown and uncertain, due to the limited data on the occurrence and toxicity of nanoparticles in waters (Good et al. 2016; Bhattacharyya et al. 2017a, b). Potential impacts on the environment and human health have been reported (Born et al. 2006; Biskos and Schmidt-Ott 2012).

According to Gottschalk and Nowack (2011), engineered nanoparticles may enter into the environment through production, incorporation of nanoparticles into products, the use of nanoparticles containing products, and through wastewater treatment plants, waste incineration, landfills, and recycling and disposal processes. In addition, during their life cycle, the characteristics of engineered nanoparticles can change (due to physical/chemical interactions such as agglomeration, dissolution), as well as aging/degradation of the nanoparticles or nanoparticles containing products (Gottschalk and Nowack 2011). Surface water, such as lakes, rivers and streams, may therefore receive engineered nanoparticles, which may represent a threat to human health if this water is used for human consumption. In developed countries, 80% of the water supply is from surface water, while smaller communities or private residences are supplied by groundwater (Westerhoff et al. 2018).

Occurrence in Surface Waters Surface waters have many sources of engineered nanoparticles, including natural, unintentional and intentional sources (Hochella et al. 2008; Park et al. 2017). Natural sources such as mineral weathering, sea spray, volcanoes and forest fires also include nanoparticles beyond other particle sizes (Hochella et al. 2008). Unintentional release usually includes non-point sources and release from products such as cosmetics (*e.g.*, sunscreens, Weir et al. 2012), wearing or washing textiles containing engineered nanoparticles (Gottschalk and Nowack 2011), paints (Mueller and Nowack 2008), urban runoff (Baalousha et al. 2016), or

combustion, wear and corrosion processes (Westerhoff et al. 2018). However, major incidental engineered nanoparticles releases into the environment occur via wastewater treatment for cosmetics, coatings, cleaning agents, and dietary supplements (Gottschalk et al. 2009). Intentional sources are usually related with the application of the engineered nanoparticles directly, for example, when used in drinking water or wastewater treatments (Brar et al. 2010), in remediation of contaminated sites because of their sorption capacities (Nowack and Bucheli 2007) or applied as agrochemicals and nanopesticides (Kah and Hofmann 2014; Iavicoli et al. 2017). Groundwater may also receive engineered nanoparticles through direct use, *e.g.*, nano zero-valent iron injected into groundwater contaminated with chlorinated solvents then directly pumped into the subsurface (Nowack and Bucheli 2007; Grieger et al. 2010). Carbon nanotubes are intentionally loaded in water and soil to detect, prevent or remove pollutants (Mauter and Elimelech 2008).

Once released into water, engineered nanoparticles can undergo various transformations, including degradation, agglomeration, dissolution and sedimentation, and their fate, mobility, and persistence in aquatic systems are largely dependent on these transformations and their stability (Nowack and Bucheli 2007). Thus, the significance of engineered nanoparticles to drinking water supplies depends upon their stability and mobility in water resources used for drinking water production, which is largely determined by engineered nanoparticles colloidal stability. Engineered nanoparticles have high surface energies, due to their high surface-to-volume ratios, so they tend to aggregate (Hu et al. 2010; Sousa and Teixeira 2013; Serrão Sousa et al. 2017). Furthermore, if repulsive electrostatic forces are dominant, an increase in ionic strength leads to reduced engineered nanoparticle stability and an increase in aggregation (Chen and Elimelech 2006; Li and Lenhart 2012; Sousa and Teixeira 2013). However, aggregation rate stops increasing with ionic strength because each collision leads to attachment and aggregation becomes diffusion-limited, at a particular electrolyte concentration known as the critical coagulation concentration (Troester et al. 2016). However, at Na^+ and Ca^{2+} concentrations typically found in surface waters, destabilization of engineered nanoparticles by Na^+ and Ca^{2+} is, respectively, too low or limited (Troester et al. 2016). The naturally occurring organic matter present in surface waters can interact with engineered nanoparticles and influence suspension stability. Organic matter surface coating of engineered nanoparticles influences the aggregation rate of particles by electrostatic stabilisation mechanisms and electrosteric repulsion (Chen and Elimelech 2007; Baalousha et al. 2008; Klaine et al. 2008; Sousa and Teixeira 2013). The extent of the stabilization is dependent of organic matter type and concentration (Chen and Elimelech 2007; Sousa and Teixeira 2013; Zhang et al. 2013). Baalousha (2009) referred that an increase of nanoparticle concentration enhances their aggregation, particularly at pH values close to the engineering nanoparticle isoelectric points. In addition, at pH equal to the engineering nanoparticle isoelectric point, particles have little or no charge, leading to a substantial weakening in the repulsive forces between nanoparticles and aggregation occurs (Baalousha 2009). For surface waters pHs, between 6.5 and 8.5, only limited electrostatic stabilization can be expected for bare cerium

oxide and bare iron oxide nanoparticles, since their isoelectric points are reported within this range (Illés and Tombác 2006; Baalousha et al. 2008; Zhang et al. 2008).

In a very simplified way, Hammes et al. (2013) evaluated the effects of the physicochemical properties of the water on the ultimate fate of nanoparticles and contaminant-colloid assemblies across Europe. These authors showed more stable conditions for contaminant-colloid assemblies in northern Europe, the alpine region and Austria, Scotland, Northern Ireland and on the north-western Iberian Peninsula. In addition, as sedimentation rates were expected to be low in these areas, they concluded that aquatic organisms may be exposed to higher to small sized nanoparticle compared to waters in Italy, southern Portugal and Spain, France, Germany, east England and eastern Europe where conditions to nanoparticle aggregate prevail.

Predicted and Measured Engineered Nanoparticles Concentrations in Surface Waters Data available on the occurrence and quantities of engineered nanoparticles in surface waters are scarce. The uncertainties about the input and production quantities, the multiple pathways for engineered nanoparticles entering into the environment, but mostly the absence of widespread adequate detection techniques for identifying low concentrations of engineered nanoparticles in natural waters contribute to these limited data (von der Kammer et al. 2012; Westerhoff et al. 2018). Rather models have been developed to predict engineered nanoparticles concentrations.

Gottschalk et al. (2013) reviewed published data on the distribution of engineered nanoparticles in surface waters, both modelled and experimental data. Troester et al. (2016) made an actualisation of that review. According to Gottschalk et al. (2013), modelled nano-titanium dioxide concentrations in rivers ranged from 0.003 to 1.6 µg/L, at high temporal and geographical resolution, and this range included other modelled concentration ranges. Nano-silver presented high variations between the highest and lowest values, approximately a factor of 1×10^5 for the difference, which might reflect the differences between initial estimates of nano-silver production (Gottschalk et al. 2013). Modelled nano-zinc oxide varied between *ca.* 1×10^{-4} and 1×10^{-1} µg/L, but only two studies have reported concentrations in aqueous systems; carbon nanotube varied between 1×10^{-5} and 1×10^{-3} µg/L; fullerenes ranged from 1×10^{-5} to 1×10^{-4} µg/L; and cerium oxide nanoparticles were in the range 1×10^{-2} to 1×10^{-1} µg/L (Gottschalk et al. 2013). More recent modelling studies revised in by Troester et al. (2016), showed concentrations ranging for titanium dioxide nanoparticles between 0.40 and 1.4 µg/L; for silver nanoparticles between 0.51 ng/L and 0.94 ng/L; for zinc oxide nanoparticles between 0.05 ng/L and 0.29 µg/L; for C60 between 0.07 ng/L and 0.28 ng/L; and for carbon nanotubes between 0.17 ng/L and 0.35 ng/L for percentile 15 and 85%, respectively (Sun et al. 2014). In addition, some studies predicted engineered nanoparticles concentrations at different distances from emission source, showing a decrease in concentrations justified by hetero-aggregation and sedimentation of the engineered nanoparticles (Troester et al. 2016). Experimental studies revealed similar concentrations of nano-titanium dioxide from the ones predicted (Gottschalk et al. 2013; Troester et al. 2016). Table 1.4 presents an overview of recent published data on

Table 1.4 Overview of the measured engineered nanoparticle concentrations in surface waters (*SP-ICP-MS* single particle inductively coupled plasma mass spectrometry, *ICP-OES* inductively coupled plasma optical emission spectroscopy, *ET-AAS* electrothermal atomic absorption spectrometry)

Material	Location	Analytical technique	Results	References
Titanium dioxide	Clear Creek, Colorado collected hourly over a 72 h period	SP-ICP-MS	5 to 28 $\mu\text{gTi/L}$; metals naturally co-occurring with Ti (Al, Fe) also showed an increase during bathing periods, suggesting the Ti increase may be partially of sediment resuspension	Reed et al. (2017)
Silver	Dutch rivers	SP-ICP-MS56–60	Silver nanoparticles (average size 15 nm) at 0.3–2.5 ng/L	Peters et al. (2018)
Cerium oxide	Dutch rivers	SP-ICP-MS56–60	Cerium oxide nanoparticles (average size 19 nm) at 0.4–5.2 ng/L	Peters et al. (2018)
Titanium dioxide	Dutch rivers	SP-ICP-MS56–60	Titanium dioxide particles (300 nm) at 0.2–8.1 $\mu\text{g/L}$	Peters et al. (2018)
Titane total	North East Italy	SP-ICP-MS	3.7–11.2 $\mu\text{gTi/L}$	Piccoli et al. (2018)
Cerium total	North East Italy	SP-ICP-MS	0.2–0.4 $\mu\text{gCe/L}$	Piccoli et al. (2018)
Zinc total	North East Italy	SP-ICP-MS	0.12–7.9 $\mu\text{gZn/L}$	Piccoli et al. (2018)
Silver total	North East Italy	SP-ICP-MS	0.64–0.80 $\mu\text{gAg/L}$	Piccoli et al. (2018)
Silver	Melana River, Malaysia	ICP-OES	0.13 \pm 0.06 to 10.16 \pm 1.32 mg/L	Syafiuddin et al. (2018)
Silver	Sekudai River, Malaysia	ICP-OES	0.10 \pm 0.00 to 9.63 \pm 0.80 mg/L	Syafiuddin et al. (2018)
Titanium dioxide	Salt River, Arizona	SP-ICP-MS	Maximum concentration of 659 ng/L	Venkatesan et al. (2018)
Silver- <i>b</i> -nanoparticles (silver-based nanoparticles)	River Isar, southern Germany	ET-AAS after cloud point extraction	1–2 ng/L; load peak of 20.88 ng/L near the wastewater treatment plant Decrease in silver- <i>b</i> -NP concentration at 1.5 km downstream of discharge wastewater treatment plant points	Wimmer et al. (2019)
Ti	Lake Taihu, China	SP-ICP-MS	0.09 to 10.2 $\mu\text{g/L}$, in October 2016 0.11 to 4.16 $\mu\text{g/L}$, in April 2018	Wu et al. (2020a)

measured engineered nanoparticles in surface waters that are dependent on the nanoparticles type and ranges within with the earlier studies presented in the table. Some studies demonstrate a remarkable decrease in measured engineered nanoparticles concentration with the distance of the point source, namely wastewater treatment plants (Syafuddin et al. 2018; Wimmer et al. 2019).

The data currently available suggest that engineered nanoparticles may be present in certain surface waters, but not at high concentrations. However, the amount of analytical data available remains too small. There is a continuing need to detect and quantify these emerging contaminants in water. The low concentrations result from the removal mechanisms occurring in surface waters, particularly in waters with moderate or high ionic strengths, and organic matter high concentrations. Nevertheless, an expected increase of engineered nanoparticles production and use might increase the concentration of engineered nanoparticles in surface waters and the risk of water contamination. Furthermore, localized high-input sources may exist and engineered nanoparticle releases that may impact drinking water treatment plants intake should be carefully analysed and monitored.

1.5 Substances of Emerging Global Concern

1.5.1 Persistent Organic Pollutants in Lake and Ocean Ecosystems

The term “persistent organic pollutant” describes a wide range of organic compounds of anthropogenic origin present in the environment. This family of substances is subdivided into four main categories, namely polycyclic aromatic hydrocarbons (PAHs), chlorinated aromatic compounds, pesticides (organochlorine pesticides) and brominated flame retardants. The best known substances are, for example, 2,4-dichlorophenoxyacetic acid herbicide (well known as 2,4-D), hexachlorobenzene (another chlorinated fungicide used to treat seeds, especially wheat), polychlorinated biphenyls commonly known as PCBs used as lubricants in transformers, or PAHs from combustion or pyrolysis. The list of substances is particularly long due to the large number of congeners and isomers for the same class of substances. For example, polychlorinated biphenyls represent a group of 209 different chemical compounds (Puzyn and Mostrag-Szlichtyng 2012; Vestergren and Cousins 2013; DeWitt 2015; Eggen and Vogelsang 2015; Harmon 2015; Kallenborn et al. 2015; Zeng 2015; Xiao 2017; Dong et al. 2018; Lorenzo et al. 2018; Brusseau 2019; Ng et al. 2019; Klemes et al. 2019; Pan et al. 2020; Salthammer 2020).

Persistent organic pollutants represent a family of substances that is not strictly speaking “new” as it has been known for more than 50 years to date, but this group of pollutants is still of concern. Indeed, their presence in the aquatic environment is not a recent phenomenon, but this problem has become more widely evident over the last decade thanks to the constant improvement of analytical techniques and

more regular monitoring of aqueous compartments, including sediments, and organisms. Persistent organic pollutants in the Arctic atmosphere have been investigated since the 1970s when the first atmospheric measurements revealed their presence in this pristine polar environment (Kallenborn et al. 2015). Nevertheless, this family of substances is regularly updated, for example, the emerging perfluoro alkyl and polyfluoro alkyl substances have been classified as persistent organic pollutants (Puzyn and Mostrag-Szlichtyng 2012; Vestergren and Cousins 2013; Zeng 2015). Only limited information is available for these “newly” identified substances.

Persistent organic pollutants are transported from primary and secondary sources (industry, agriculture, urbanized areas, transport, etc.) through the atmosphere, and they can be transported over long distances to areas of the World through natural atmospheric and oceanic processes where there are no anthropogenic activities, *e.g.*, in Arctic soils (Gioia et al. 2011; Cabrerizo et al. 2018). Indeed, they are found all over the World, even in areas where these substances have never been used or produced (Puzyn and Mostrag-Szlichtyng 2012; Kallenborn et al. 2015).

The majority of persistent organic pollutants identified so far are banned or restricted worldwide due to concerns about their harmfulness to human health and ecosystems. They are indeed substances of global concern due to their toxicity, persistence, bioaccumulation and long-range transport (Puzyn and Mostrag-Szlichtyng 2012; Datta et al. 2018). Once released into the environment, persistent organic pollutants, that remain intact for exceptionally long periods of time (even some long-banned substances persist in the environment), are widely distributed in all environmental compartments (water, sediment, soil and atmosphere). They accumulate in the fatty tissue of living organisms (due to their low solubility and high lipophilicity, the molecules are subject to bioaccumulation in human and animal fatty tissues, and then biomagnify along food chains), being toxic to humans and wildlife (Mortimer 2013; Harmon 2015). Indeed, due to their special intrinsic physical and chemical properties, they are resistant to environmental degradation through physical, chemical and biological processes (Harmon 2015; Zeng 2015). Exposure to persistent organic pollutants can lead to serious health effects, including certain cancers, birth defects, immune and reproductive system dysfunction, increased susceptibility to disease and damage to the central and peripheral nervous systems. Some substances are also known as disrupting endocrine compounds.

In order to eliminate or reduce the release of persistent organic pollutants into the environment, several international treaties have been established, which call for efforts and actions by the international community, such as the Protocol to the UNECE Regional Convention on Long Range Transboundary Air Pollution (CLRTAP) and the Stockholm Convention on persistent organic pollutants. The Stockholm Convention (signed in 2001; Puzyn and Mostrag-Szlichtyng 2012), which has 184 countries/regions member signatories, listed 12 original persistent organic pollutants in 2004 and has updated it over the last decades. These instruments have established strict international regimes for lists of persistent organic pollutants, including 16 chemicals in the UNECE Protocol and 12 original chemicals (the “dirty dozen” including DDT, aldrin, endrin, heptachlor, polychlorinated

biphenyls, polychlorinated dibenzofurans and polychlorinated dibenzo dioxins) and 16 newly added chemicals in the Stockholm Convention.

Lake ecosystems, composed of the water body, sediments, organisms, surrounding soils and the atmosphere, are one of the major sinks for persistent organic pollutants and are also an important part of surface water systems. Persistent organic pollutants in lakes can accumulate in the fatty tissue of living organisms through the food chain and pose potential risks to humans (Puzyn and Mostrag-Szlichtyng 2012; Duedahl-Olesen 2013; Schrenk and Chopra 2013; Mortimer 2013). Legacy persistent organic pollutants, such as polycyclic aromatic hydrocarbons, organochlorine pesticides, polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins and dibenzofurans and polybrominated diphenyl ethers, have been commonly detected and reported in various lake ecosystems, while emerging persistent organic pollutants such as perfluorinated compounds, polychlorinated naphthalenes, tetrabromobisphenol A and hexabromocyclododecane have been relatively less detected or reported, but these chemicals are also of great concern. Figure 1.6 shows the average concentrations of various persistent organic pollutants in the Chinese Taihu lake ecosystem. Lake Taihu, located in the southern Jiangsu province and northern Zhejiang province, is the third largest freshwater lake in China and has provided local communities with valuable fisheries for centuries. There are 38 cities and more than 40 million people living around the lake, Taihu Basin being one of the most developed regions in China (Li et al. 2009; Wang et al. 2009).

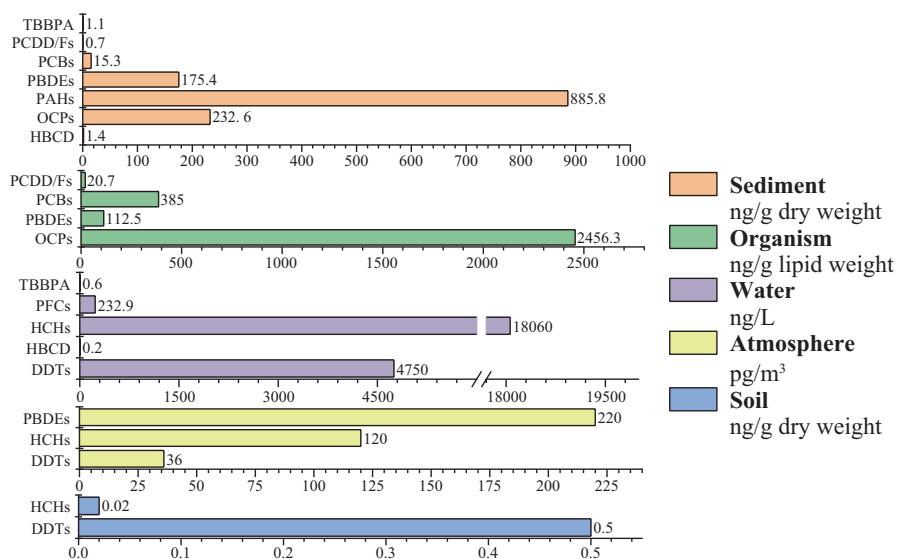


Fig. 1.6 Average concentrations of various persistent organic pollutants in the Chinese Taihu lake ecosystem (TBBPA tetrabromobisphenol A, PCDD/Fs polychlorinated dibenzo-p-dioxins and dibenzofurans, PCBs polychlorinated biphenyls, PBDEs polybrominated diphenyl ethers, PAHs polycyclic aromatic hydrocarbons, OCPs organochlorine pesticides, HBCD hexabromocyclododecane, DDT dichlorodiphenyltrichloroethane, DDTs DDT-related compounds)

Various carcinogenic persistent organic pollutants from the past are commonly detected in typical lake ecosystems in Europe and Asian. Organochlorine pesticides, polychlorinated biphenyls, and polycyclic aromatic hydrocarbons are the main persistent organic pollutants in water bodies (Javedankherad et al. 2013), sediments (de Mora et al. 2004; Boehm et al. 2005; Nemirovskaya and Brekhovskikh 2008; Varnosfaderany et al. 2015; Baniemam et al. 2017), organisms (Rajaei et al. 2011; Mashroofeh et al. 2015), and the surrounding soils and atmosphere (Aliyeva et al. 2012, 2013; Shahbazi et al. 2012) of the Caspian Sea located between Europe and Asia, the World's largest lake.

The levels of these persistent organic pollutants in the Caspian Sea ecosystems are at a scale of approximately ng/g, with polycyclic aromatic hydrocarbons having a relatively higher concentration. However, persistent organic pollutants newly added to the Stockholm Convention, such as polychlorinated naphthalenes, perfluorinated compounds, hexabromocyclododecane, etc., are rarely studied in the Caspian Sea at present. Persistent organic pollutants, including organochlorine pesticides, polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins and dibenzofurans, polycyclic aromatic hydrocarbons, polybrominated diphenyl ethers, polychlorinated naphthalenes, hexabromocyclododecane, perfluorinated compounds and tetrabromobisphenol A, are also present in different environmental compartments and biota in Chinese lake ecosystems (Qiu et al. 2004; Zhang and Jiang 2005; Qiao et al. 2006; Wang et al. 2007; Wen et al. 2008; Yang et al. 2011; Yu et al. 2012; Zhang et al. 2012; Zhou et al. 2012a, b; Xu et al. 2013, 2015; Wang et al. 2016a, b; Cui 2018; Liu et al. 2018; Wei et al. 2019; Xiang et al. 2019).

Recently, the presence of perfluorinated compounds in the environment has been of great concern. Levels of perfluorinated compounds in the water body of Chinese lakes have averaged between 30 and 50 ng/L and perfluorooctanoic acid and perfluorooctane sulfonate were the most frequent perfluorinated compounds (Yang et al. 2011; Gao et al. 2016). Mean concentrations of organochlorine pesticides, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, polybrominated diphenyl ethers, polychlorinated dibenzo-p-dioxins and dibenzofurans, perfluorinated compounds and hexabromocyclododecane in samples of biota from various Chinese lakes are usually at ng/g levels (Liu et al. 2018). In summary, European and Asian lake ecosystems are contaminated to varying degrees by various persistent organic pollutants. There are large differences in the levels of persistent organic pollutants between different lake ecosystems and other environmental media. Further studies on newly added persistent organic pollutants are needed in the future to better understand their environmental fate and ultimate control.

Persistent organic pollutants, old and new, are also widely distributed in the water bodies, sediments, organisms, surrounding soils and atmosphere of lake ecosystems typical of North America and Africa. Lake Superior is the largest freshwater lake in the World and also the largest of the Great Lakes in North America. Polychlorinated biphenyls and organochlorine pesticides occurring in the Lake Superior water body in the 1990s were at ng/g range and by 2018 they were at pg/g levels, which is lower than in lakes in Europe and Asia (Jeremiason et al. 1994; Ruge et al. 2018). Polychlorinated dibenzo-p-dioxins and dibenzofurans,

polybrominated diphenyl ethers and polychlorinated biphenyls were found in Lake Superior sediments at ng/g magnitude, which was comparable to that of European and Asian lakes (Pearson et al. 1998; Shen et al. 2009).

In addition to organochlorine pesticides and polychlorinated biphenyls, some emerging persistent organic pollutants such as polybrominated diphenyl ethers, hexabromocyclododecane, polychlorinated naphthalenes and perfluorinated compounds were also present in Lake Superior organisms (Kannan et al. 2000; Luross et al. 2002; Dykstra et al. 2005; Fernie and Letcher 2010; Furdui et al. 2015). Polycyclic aromatic hydrocarbons, polybrominated diphenyl ethers, organochlorine pesticides, polychlorinated naphthalenes and polychlorinated biphenyls were present in the surrounding atmosphere (Hillery et al. 1997; Strandberg et al. 2001; Fernandez et al. 2002; Helm et al. 2003). Lake Tanganyika is a freshwater lake located in Central Africa. Reports of persistent organic pollutants in Lake Tanganyika are mainly related to lake organisms. Organochlorine pesticides, polychlorinated biphenyls, polybrominated diphenyl ethers and hexabromocyclododecane were detected in fish samples from Lake Tanganyika (Mahugija et al. 2018; Polder et al. 2014). Among these reported persistent organic pollutants, the concentration of polychlorinated biphenyls in fish samples ranged from 36 to 167 ng/g, which is generally lower than in Asian lakes. In addition, the contamination of persistent organic pollutants in Lake Tanganyika was lower or comparable to that in other parts of Africa (Manirakiza et al. 2002).

Polybrominated diphenyl ethers have raised new concerns in recent decades. Some studies have focused on polybrominated diphenyl ether contamination in the North Pacific Ocean, where the World's largest fishery, that of Hokkaido, is being lacerated. It is the main source of seafood for people living in countries along the North Pacific coast, especially those living in Japan, South Korea and China. However, this coast is also the World's largest producer and consumer of polybrominated diphenyl ethers. The use and emissions of polybrominated diphenyl ethers in this region are significant, and pollution by polybrominated diphenyl ethers is becoming an increasingly serious problem. Xiang et al. (2019) showed that the current concentration of polybrominated diphenyl ethers in the atmosphere, water, sediments and organisms in the North Pacific Ocean is 0.14 to 896 $\mu\text{g}/\text{m}^3$, 3 to 4360 $\mu\text{g}/\text{L}$, 0.24 to 7397.7 ng/g dry weight and 0.56 to 3930 ng/g lipid weight, respectively. The predicted concentration of polybrominated diphenyl ethers in the Hokkaido fishery could be 4.6 to 9 $\mu\text{g}/\text{m}^3$ (air), 106 to 341 $\mu\text{g}/\text{L}$ (water), 3.4 to 248 ng/g dry weight (sediment) and 5 to 64.7 ng/g lipid weight (biota). The concentration of polybrominated diphenyl ethers in the atmosphere, water bodies, sediments and organisms in the North Pacific has a characteristic near-shore > ocean or low latitude > high latitude distribution (Xiang et al. 2019).

From a global perspective, lake ecosystems are contaminated to varying degrees by several persistent organic pollutants, both from past and recent contamination. Although many studies have been conducted on these substances in lake ecosystems, these studies have mainly focused on traditional persistent organic pollutants such as organochlorine pesticides, polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins and dibenzofurans, while emerging persistent organic pollutants

such as polychlorinated naphthalenes, perfluorinated compounds, hexabromocyclododecane, etc. are relatively less reported. The extent and significance of all these substances are still largely unknown. Environmental risk assessing of persistent organic pollutants remains particularly difficult, not only in lake ecosystems, but also in freshwater and marine ecosystems.

These ecosystems are fragile, living at the rate of anthropogenic disturbances (pollution, artificialization, withdrawals), increasingly vulnerable for example to climate change, but essential to life in general. Indeed, lake ecosystems are important freshwater resources closely linked to human life, but our understanding of pollution by persistent organic pollutants in lake ecosystems is not yet sufficient. A better understanding of these substances, in terms of their degradation, behavior, accumulation, transfer, toxicity and impact, still requires research in the different environmental compartments and living organisms of these systems. More comprehensive international health policies and standards are also needed in the future.

1.5.2 Monitoring of Emerging Contaminants in Portuguese Rivers

Portugal is on the top three of countries with more studies in the field of surface water even by normalizing the amount of reports by the number of inhabitants per country, according to a recent review on the environmental monitoring of water organic pollutants dedicated to the literature published between 2012 and 2018 (Sousa et al. 2018). That review paper provides an overview of the worldwide occurrence of contaminants identified by European Union guidelines, namely priority substances of European Directive 39/2013/EU and contaminants of emerging concern of Watch Lists of European Decisions 495/2015/EU and 840/2018/EU, and presenting also comprehensive data about other specific organic pollutants not considered in those European Union documents and with reported high concentrations and frequencies. Another review paper covering the period between 2001 and 2015 systematically overviewed the published data on the monitoring of industrial compounds, natural and synthetic estrogens, phytoestrogens and phytosterols, pharmaceuticals, and pesticides in the Portuguese aquatic environment (Ribeiro et al. 2016b). The data collected in that review show that some compounds were determined at high concentrations in the studies performed between 2001 and 2015, namely industrial and household compounds (*e.g.*, bisphenol A, alkylphenols and alkylphenol polyethoxylates) found from few ng/L to dozens of µg/L, in agreement with other European countries such as Spain, Switzerland, Netherlands, and France (Ribeiro et al. 2016b). In the case of natural and pharmaceutical estrogens, they were detected always at ng/L levels in Portuguese surface waters in the reviewed literature, similar or higher than those concentrations reported in European countries (Ribeiro et al. 2016b). While phytoestrogens are described as frequently studied and detected at µg/L range, the authors pointed out that most publications about pharmaceuticals in Portuguese surface waters published before 2016 referred only

few therapeutic classes in the north of Portugal and the majority of them consisted in the application of new analytical methods rather than consistent monitoring data (Ribeiro et al. 2016b). A wide range of classes of pesticides including priority substances of European Directive 39/2013/EU were compiled in that review from 2001 to 2015, some of them up to $\mu\text{g/L}$, including atrazine that was already banned in Europe (Ribeiro et al. 2016b). The present section aims to update the information about the occurrence and distribution of emerging contaminants in Portuguese rivers (Fig. 1.7) and results from a literature survey comprising reports published since 2015 in Scopus database, using as keywords: “river water”, “surface water” or “estuarine water” and “Portugal” or “Portuguese”, and “monitor” or “occurrence”.

In the last years, natural organic compounds have been studied in Portuguese rivers, namely phytoestrogens and phytosterols that are found in many plants and mycotoxins produced by fungi. One study monitoring these classes in the Douro River estuary reported the maximum concentration of daidzein (up to 277.4 ng/L) in the summer (Ribeiro et al. 2016a), whereas the highest value in another seasonal study performed by the same research group in the Ave River was determined in the spring (up to 404.0 ng/L) (Ribeiro et al. 2016c). In that river, a seasonal trend for phytoestrogens and phytosterols was verified and the largest level of coumestrol (up to 165.0 ng/L) was observed in the summer. Interestingly, this compound was not detected in any sample collected in the Douro monitoring campaign (Ribeiro et al. 2016a). Both reports showed that the mycotoxin deoxynivalenol was ubiquitously found up to 373.5 ng/L in the Douro (Ribeiro et al. 2016a) and between 59.5 to 642.4 ng/L in the Ave (Ribeiro et al. 2016c), whereas the micotoxin zearalenone and its metabolite α -zearalenol were only detected in spring and summer in the Douro (Ribeiro et al. 2016a). This last finding is in agreement with another monitoring study in seven Portuguese rivers and one creek, where the highest concentration of

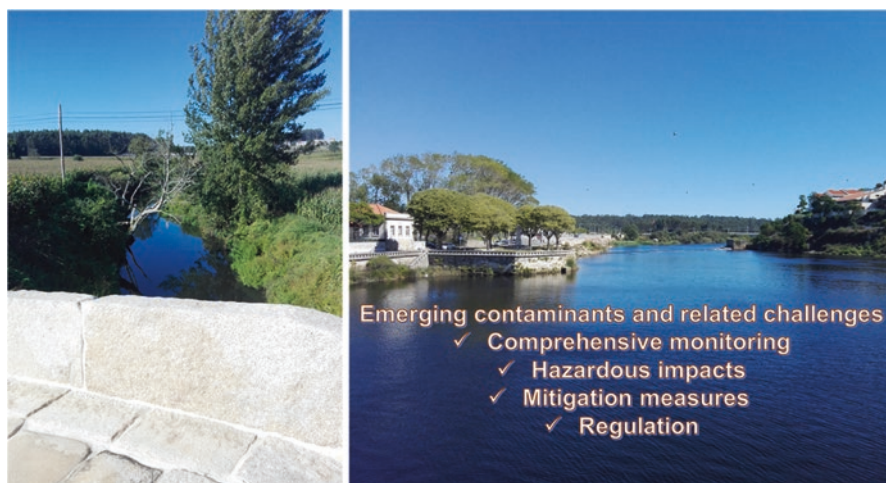


Fig. 1.7 River pollution by emerging contaminants and related challenges for their management. Ave River (left) and Leça River (right). (Source: Ana Rita Lado Ribeiro, Porto, Portugal)

zearalenone was reported during spring. In that survey, it was estimated a contamination frequency of 23.7% for this mycotoxin, with concentrations ranging between 5.6 and 82.6 ng/L (Laranjeiro et al. 2018). In general, the highest values found in the last years are quite lower than those reviewed in the previous period 2001–2015 by Ribeiro et al. (2016b). Industrial and household compounds have been also monitored in Portuguese rivers. In a monitoring program developed in Mira River over a 1-year period, including also natural and pharmaceutical estrogens, phytoestrogens and the phytosterol sitosterol, both estrogens and industrial/household pollutants were found at high concentrations in all sampling locations, including some positioned in environmental protected areas (Rocha et al. 2016). Specifically, the annual average of industrial/household pollutants was of ca. 1.3 µg/L, whereas values at ng/L levels were described for phytoestrogens and sitosterol (Rocha et al. 2016). Another recent study targeting endocrine disruptor compounds in Minho, Ave and Mondego River estuaries, reported quite high concentrations of alkylphenols and alkylphenol ethoxylates (up to 4855 ng/L) despite those of the natural estrogens were markedly lower than previous surveys (Rocha et al. 2016).

Regarding personal care products, one study performed in northern Portuguese rivers in the summer (2018) targeted 43 compounds and detected 28 substances (Celeiro et al. 2019): fragrances up to 200 ng/L (citronellol), limonene, α -isomethylionone, tonalide and galaxolide in all samples, the latter up to 379 ng/L; phthalates up to 92 ng/L (benzylbutylphthalate), including the priority substance diethylhexylphthalate determined at 88 ng/L in one sampling point; the priority substance antioxidant butylhydroxytoluene between 8 and 25 ng/L in half of the samples; and UV filters up to 254 ng/L (benzophenone 3).

In the last years, pharmaceuticals have been extensively monitored by some research groups. A wide group of 66 human and veterinary pharmaceuticals belonging to seven therapeutic groups was monitored in Tejo estuarine waters and the therapeutic families with an overall frequency of detection higher than 90% were antibiotics, β -blockers, antihypertensives, lipid regulator and anti-inflammatories (Reis-Santos et al. 2018). The highest concentrations of each class were 304 ng/L for antidepressants (sertraline), 51.8 ng/L for non-steroidal anti-inflammatories (diclofenac), 77.0 ng/L for lipid regulators (gemfibrozil), 161.9 ng/L for antihypertensives (ibersartan) and 128.0 ng/L for antibiotics (doxycycline) (Reis-Santos et al. 2018). Another one-year occurrence study published before targeting 23 pharmaceuticals in Tejo and Mondego Rivers (Pereira et al. 2017a), showed one site in Tejo River with comparable concentrations of diclofenac, gemfibrozil and bezafibrate. In that study, pharmaceuticals were found in 27.8% of the samples at ng/L levels, with the following therapeutic families having the highest detection frequencies and mean concentrations: selective serotonin reuptake inhibitors, anti-inflammatories and antibiotics (Pereira et al. 2017a). The authors confirmed the impact of wastewater treatment plants by an increase of the mean concentrations downstream and the impact of lower river flow rates on increasing detection frequencies and concentrations (Pereira et al. 2017a). In this sense, despite the risk quotients were higher than one only for two pharmaceuticals, the authors stressed the ecotoxicological pressure especially due to water scarcity in drought periods, which may raise the risk in

rivers located in the Iberia region (Pereira et al. 2017a). A study carried out in the Lisbon's drinking water supply system included the analysis of 31 pharmaceuticals in surface waters from Tejo and Zêzere Rivers, where 15 and 10 pharmaceuticals were detected at ng/L levels, respectively (de Jesus Gaffney et al. 2015). Caffeine, erythromycin, acetaminophen, sulfadiazine, sulfapyridine, sulfamethoxazole, carbamazepine and atenolol were quantified in both rivers; propranolol, sulfamethazine, gemfibrozil, indomethacin, ibuprofen, diclofenac, and naproxen were present in the Tejo River; and nimesulide was only quantified in the Zêzere River (de Jesus Gaffney et al. 2015). In that study, the risk assessment was performed for human health and it was suggested that the exposure to residual pharmaceuticals in drinking water would be particularly improbable. One environmental relevant therapeutic class is the cytostatics as the cancer incidence has raised worldwide and thus their consumption has evidently increased over the last years. From the seven cytostatics (cyclophosphamide, capecitabine, mycophenolic acid, imatinib, bicalutamide, prednisone and 5-fluorouracil) determined in river water samples in a very recent study encompassing also wastewaters, only mycophenolic acid was detected in Uíma, Douro and Leça Rivers, at average concentrations of 210, 211 and 541 ng/L, respectively (Santos et al. 2018). Twenty-seven pharmaceuticals including antibiotics and psychiatric drugs were also analysed in Douro and Leça Rivers (Fernandes et al. 2020). In that study, higher frequency and concentrations of pharmaceuticals were found in the Leça River, where six antibiotics (azithromycin, ciprofloxacin, clarithromycin, moxifloxacin, ofloxacin, and trimethoprim) were found, the highest concentration was registered for azithromycin (2819 ng/L), and fluoxetine was the most detected pharmaceutical (Fernandes et al. 2020). Interestingly, in the same report, none of the studied antibiotics was detected in river samples of Douro River (Fernandes et al. 2020).

Some occurrence studies have been developed in the last years, by simultaneously targeting pharmaceuticals and other classes of compounds, namely pesticides. One recent monitoring program performed recently in four rivers (Ave, Antuã, Cértima, and Leça) described the spatial and temporal variations of 39 priority substances and contaminants of emerging concern, some belonging to European Directive 39/2013/EU, European Decisions 840/2018/EU and 495/2015/EU (Barbosa et al. 2018). From the 13 pollutants detected in all the rivers, various pharmaceuticals were detected (up to 396 ng/L) and the priority pesticide isoproturon was found up to 92 ng/L (Barbosa et al. 2018). The industrial priority substance perfluorooctanesulfonic acid was detected below its quantification limit in the Antuã, Cértima, and Leça (Barbosa et al. 2018). Atrazine, a priority substance of European Union Directive 39/2013 already banned, was also detected in Ave, Antuã and Leça (up to 41 ng/L), whereas simazine was found in the Cértima and Leça (Barbosa et al. 2018), both pesticides being found at higher concentrations than those reported in the Arade River by Gonzalez-Rey et al. (2015). The neonicotinoids acetamiprid and imidacloprid of the European Decision 840/2018/EU were only detected during the dry season in the Ave (Barbosa et al. 2018).

In the same report, higher concentrations were observed downstream of industrial areas and urban wastewater treatment plants (Barbosa et al. 2018). In another

study published by the same group, all the contaminants of emerging concern pre-recognized in the Watch List in force at the time of that monitoring program (European Decision 495/2015/EU) were monitored during four seasons in two Portuguese rivers located in the northern region, Ave and Sousa (Sousa et al. 2019). In that study, 13 contaminants of emerging concern were found, being diclofenac, 2-ethylhexyl 4-methoxycinnamate, and azithromycin the most frequent compounds and diclofenac, 2-ethylhexyl 4-methoxycinnamate and imidacloprid those determined at the highest concentrations (Sousa et al. 2019). The same authors reported the first spatial distribution of 37 pollutants in the entire Portuguese coast, including the ocean shore and the nearest river discharging on it (Sousa et al. 2019). This monitoring program included some priority substances and contaminants of emerging concern of the European Watch List (European Decisions 495/2015/EU and 840/2018/EU; EU 2015, 2018). In general, the authors found high concentrations of diclofenac, tramadol and carbamazepine, the latter being ascribed as having medium to high risk for algae (Sousa et al. 2020). While some pharmaceuticals and perfluorooctane-sulfonic acid were largely distributed, atrazine and alachlor were also determined in most samples, with the concentrations of alachlor in some locations being considered as medium to high risky (Sousa et al. 2020). Interestingly, higher levels were described in some seawater samples in comparison to that of the nearest estuarine site, which was attributed to the possible direct discharge into the sea (Sousa et al. 2020). The first study on the presence of pharmaceutical compounds and pesticides in the Arade River estuary included 19 pharmaceuticals and 47 pesticides, some of which defined as priority substances of European Directive 39/2013/EU or included in the European Decision 495/2015/EU (EU 2013; Gonzalez-Rey et al. 2015). In that study, the detected compounds varied temporally and seasonally, except the stimulant caffeine (804 ng/L), which occurred without any remarkable differences. Other study targeting caffeine as anthropogenic indicator in the Lis River over an 11-month period, reported its presence in all river samples ranging from 25.3 to 321 ng/L, with its highest levels found downstream of effluent discharge points, confirming that it could be an effective indicator of human-born pollution (Paíga et al. 2019). Besides caffeine, those compounds found at highest concentrations in the Arade River were the antiasthmatic theophylline (184 ng/L), the analgesic paracetamol (88 ng/L) and the fungicide carbendazim (45 ± 18 ng/L) (Gonzalez-Rey et al. 2015). In turn, atrazine, diuron, isoproturon and simazine were found at few ng/L and below the environmental quality standards.

Some monitoring surveys focusing on pesticides have been also published. Surface waters of the Lezíria do Tejo agricultural area were monitored and the measured environmental concentrations for the 19 pesticides were compared with their environmental quality standards for risk assessment, being the risk demonstrated in 100% of the samples containing insecticides, which represented 60% of the total risk identified (Pereira et al. 2017b). One occurrence study was performed between 2002 and 2004 in the river basins Mondego, Sado and Tejo in order to assess the risk of 29 pesticides and metabolites, including priority substances and other compounds used in dominant crops of a number of agricultural areas within the catchment of these Mediterranean river basins (Silva et al. 2015a, b). In that study, 20 substances

were detected, from which seven are priority substances (alachlor, atrazine, chlorfenvinphos, chlorpyrifos, endosulfan, simazine and terbuthryn) and remarkably all exceeded their individual environmental quality standards values. Other specific pollutants namely molinate, oxadiazon, pendimethalin, propanil, terbuthylazine, and the metabolite desethylatrazine, had non-acceptable aquatic risks (Silva et al. 2015a). The authors highlighted the need to monitor such substances not only at European Union, but also at local/river-basin/national level, allowing to describe the exceedances of the environmental quality standards (Silva et al. 2015a). The most frequently found compounds in a previous study reporting 29 pesticide compounds (21 herbicides, 5 insecticides and 3 metabolites) in surface waters of Mondego, Sado and Tejo from 2002 and 2008 were: chlorfenvinphos (mean 0.16µg/L), propanil (mean 0.007µg/L) and the metabolite 3,4-dichloroaniline (mean 0.33µg/L) in all rivers; molinate (mean 1.03µg/L) and oxadiazon (mean 0.006µg/L) in Mondego and Sado Rivers; and atrazine (mean 0.16µg/L), simazine (mean 0.08µg/L) and metolachlor (mean 0.06µg/L) in Mondego and Tejo Rivers (Silva et al. 2015a). Endosulfan was also detected in all rivers, but less frequently (3–7%) and with a quite lower mean value of 0.0008µg/L (Silva et al. 2015a). In that study, the authors predicted the aquatic risk of the measured pesticide mixtures for primary producers, arthropods and fish in the three Portuguese river basins and proposed a ranking per taxonomic group and river basin for the relative contribution of individual compounds or groups sharing the same mode of action, where the highest toxicity role was observed for oxadiazon on primary producers and for the organophosphorus insecticides chlorfenvinphos and chlorpyrifos on arthropods and fish, respectively. It is noteworthy that a study conducted between 2010 and 2011 in the Mondego estuary, comprising 56 priority pesticides (insecticides, herbicides and fungicides), reported more than half of the quantified pesticides above the maximum values set by the European Directives (98/83/EC and 2013/39/EU), a potential risk for the pesticide mixture at the maximum concentrations found, and a significant toxic effect for *Artemia salina*, with observed affected locomotion (Cruzeiro et al. 2016).

In another spatial and temporal monitoring study encompassing the pesticides atrazine, azoxystrobin, bentazon, λ-cyhalothrin, penoxsulam and terbuthylazine in the Mondego estuary, azoxystrobin was found as the most frequently detected pesticide (Rodrigues et al. 2018a), which had been also reported in all aqueous samples collected seasonally during 2012–2013 in a wetland of worldwide interest (Ria Formosa Lagoon) (Cruzeiro et al. 2015a), where pesticide concentrations surpassed those recommended by European Directive 2013/39/EU in two monitoring studies (Cruzeiro et al. 2015a, b). In the Mondego (Rodrigues et al. 2018a), atrazine was the second most detected, reinforcing that this priority substance should be monitored despite its ban. Although the concentrations of pesticides in estuarine water were estimated to lead to low risk to estuarine organisms, all pesticides were bioaccumulated by bivalves and triazine pesticides were found also in macroalgae (Rodrigues et al. 2018a). In the same study, the pesticides were quantified typically during summer concurring with the pesticide usage period and no severe contamination occurred during a flood event that was expected to promote the runoff of pesticides from the adjacent agricultural areas (Rodrigues et al. 2018a). The quantified

residues of pesticides were also more frequent during the summer and thus in the pesticide application period in another spatial and temporal monitoring program performed in 2017 in the Sado estuary (Rodrigues et al. 2019a). That report suggested a long-term aquatic exposure for five herbicides, namely alachlor, bentazon, metobromuron, metribuzin and triclopyr, which were determined in the water samples before and after the production season (Rodrigues et al. 2019a). Regarding the potential adverse effects of the application of agricultural pesticides on the aquatic organisms in this estuary, it was not found any severe effect, even considering the potential mixture effect of pesticides (Rodrigues et al. 2019a).

The problematic of microplastics in river waters has received little attention in comparison to marine system. Two recent studies performed in Antuã River (Rodrigues et al. 2018b) and Douro river estuary (Rodrigues et al. 2019b) targeted this environmental issue. The first study on the occurrence of microplastics in freshwater systems performed in Portugal was developed in the Antuã River during March and October 2016, showing a correlation of their occurrence with the urbanization and industrial activities, with an abundance in water up to 193 items/m³ in March and up to 1265 items/m³ in October (Rodrigues et al. 2018b). It was verified a higher abundance in October than in March for almost all sampling sites (one exception) and a decrease from upstream to downstream areas (Rodrigues et al. 2018b). Generally, the most frequently found plastic type was foam (>50%) and the least was pellets, but fibers were the dominant type during March (Rodrigues et al. 2018b). In the Douro report performed between from 2016 and 2017, the authors found a total of 2152 particles, with an average density of 17.06 items/100 m³, including fibers, soft and hard plastic, colourful and transparent plastic, being hard fragments and fibers the most frequent (Rodrigues et al. 2019b). In the same study, an average ratio of fish larvae to microplastics was found to be greater than one in some months, highlighting the possible ingestion by fish and the resulting impact in these communities (Rodrigues et al. 2019b).

All these results show that we still need to mobilise to protect water resources in order to guarantee the sustainability of the ecosystems that are essential to Portugal's economy. Indeed, the spatial distribution of pollutants along the entire Portuguese mainland coast shows the need for mitigation measures to enhance the elimination of pharmaceuticals in wastewater treatment plants and measures to control the use and discharge of pesticides and industrial compounds.

1.5.3 Presence of Emerging Contaminants in the Aquatic Environment in Latin America

With about one-third of the World's water resources and 24,400 m³ of water per capita per year, Latin America is a region with abundant freshwater resource availability. This resource is nevertheless fragile, particularly impacted by increasing economic development (Peña-Guzmán et al. 2019). Indeed, in many Latin America countries, there is a high population density in areas suffering from poor sanitary

conditions, which contributes to the contamination/pollution of rivers and reservoirs that supply water (Caldas et al. 2019; Peña-Guzmán et al. 2019; Starling et al. 2019). The chemical and physicochemical properties (*e.g.*, water solubility, high adsorption capacity and low biodegradability) of many substances in daily use facilitate their flow without resistance reaching water sources, which can trigger problems not only for the environment but also for the health of living organisms (Janssens et al. 1997; Knepper et al. 1999; Kuster et al. 2008; Hernández et al. 2011a, b; Peña-Guzmán et al. 2019).

In a recent comprehensive review by Peña-Guzmán et al. (2019), it was addressed the water quality involving various aqueous compartments of Latin American countries (Argentina, Bolivia, Brazil, Chile, Colombia, Costa Rica, Ecuador, Guatemala, Mexico, Uruguay, and Venezuela), such as water reservoirs for human consumption, drinking water treatment plants, groundwater, surface waters, rivers and wastewater treatment plants. The authors of this survey concluded that the most frequently detected emerging substances are pharmaceuticals (mainly antibiotics), followed by personal care products, and that the most common molecules are 17- β -estradiol, bisphenol A, estrone and caffeine. Most of these chemical substances are not yet regulated by any environmental law. Peña-Guzmán et al. (2019) indicated that a total of 51 emerging pollutants were found in studies related to wastewater, with Ecuador being the country with the largest number of samples, followed by Mexico, Brazil and Colombia. In wastewater, caffeine had the highest concentrations (5597 $\mu\text{g/L}$), followed by the cocaine metabolite benzoylecgonine (1065 $\mu\text{g/L}$) and carbazepine (830 $\mu\text{g/L}$). In the drinking water supply, the substance with the highest concentration (625 $\mu\text{g/L}$) was ibuprofen (Brazil, Colombia, and Venezuela). For surface water sources, the contaminants with the highest concentrations were cholesterol (301 $\mu\text{g/L}$), caffeine (106 $\mu\text{g/L}$), stigmasterol (85.5 $\mu\text{g/L}$) and bisphenol A (64.2 $\mu\text{g/L}$) (Brazil, Costa Rica, Colombia, Bolivia, Chile, Mexico and Argentina). Mexico is the only country that has recorded cases of emerging contaminants in groundwater in the urban water cycle, with the highest concentrations for naproxen (2 $\mu\text{g/L}$), sulfasalazine (0.78 $\mu\text{g/L}$), ibuprofen (0.51 $\mu\text{g/L}$), and salicylic acid (0.464 $\mu\text{g/L}$). For drinking water treatment plant effluents (Brazil only), the substances identified were caffeine (4.083 $\mu\text{g/L}$), nonylphenol (0.228 $\mu\text{g/L}$), 17- α -ethinylestradiol (0.798 $\mu\text{g/L}$), bisphenol A (0.0005 $\mu\text{g/L}$), estriol (0.0003 $\mu\text{g/L}$), and estrone (0.00003 $\mu\text{g/L}$).

Other recent studies have also shown that pharmaceuticals, personal care products, industrial substances and pesticides are widely detected at concentrations of the same order of magnitude (Machado et al. 2016; Hernández-Padilla et al. 2017; Botero-Coy et al. 2018; Gilabert-Alarcón et al. 2018; Sodr e et al. 2018; Montagner et al. 2019; Starling et al. 2019). All studies concluded that these types of chemicals are persistent in the environmental compartments of Latin America; at the same time, their continuous introduction into rivers yields a complex mixture with potential synergistic effects that can result in a serious ecological risk.

As in many other countries around the World, emerging substances enter the aquatic environment of Latin America by many pathways, with the main one being the conventional wastewater treatment plants not designed to remove these type

pollutants, and their discharge containing organic substances and some metabolites (Dougherty et al. 2010; Hernández-Padilla et al. 2017; Starling et al. 2019). Besides, it is estimated that only 20% of municipal wastewater is treated, and in some Latin America countries, many water treatment plants are abandoned due to the high operating costs or low performance (Hernández-Padilla et al. 2017). In Mexico, less than 50% of wastewater is treated and wastewater treatment plants are not financially self-sustaining, resulting in uneven water quality (Gilabert-Alarcón et al. 2018). In Brazil, a country of more than 200 million inhabitants, the percentage of households with access to the wastewater treatment system does not exceed 50%, and a large part of the collected wastewater does not receive appropriate treatment before being discharged into rivers (Machado et al. 2016). In Colombia, raw wastewater is sometimes discharged directly into surface waters in certain Colombian regions such as Florencia and Tumaco (Botero-Coy et al. 2018). When untreated water is released, this contamination further reduces the availability of freshwater for domestic purpose and other uses, as well as damage to ecosystems is caused.

However, this is not just a domestic water problem. Indeed, treated industrial wastewater from the pharmaceutical, chemical, textile or metal industries, as well as water from agricultural activities including irrigation, livestock and aquaculture, can also contain a cocktail of substances, which end up in rivers. All these water uses can also pollute freshwater resources. Before being discharged, like municipal wastewaters, industrial effluents must nevertheless comply with regulations concerning a number of “conventional” substances such as metals and water parameters, namely suspended solids, chemical and biochemical oxygen demand, but organic substances are rarely registered in industrial wastewater (Hernández-Padilla et al. 2017; Gilabert-Alarcón et al. 2018).

The assessment of the occurrence of new contaminants in rivers is one of the major challenges for the scientific community. This task is important because there is a lack of information in most Latin American countries (Hernández-Padilla et al. 2017; Peña-Guzmán et al. 2019; Starling et al. 2019). Unlike Europe and other regions, many Latin American countries do not have an established list of priority pollutants or laws controlling their production or release into the environment. However, regulations are beginning to evolve, particularly in Mexico, Colombia and Brazil, for example with regard to the treatment of municipal and industrial wastewater before discharge. Treatment plants and industries in Latin America do not have a formal structure to detect, assess, control and manage new compounds. Researchers and industrialists in Mexico, Colombia and Brazil draw on the experience of other developed countries in order to protect the aquatic environment of their respective regions, which have different conditions, environmental culture and pollutions levels (Hernández-Padilla et al. 2017).

1.5.3.1 Pharmaceuticals, Personal Care Products and Pesticides in the Aquatic Environment in Mexico

Based on data of the Federal Agency of Consumer (PROFECO) of Mexico, this country is one of the main economies in Latin America, which has registered a strong growth in the personal care products market during the last decade, where around 40% of the demand is related to hair and skin care products. On the other hand, according to the Ministry of Health (Mexico), it is estimated that more than 80% of the Mexicans self-medicate, which means that they use drugs regardless medical prescription. As an example, diabetes is one of the main health issues in Mexico, and high pharmaceuticals consumption is associated to this disease. Unfortunately, similar to other countries, the uncontrolled use of drugs and personal care products, coupled to the discharge of untreated domestic wastewater or the inefficient removal of this type of substances in conventional wastewater treatment plants, can increase the contamination levels in the aquatic environment of various Mexican regions (Gilabert-Alarcón et al. 2018; Lesser et al. 2018; Pérez-Alvarez et al. 2018).

In some States, the reuse of wastewater has been implemented without integrative planning and assessment of the impact on ecosystems and public health (Gilabert-Alarcón et al. 2018). Despite emerging contaminants are rarely monitored in Mexico, the occurrence of pharmaceuticals and personal care products in effluents and surface waters has been investigated. With that aim, measurements of trimethoprim (0.11–0.15 µg/L, 0.28–0.32 µg/L), clarithromycin (0.37–0.45 µg/L, 1.10–1.40 µg/L), naproxen (6.2–6.74 µg/L, 2.84–3.16 µg/L), and diclofenac (0.25–0.34 µg/L, 0.42–0.50 µg/L) were determined in wastewater from Mexico City-Mezquital Valley (Pumping station “Gran Canal” and Emisor Profundo “El Salto”). The concentrations of these substances were found to be similar to levels reported for sewage in Europe, Japan, and USA. Levels of metoprolol (0.21–0.25 µg/L) in water from the Gran Canal were comparative to the concentrations detected in wastewater in Switzerland (0.14–0.29 µg/L), but these levels were higher than those found in sewage in Spain (< 0.005–0.09 µg/L). The concentration of ibuprofen had been previously reported close to 0.3 µg/L for both sampling points (Siemens et al. 2008).

Lesser et al. (2018) carried out analyses of untreated wastewater used for agricultural irrigation, from different points in Mezquital Valley (located in Central Mexico), reporting that from the group of 7 reproductive hormones and 118 pharmaceuticals measured, 3 hormones and 65 drugs were detected. Some examples include acetaminophen (39,900 ng/L), ciprofloxacin (1190 ng/L), sulfamethoxazole (5360 ng/L), oxytetracycline (134 ng/L), naproxen (11,800 ng/L) and metformin (82,900 ng/L).

In the same way, hospital wastewater from Toluca City (the capital city of the State of Mexico) was studied by the quantification of different pharmaceuticals, where antidiabetics (*e.g.*, 1.92 µg/L and 1.31 µg/L for glibenclamide and metformin, respectively), β -blockers (0.20 µg/L for atenolol and 2.02 µg/L for metoprolol), β -lactams (3.77 µg/L for penicillin G and 0.42 µg/L for penicillin V), hormones

(0.08µg/L for 17-β-estradiol), and anti-inflammatory drugs (0.59µg/L for diclofenac, 0.62µg/L for ibuprofen, 1.79µg/L for naproxen and 2.66µg/L for acetaminophen), were detected (Pérez-Alvarez et al. 2018).

Similarly, the presence of some emerging contaminants was also investigated in five effluents of domestic wastewater produced in the coastal zone of Cihuatlan, Jalisco (a State of Mexico on the edge of the Pacific Ocean) (Arguello-Pérez et al. 2019). These authors specified that diclofenac, ibuprofen and ketorolac were determined in all the analyzed effluents at concentration considered as “toxic”, whilst estradiol was found in two of the effluents at concentrations that fall into a very toxic range.

Díaz and Peña-Alvarez (2017) previously reported an analytic method for the detection of ibuprofen, 2-benzyl-4-chlorophenol, naproxen, triclosan, ketoprofen, diclofenac, bisphenol A and estrone in river sediments. Their analyses showed that sediment samples from the Tula River (Hidalgo, in central Mexico) had ibuprofen, naproxen and triclosan at concentrations in the order of ng/g. The authors remarked that the water sample with higher naproxen concentration (240 ng/L) was taken from the riverside where wastewater from Ixmiquilpan City was discharged.

Others monitoring studies exhibited the occurrence of pharmaceuticals in influent/effluent of the wastewater treatment plant “Acapantzingo” and surface water (Apatlaco River in Cuernavaca, the capital of the State of Morelos in south-central Mexico) (Rivera-Jaimes et al. 2018). The total concentrations of pharmaceuticals were higher in surface water and influent wastewaters as compared to those detected in effluent wastewaters, showing the important role of wastewater treatment plants. Rivera-Jaimes et al. (2018) indicated that the discharge of untreated wastewater increased the concentration of pharmaceuticals in the river, where naproxen (732–4880 ng/L), acetaminophen (354–4460 ng/L), diclofenac (258–1398 ng/L) and bezafibrate (286–2100 ng/L), were the most abundant.

Recently, Pérez-Coyotl et al. (2019) analyzed water samples from an urban reservoir (Madín dam, located in the municipalities of Naucalpan and Atizapán in the metropolitan area adjacent to Mexico City) that is a source of drinking water and represents an area for recreational activities, including carp fishing. Their results showed different concentrations of personal care products (especially sunscreens) and pharmaceuticals. As example, 2,2',4,4'-tetrahydroxybenzophenone (13.7 ng/L), 2-ethylhexyl 4-(dimethylamino) benzoate (29 ng/L), 4-methylbenzylidene camphor (134 ng/L) and methyl benzotriazol (250 ng/L), antidiabetic agents glibenclamide and metformin (2148 ng/L and 9557 ng/L, respectively), and the analgesic acetaminophen (9156 ng/L) were detected. Hence, it is notably essential to implement a monitoring program of these emerging contaminants in drinking water sources of this region.

Another important problem in Mexico, as in other Latin American countries, is the presence of pesticides in water resources (García-de la Parra et al. 2012; Arellano-Aguilar et al. 2017). The high availability and convenient cost of agrochemicals, as well as flexible environmental laws have led to an overuse of pesticides in Mexico, in order to satisfy the global demand of agricultural products. Nevertheless, residual agrochemicals in agricultural runoff are rarely monitored by

farmers, and some of their leachates drain these pollutants to lakes or rivers (sources of drinking water), which eventually contaminate bays and coasts (Fig. 1.8) (Osuna-Flores and Riva 2002; Arellano-Aguilar et al. 2017). In particular cases, people of various villages are in contact with this type of hazardous leachates; furthermore, private wells for drinking water, which is untreated (used directly), are located close to agricultural fields (Picos-Corrales et al. 2020). In this regard, some pesticides are regulated in Mexico by the Federal Commission for the Protection against Sanitary Risk, an organ of the Health Secretary of Mexico. Based on this environmental regulation (NOM-127-SSA1-1994), the maximum limits for the main



Fig. 1.8 Contamination sequence involving river pollution in Sinaloa from agricultural wastewater (Sinaloa is an important agricultural region of Mexico; source: Lorenzo A. Picos-Corrales, Sinaloa, Mexico)

organochloride pesticides for drinking water are: 30µg/L for 2,4-D (2,4-dichlorophenoxyacetic acid), 20µg/L for methoxychlor, 2µg/L for γ-lindane, 1µg/L for DDT (dichlorodiphenyltrichloroethane, total) and hexachlorobenzene, 0.2µg/L for chlordane, 0.03µg/L for heptachlor, aldrin and dieldrin (separated or combined).

Sinaloa is an example of an industrialized agricultural region in Northwestern Mexico that is characterized by a variety of crops and high production. In this State of Mexico, pesticides have been found in sediments of agricultural drainages (García-de la Parra et al. 2012). From this assessment, concentrations of organochlorine compounds (15 substances) and organophosphorus compounds (8 substances) were within the ranges 0.1–20.19 ng/g and 0.03–1294 ng/g, respectively, being diazinon the compound with the highest concentration. Arellano-Aguilar et al. (2017) also reported that this industrialized agricultural region has a documented pesticides usage of 700 t/year, being at least 17 of the molecules classified as moderately to highly toxic.

With the same focus, Leyva-Morales et al. (2017) assessed the quality of river water from central Sinaloa (Humaya, Tamazula and Culiacan rivers) by monitoring residual pesticides. Their results showed that the following chemicals were present: lindane (0.0041–0.0104µg/L), endosulfan (0.0198–0.03601µg/L), heptachlor, dichlorodiphenyltrichloroethane (0.0525µg/L), diazinon (0.0211–0.0403µg/L), chlorpyrifos, methyl parathion, cyromazine (0.1961µg/L), permethrin (0.2351µg/L), ethion, carbofenothion, lambda cyhalotrine, pyrimicarb, aldrin (0.0099–0.1023µg/L) and malathion. Leyva-Morales et al. (2017) suggested that pesticide contamination derived mainly from runoffs of polluted soil toward rivers.

Besides, the connection between agrochemical loading in drains/rivers and pollution in coastal lagoons of the Mexican Pacific has been studied (Arellano-Aguilar et al. 2017). The authors indicated that the organochlorine chemicals were clearly accumulated in the coastal lagoons from the drains and rivers, with hexachlorocyclohexanes (organochlorine) showing the highest concentration. In another work regarding pesticides accumulation, levels of dichlorodiphenyltrichloroethane (\sum DDTs ~0.6–137µg/kg) were quantified in sediments samples taken from Texcalac River in Tlaxcala (Mexico), exceeding the guidelines for protection of aquatic life according to the authors (García-Nieto et al. 2019).

From the literature, Yucatan (southeastern Mexico) is a state with high levels of groundwater pollution, where different pesticides have been detected (3.2 mg/L for endrin, 10.86 mg/L for δ-lindane, 5.23 mg/L for γ-lindane, 6.53 mg/L for α-lindane and 12.54 mg/L for heptachlor) (Polanco-Rodríguez et al. 2018). This type of hazardous chemicals has been also identified in the drinking water source “Madín dam” of Naucalpan and Atizapan (Mexico), namely diazinon up to 12.592 ng/L and fenthion sulfoxide up to 2.465 ng/L (Pérez-Coyotl et al. 2019). Based on the current literature, it is recommended to increase the monitoring work regarding pesticides content in surface water in Mexico.

In addition to monitoring, examples related to the impact of emerging pollutants on human health and ecosystems in Mexico have also been reported. Researchers developed a strategy for the determination of some residual personal care product ingredients in hydroponic French lettuce from a local supermarket in Mexico

(Cabrera-Peralta and Peña-Alvarez 2018). The results indicated that the use of wastewater to irrigate crops can result in contaminated food since the absorption by plants is favored in the presence of compounds with intermediate polarity.

Martinez-Gomez et al. (2015) previously assessed the effect of pharmaceuticals and personal care products on aquatic life using the rotifer *Platyonus patulus*, which is a member of riverine food networks in Mexico. Results indicated that the continuous exposure to emerging contaminants could reduce rotifer population growth. Hence, the constant discharge of treated wastewater to aquatic ecosystems could represent a risk for the zooplankton community.

In another work, the toxicological risk of a hospital effluent from Toluca (the capital of the State of Mexico) was evaluated using two bioindicator species, i.e. *Xenopus laevis* and *Lithobates catesbeianus* (Pérez-Alvarez et al. 2018). This research group suggested that the hospital effluents represent a latent risk for the ecological balance and diverse organisms, being necessary a prior treatment for the removal of the pharmaceuticals (Pérez-Alvarez et al. 2018).

Based on hazard quotients for pharmaceuticals detected in the Apatlaco River in Cuernavaca (the capital of the State of Morelos in south-central Mexico), Rivera-Jaimes et al. (2018) found that contamination levels of this river could represent a risk for the aquatic ecosystem, due to the high concentrations of naproxen, ibuprofen, diclofenac and sulfamethoxazole. Similarly, experiments performed using samples from the drinking water source “Madín dam” (Naucalpan-Atizapán, State of Mexico) revealed that residual pharmaceuticals, personal care products and pesticides originated embryotoxicity, embryoletality, congenital abnormalities and oxidative stress on the common carp embryos. This was a rational explanation regarding the reduction in the population of *Cyprinus carpio* species of this ecosystem (Pérez-Coyotl et al. 2019). Also, in past years in the Bay of Ohuira (Topolobampo, a port on the Gulf of California in northwestern Sinaloa), the decrease in shrimp production was associated, among other causes, with the high coastal pollution by pesticides (Osuna-Flores and Riva 2002). In Chiapas (Southern Mexico), concentrations of organochlorine pesticides were found in a greater amount in cow’s milk and forage than in water samples. Despite the content of contaminants was below the limits established by Mexican government, a monitoring program was recommended by the authors (Murga et al. 2016).

It is also estimated that in Yucatan (southeastern Mexico) around 30% of the residents drink water from contaminated sources, and investigations revealed high levels of pesticides (7.352 mg/L for endosulfan I, 2.336 mg/L of 4,4'-dichlorodiphenyldichloroethane, 3.695 mg/L for aldrin and 1.434 mg/L for heptachlore) in the blood of women having cervical uterine cancer. Additionally, other studies showed the high levels of these chemicals in breast milk (18.436 mg/L for heptachlor epoxide and 2.10 mg/L for dieldrin) (Polanco-Rodríguez et al. 2018).

In conclusion, Mexico is facing the problem of emerging substances in its aqueous compartments. This is not a novelty itself, but this problem is accentuated by the diversity of the substances found and the levels of quantified concentrations. Table 1.5 summarizes examples of contamination by emerging substances reported in water compartments in Mexico, comparing them with those reported by

Table 1.5 Contamination by emerging substances reported in water compartments in Columbia, Mexico and Brazil (from 2013 onward)

Country	Water type	Emerging substance	Concentration (ng/L)	References
Columbia (La Fe)	Drinking water supply reservoir	Ibuprofen	7–39	Aristizabal-Ciro et al. (2017)
Columbia (Rio Grande)	Drinking water supply reservoir	Ibuprofen	5–62	Aristizabal-Ciro et al. (2017)
Mexico (Mexico City)	Surface water	Ibuprofen	15–45	Félix-Cañedo et al. (2013)
Mexico (Toluca City)	Hospital wastewater	Ibuprofen	620	Pérez-Alvarez et al. (2018)
Mexico (Morelos)	Surface water	Diclofenac	258–1398	Rivera-Jaimes et al. (2018)
Mexico (Mexico City)	Surface water	Diclofenac	28–32	Félix-Cañedo et al. (2013)
Mexico (Morelos)	Wastewater	Diclofenac	600–2500	Rivera-Jaimes et al. (2018)
Mexico (Cuernavaca)	Wastewater	Diclofenac	258–1398	Rivera-Jaimes et al. (2018)
Mexico (Toluca City)	Hospital wastewater	Diclofenac	590	Pérez-Alvarez et al. (2018)
Mexico (Morelos)	Surface water	Naproxen	732–480	Rivera-Jaimes et al. (2018)
Mexico (Tula River)	Surface water	Naproxen	240	Díaz and Peña-Alvarez (2017)
Mexico (Mexico City)	Surface water	Naproxen	52–186	Félix-Cañedo et al. (2013)
Mexico (Mezquital Valley)	Wastewater	Naproxen	11,800	Lesser et al. (2018)
Mexico (Cuernavaca)	Wastewater	Naproxen	732–4880	Rivera-Jaimes et al. (2018)
Mexico (Morelos)	Wastewater	Naproxen	800–4200	Rivera-Jaimes et al. (2018)
Mexico (Toluca City)	Hospital wastewater	Naproxen	2660	Pérez-Alvarez et al. (2018)
Brazil (São Paulo)	Surface water	Paracetamol	30,421	Campanha et al. (2015)
Brazil (São Paulo)	Surface water	17- α -ethynylestradiol	777	Montagner et al. (2019)
Brazil (São Paulo)	Surface water	Caffeine	19–127,000	Montagner et al. (2019)
Brazil	Surface water	Caffeine	40–19,000	Machado et al. (2016)
Brazil (São Paulo)	Surface water	Caffeine	129.585	Campanha et al. (2015)
Brazil	Drinking water	Caffeine	1.8–2000	Machado et al. (2016)

(continued)

Table 1.5 (continued)

Country	Water type	Emerging substance	Concentration (ng/L)	References
Brazil (São Roque)	Drinking water	Caffeine	4083	Peña-Guzmán et al. (2019)
Brazil (São Paulo)	Drinking water	Caffeine	121	Montagner et al. (2019)
Brazil (Rio Grande)	Drinking water supply reservoir	Caffeine	18,828	Machado et al. (2016)
Brazil (São Paulo)	Surface water	Bisphenol A	2–13,016	Montagner et al. (2019)
Brazil (Rio Grande)	Drinking water supply reservoir	Bisphenol A	11	Machado et al. (2016)
Brazil (São Paulo)	Drinking water	Bisphenol A	23	Montagner et al. (2019)
Brazil (São Roque)	Drinking water	Bisphenol A	0.5	Peña-Guzmán et al. (2019)
Brazil (São Paulo)	Surface water	Cocaine	10	Montagner et al. (2019)
Brazil (São Paulo)	Surface water	Benzoylcegonine	133	Montagner et al. (2019)
Colombia (Bogotá)	Wastewater	Benzoylcegonine	4000	Bijlsma et al. (2016)
Colombia (Bogotá)	Wastewater	Amphetamines	12–68	Bijlsma et al. (2016)
Brazil (São Paulo)	Drinking water	Triclosan	2–37	Montagner et al. (2019)
Brazil (Rio Grande)	Surface water	Atrazine	5–49	Caldas et al. (2019)
Brazil (São Paulo)	Drinking water	Atrazine	687	Montagner et al. (2019)
Brazil (Rio Grande)	Drinking water	Atrazine	5–37	Caldas et al. (2019)
Brazil	Drinking water	Atrazine	2–6000	Machado et al. (2016)
Mexico (Yucatan)	Groundwater	Endrin	3.2 mg/L	Polanco-Rodríguez et al. (2018)
Mexico (Yucatan)	Groundwater	γ -Lindane	10.86 mg/L	Polanco-Rodríguez et al. (2018)
Mexico (Yucatan)	Groundwater	Heptachlore	12.54 mg/L	Polanco-Rodríguez et al. (2018)

Columbian and Brazilian colleagues. It is necessary to mobilize all the stakeholders and the population to protect aquatic ecosystems in order to ensure the production of quality water. To achieve this goal, a thorough monitoring of surface waters is necessary and indispensable as part of a vast program at several spatial and temporal scales, not only at the national level but also as part of a more comprehensive water policy in collaboration with Mexico neighboring countries. In addition, attention

should also be paid to treatment plants and their purification performance, as part of a more organizational water management at national and regional levels.

1.5.3.2 Emerging Contaminants in Colombian Rivers

Colombia is a country in South America with an area of 1,141,748 km², a large marine area covering 928,660 km² and a population of 46,581,823 (*Departamento Administrativo Nacional*, DANE 2011). Colombia is a privileged country because of its geographical position in the continent, which gives it direct access to both ocean Atlantic and Pacific. Colombia has many water sources throughout its territory and the most important biodiversity not only in the region but also in the World. The country has indeed many rivers, the most important of which are the following: Amazon (6992.6 km, shared with Peru and Brazil), Caquetá (Japura, 2816.3 km, shared with Brazil), Negro (2230.5 km, shared with Brazil and Venezuela), Orinoco (2140.4 km, shared with Venezuela), Putumayo (1609.3 km, shared with Peru and Brazil), Guaviare (1496.6 km, shared with Venezuela), Arauca (1049.2 km, shared with Venezuela), Cauca (965.6 km), Goal (804.6 km, shared with Venezuela), Magdalena (528.8 km) and its affluent Rio Bogotá. Concerning the latter river, it originates in the northeastern region of Cundinamarca, in the lagoon valley of Paramo Guacheneque, municipality of Villa Pinzon, Eastern Cordillera of Colombia, at 3300 m above sea level. The waters of the Bogotá River flow for 380 kilometers to Girardot, where they flow into the Magdalena River. Its basin is located in the center of the country, in the department of Cundinamarca, with an area of approximately 6.000 km² (Hernández et al. 2015; Bedoya-Ríos et al. 2018; Bedoya-Ríos and Lara-Borrero 2018).

Colombia bases its income mainly on the production of raw materials to export and to manufacture consumer products for the domestic market. Its main activities are the production of oil for exportation (fourth in Latin America and sixth in the continent) and mining, particularly carbon, gold, emeralds, sapphires and diamonds (*Ministerio de Ambiente y Desarrollo Sostenible*, 2016). The strongest industrial sectors in Colombia are petrochemicals, textiles, automobiles, and chemicals.

Colombia, like most countries in the World, is not immune to the problem of emerging compounds and Colombian developing regions are concerned (Martínez Vidal et al. 2006; Barceló and Petrovic 2008; Ibáñez et al. 2008, 2009; Klammerth et al. 2009; Teijón et al. 2010; Tobón-Marulanda et al. 2010; Gil et al. 2012; Díaz-Casallas et al. 2019; Reichert et al. 2019). As in many other developing countries, Colombia's indiscriminate industrial growth has led to severe pollution of its waterbodies. Indeed, numerous studies have shown that several of its water sources are heavily contaminated, including by emerging contaminants. The sources of contamination are industrial, agricultural and domestic, the latter often uncontrolled. Once entered into the environment, chemicals and their metabolites can produce subtle effects on aquatic and terrestrial organisms, especially on the former since they are exposed to long-term continuous influx of wastewater effluents. Recently, Díaz-Casallas et al. (2019) proposed a comprehensive analysis of the water quality

at the upper basin of the Bogotá River between 2008 and 2017, pointing out an insufficient quality of water. This study highlighted the necessity for further efforts on the continuous monitoring of Colombian rivers basins.

Indeed, Colombia is currently focusing its efforts on the detection and the quantification of emerging substances, in order to compile a list of priority substances adjusted to the needs and characteristics of Latin America. Research programs are also underway to provide recommendations for future monitoring, prevention and elimination programs for these chemicals. It is indeed important not only to monitor discharge waters from municipal treatment plants and industrial wastewaters but also to encourage the improvement of their systems and treatment techniques in order to achieve better removal efficiencies.

The list of substances that have been found in effluents from wastewater treatment plants, and consequently in Colombian waters (surface water, groundwater, etc.) is extremely varied, ranging from pharmaceuticals, hormones and steroids to surfactants, cosmetics and pesticides (Hernández et al. 2005, 2012, 2015; Martínez Vidal et al. 2006; Ibáñez et al. 2008, 2009; Tobón-Marulanda et al. 2010; Bijlsma et al. 2016; Sarria-Villa et al. 2016; Portilla et al. 2017; Botero-Coy et al. 2018; Serna-Galvis et al. 2019; Reichert et al. 2019). These studies also helped to improve the understanding about the dynamics and behavior of the target compounds.

The substances most frequently found in Colombian water sources were pharmaceuticals such as antihypertensives, antibiotics, analgesics and psychiatric products, and illicit substances, *e.g.*, cocaine and its main metabolite, heroine, and amphetamines (methamphetamine). They are detected at trace levels, usually between ng/L and µg/L, depending on the molecule. Raw wastewater from the cities of Bogotá, Medellín and Florencia contain levels of several pharmaceuticals above 1µg/L, while the concentrations for antibiotics are commonly above 5µg/L in raw hospital wastewater. A survey of the Latin American literature, including Colombian data, shows that all these substances are often identified and quantified by gas chromatography coupled to mass spectrometry (Peña-Guzmán et al. 2019). Continual improvements in analytical equipment and methodologies enable the determination of pharmaceuticals and their metabolites at lower and lower concentration levels in water samples and also in other environmental matrices.

Colombia is facing the problematic of the high use of pharmaceutical products and cosmetics (Fig. 1.9). Pharmaceuticals include antihypertensives (valsartan, irbesartan), antibiotics (ciprofloxacin, norfloxacin), anticonvulsants (carbamazepine), diuretics (furosemide), psychiatric products (gabapentin, benzodiazepine derivatives, antiepileptics), and psychoactive agents (hallucinogens). Benzophenones (benzophenone-1, benzophenone-2, benzophenone-3, benzophenone-4), parabens (methylparaben, ethylparaben, butylparaben, propylparaben), triclosan and bisphenols are examples of cosmetic ingredients considered as endocrine disruptors. Among these substances, antihypertensives (valsartan, irbesartan), antibiotics (ciprofloxacin, norfloxacin) and endocrine disruptors are of great concern and their hazardous effects are already reported (Darbre 2015; Gee et al. 2015). Triclosan is also a substance of concern. This hydrophobic substance can accumulate in fatty tissues, such as fish and human samples (urine, breast milk and serum). Moreover, triclosan

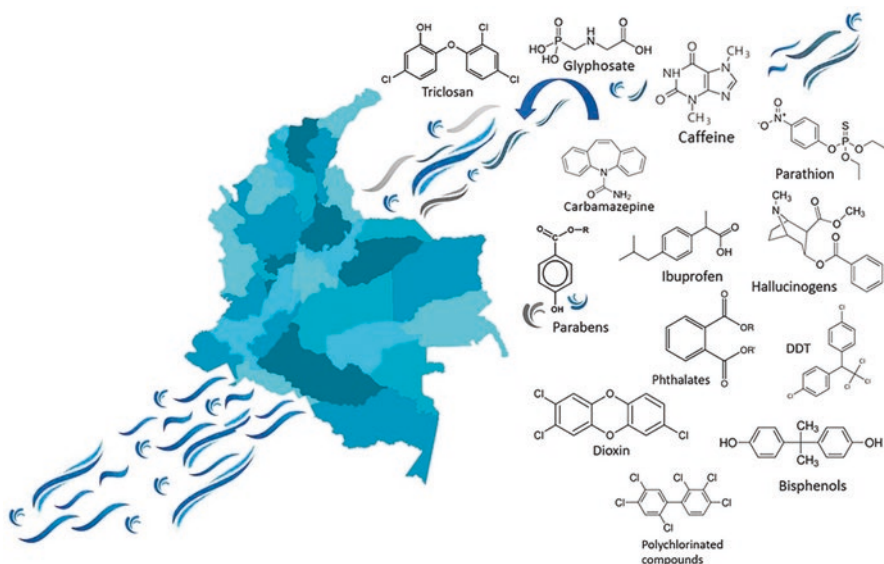


Fig. 1.9 Example of emerging contaminants in Colombian Rivers. (Source: Juan Carlos Moreno-Piraján, Bogotá, Colombia)

has been shown to have toxic effects in aquatic organisms at environmental concentrations and its degradation products can be more toxic and persistent than the parent compound (Kosma et al. 2014; Juliano and Magrini 2017; Machado et al. 2016; Montagner et al. 2019).

A first typical example is the presence of losartan, an antihypertensive widely used in Colombia (Portilla et al. 2017; Serna-Galvis et al. 2019). Another typical example is ciprofloxacin that is among the top five most common antibiotics prescribed in Colombian hospitals. Botero-Coy et al. (2018) and Serna-Galvis et al. (2019) have reported its frequent presence in hospital effluents. However, the load from hospital wastewater varied from study to study. Another problem is the presence of endocrine disruptors, which are capable of blocking and altering every hormonal function, disrupt the endocrine system. Endocrine disruptors are compounds that mimic the hormones produced by living organisms and interfere with various functions (Darbre 2015). These chemical compounds include the natural (17- β -estradiol) and synthetic (17- α -ethynylestradiol) hormones used in birth control pills, fertility treatments and hormone replacement therapy. All these endocrine disruptors end up in water via domestic, industrial and/or hospital discharges. However, conventional municipal wastewater treatment plants are not designed to deal with these substances, and consequently such molecules and their metabolites can reach the aquatic environment. Endocrine disrupting effects such as intersexuality and reproductive disorders have been reported in fish and other aquatic organisms living downstream from wastewater treatment plant outfalls (Vajda et al. 2008; Gagné et al. 2011; Tetreault et al. 2011).

Cocaine is a highly consumed illicit drug in populated Colombian cities such as Bogotá, and consequently, its main metabolite (benzoylecgonine) has a high prevalence in wastewaters (Bijlsma et al. 2016; Hernández et al. 2015; Serna-Galvis et al. 2019). Bijlsma et al. (2016) conducted for the first time a wastewater-based epidemiology in Colombia, reporting that cocaine was the most consumed illicit drug, particularly in Medellín (department of Antioquia). Benzoylecgonine, a cocaine metabolite, exceeded 4000 ng/L in all samples from wastewater treatment plants. Amphetamines were also found in all samples at concentrations between 12 ng/L and 68 ng/L (Bijlsma et al. 2016). Illicit substances, together with pharmaceuticals, are commonly measured in Colombian effluents as both groups of substances are not completely removed with conventional treatments (Serna-Galvis et al. 2019).

Another important issue is the presence of pesticides, such as glyphosate, dichlorodiphenyltrichloroethane (DDT), parathion and clofibric acid, in water, since Colombia is a major agricultural country that uses phytosanitary products. A typical example is the presence of glyphosate used to protect illicit crops. The frequent detection of this substance suggests that it is a widespread environmental contaminant. Another typical example is the insecticide DDT which has well know adverse health consequences, namely an established link with malformations in newborns. Studies have also shown significant impacts on fish and reptiles (deformities, reduced fertility, and abnormal behavior).

There are also industrial products such as phthalates, bisphenol A and its analogues (bisphenol F and bisphenol S) used in the production of resins and plastics, paints/lacquers and binding materials, or cleaning agents (nonylphenol). Another example is triclosan used as a broad spectrum antibacterial agent into many consumer products and as preservative in products of domestic use. It is also found in cosmetics, textiles and antibacterial fibers. These substances have been identified and quantified in industrial wastewaters and in rivers.

In Colombia and in other Latin America countries, the situation is worrying not only from a water pollution point of view but also from a health point of view, with the appearance of resistance phenomena for certain bacteria. Antibiotics are antimicrobial drugs that kill or reduce the growth of bacteria. They have been used in large quantities for several decades around the World and antibiotic resistance of pathogens has been for long a focus of research in clinical settings and, more recently, in environmental research. Incorrect use of antibiotics increases resistance to them, a process called antimicrobial resistance, the antibiotic being ineffective on a bacterial infection. The more antibiotics are consumed, the greater the risk of developing resistant bacteria (García et al. 2020). One widely reported case is that of *Staphylococcus aureus*, which has developed resistance to methicillin (MRSA). This bacterium is a clear example of hospital infections originated when a certain patient stays in a hospital for long periods of time, creating a big problem in terms of hospital hygiene. There are three main routes of entry of antibiotics into freshwater: (1) effluents from wastewater treatment plants, (2) chemical manufacturing plants, and (3) livestock, agricultural and aquaculture sites. Indeed, antibiotics can bypass water treatment processes and end up directly in the environment. They are detected in Colombian rivers at very low concentrations and are diluted more than a

million times compared to concentrations in the human body. However, these residual concentrations are highly likely to generate antimicrobial resistance, having direct and indirect effects on the microbial component of aquatic communities. Indeed, even at low concentrations, these antibiotics could have significant consequences for ecosystems and human health.

In conclusion, the presence of emerging substances in Colombian waters is a concern that is becoming increasingly important in society. The demand for water, whether for domestic, agricultural or industrial use, is constantly increasing, with the consequences of water pollution and ecosystem degradation, as a significant amount of wastewater is either untreated or poorly treated. This scenario is complicated by a climate context that is affecting the predictability of our most precious resource. All water stakeholders are concerned by this issue and mobilized. There is a growing consensus that the challenges can be tackled by adopting an integrated approach for water resources management. In particular, special efforts need to be made in the operation of municipal wastewater treatment plants and in the protection of the ecosystems and water resources.

1.5.3.3 Analysis of Emerging Contaminants in Brazilian Water Resources

As in Mexico and Colombia, the presence of the same vast group of emerging contaminants (pharmaceuticals, personal care products and cosmetics, industrial substances and pesticides) in Brazil's water resources, including rivers, lakes, drinking water reservoirs and tap water, has been reported at the same orders of magnitude of concentrations, showing that the conventional wastewater treatments are not effective for their removal, even in regions that have adequate sanitation. Indeed, numerous studies indicated that the conventional applied wastewater treatments are not efficient enough to remove these substances from wastewater and sludge, and as a result they find their way into the environment (Barbosa et al. 2015; Campanha et al. 2015; Albuquerque et al. 2016; Machado et al. 2016; Caldas et al. 2019; Starling et al. 2019).

The collection, treatment and reuse of wastewater from households and industry, the reduction of diffuse pollution and the improvement of water quality are major challenges for Brazilian water stakeholders. Freshwater quality is indeed under threat. Its pollution is widespread and increasing in many regions. In Brazil, regulations concerning emerging contaminants in both natural waters and drinking water require a commitment among researchers and regulatory authorities, since this issue has not been considered as a priority by the government (Machado et al. 2016).

The substances that have been analyzed in Brazilian waters include mainly, hormones, antibiotics, endocrine disruptors, caffeine (as licit drug), illicit drugs (methamphetamine, cocaine, heroin), industrial compounds (bisphenols, triclosan), and pesticides. Among them, pesticides in particular have been monitored, as Brazil is the World's largest consumer of herbicides, fungicides and insecticides (Barbosa et al. 2015; Albuquerque et al. 2016; Caldas et al. 2019; Starling et al. 2019), which means that these substances may end up in the environment, especially in aquatic

systems and reservoirs used for drinking water production. There are 381 active ingredients authorized by the Brazilian Ministry of Agriculture for pesticides used on crops and 1670 formulated plant protection products in the market (Albuquerque et al. 2016). Brazil has regulations on the use of pesticides and their presence in water. For example, the Brazilian drinking water norm (Ordinance 2914/2011 of the Ministry of Health) includes 64 chemical substances, of which 27 are pesticides that must be monitored every 6 months. However, this number represents <10% of the current pesticide active ingredients approved for use in the country (Barbosa et al. 2015). Of the 27 pesticides, 21 are banned in Europe due to the risks they offer to health and the environment. A comprehensive review on the presence of pesticides in Brazilian freshwaters was published by Albuquerque et al. (2016). They reported that data in peer-reviewed literature are scarce and often incomplete, concluding that, without the implementation of a nationwide pesticide freshwater monitoring program and a clear definition of proper water quality standards, it is not possible to evaluate the risks posed by pesticides to the aquatic life in Brazil.

Among the most widely used pesticides in Latin America, glyphosate and atrazine occupy prominent positions as the best-selling active ingredients in Brazil (Brazil 2011; Barbosa et al. 2015; Marin et al. 2019). Since its introduction as an herbicide active ingredient in 1971, glyphosate became and remains the market leading herbicide worldwide (glyphosate-based formulations are mainly represented by Roundup). The limit of glyphosate in drinking water in Brazil is 0.5µg/L (Brazil 2011; Barbosa et al. 2015), while in Europe only 0.1µg/L is permitted (0.9µg/L for World Health Organization, 0.8µg/L for Canada). The 0.1µg/L value is also the maximal residue level of glyphosate in European surface and ground water. The maximum contaminant level in the U.S. in drinking water is 700µg/L (sum of glyphosate and its residues) and the health-based guideline value in Australia is 1000µg/L (Székács and Darvas 2018). The contamination of the environment by glyphosate is worrying since it impairs enzymatic activity, causes cytotoxicity and DNA damage in human cells (Marin et al. 2019).

In drinking and surface waters, acceptable limit for atrazine (herbicide of the triazine class) and methyl parathion (organophosphate insecticide) are 9 and 2µg/L, respectively (Ordinance 2914/2011 of the Ministry of Health). These limits are based on toxicological and neurotoxicological trials, but they do not take into account possible estrogenic effects that atrazine can cause when human and wildlife are chronically exposed to low concentrations (Machado et al. 2016). In Canada, the maximum acceptable concentration for atrazine in drinking water is 5µg/L (this value is applicable to the sum of atrazine and its metabolites) while for the United States Environmental Protection Agency, the maximum concentration in water is 3µg/L. In the European Union, a limit of 0.1µg/L has been set for all pesticide residues in drinking water and groundwater. This value of 0.1µg/L for each substance represents a standard for water quality, not for the health risk. If more than one pesticide is found in drinking water, the sum of all pesticides has a legal limit of 0.5µg/L (source: French Agency for Food, Environmental and Occupational Health & Safety).

Sodré et al. (2010) investigated the occurrence of endocrine disruptors in drinking water of the city of Campinas. Six emerging contaminants (stigmaterol,

cholesterol, bisphenol A, caffeine, estrone, and 17- β -estradiol) were found in twelve samples. Estrone and 17- β -estradiol were detected only during the dry season, with concentrations below quantification limits. Stigmasterol showed the highest average concentration ($0.34 \pm 0.13\mu\text{g/L}$), followed by cholesterol ($0.27 \pm 0.07\mu\text{g/L}$), caffeine ($0.22 \pm 0.06\mu\text{g/L}$), and bisphenol A ($0.16 \pm 0.03\mu\text{g/L}$). Alarmingly, the level of bisphenol A detected in drinking water ($0.0005\mu\text{g/L}$) was higher than the average effluent from effluent treatment plants ($0.00002\mu\text{g/L}$) (Sodré et al. 2010). Ten years later, Peña-Guzmán et al. (2019) also reported similar levels of concentrations. Sodré et al. (2010) concluded that, in Campinas, where surface drinking water supplies receive large amounts of raw sewage inputs, the emerging contaminants levels in drinking waters were higher than median values compiled for drinking and finished water samples around the World. Montagner and Jardim (2011) also reported that among endocrine disruptors, bisphenol A (a compound used as a manufacturing intermediate) is distinguished by its widespread presence in the environment. In the State of São Paulo, this substance was detected in all surface water sampling campaigns with concentrations between 204 and 13,016 ng/L (Montagner and Jardim 2011).

A special substance in Latin America is caffeine. It is consumed by people of all ages, cultures and socio-economic status (Campanha et al. 2015; Sodré et al. 2018; Peña-Guzmán et al. 2019; Starling et al. 2019). As caffeine is present in everyday beverages such as coffee, tea, chocolate and cola drinks, a large amount of caffeine waste is generated, which enters the aquatic environment. Many drugs also contain caffeine, namely analgesics, antihistamines, diet pills, cold remedies, and stimulants of psychophysical activity. Campanha et al. (2015) reported a three-year study on the occurrence of pharmaceuticals and hormones in surface waters of a central urban region of São Paulo State of Southeast Brazil (the Monjolinho River in São Carlos). The most frequently detected compounds at highest concentrations were caffeine, paracetamol, and atenolol (maximum concentrations $129.585\mu\text{g/L}$, $30.421\mu\text{g/L}$, and $8.199\mu\text{g/L}$, respectively), while the hormones estrone and 17- β -estradiol were the least detected, at levels up to 0.0148 ng/L . The results also showed that there was an increasing trend in concentrations of most of the compounds along the river course, especially downstream of the river where there are discharges of both wastewater treatment plant effluent and raw sewage from a particular region of São Carlos city. The concentrations of contaminants were higher during dry periods as a result of the decline in the water levels. A decrease of concentrations occurred near the river mouth at different extents for each compound, being high for caffeine and atenolol and very low for carbamazepine and diclofenac.

The first nationwide survey of emerging contaminants in Brazilian waters has been published by Machado et al. (2016). One hundred drinking water samples were investigated in 22 Brazilian State capitals during two campaigns between July and September of 2011 and 2012. In addition, seven source water samples from two of the most populous regions of the country were evaluated. The analytical monitoring showed that caffeine, triclosan, atrazine, phenolphthalein and bisphenol A were found in at least one of the samples collected in the two sampling campaigns. Caffeine and atrazine were the most frequently detected substances in both drinking

and source water, in agreement with the results published by Campanha et al. (2015). Caffeine concentrations in drinking water ranged from 1.8 ng/L to values above 2.0 µg/L while source-water concentrations varied from 40 ng/L to approximately 19 µg/L. The frequency of detection of caffeine corresponded to 93%, corresponding to a higher frequency than those found in similar Spanish and Chinese studies (<88% in the two cases). For atrazine, concentrations were found ranging from 0.002 to 0.006 µg/L in drinking water and at concentrations of up to 0.15 µg/L in source water. The levels of atrazine were between two and three orders of magnitude below the maximum limit established by the Brazilian regulations (2.0 µg/L is the authorized value in drinking and surface water). Atrazine was found in 75% of the drinking water samples collected in both campaigns. Only two other substances, triclosan and phenolphthalein, were detected in drinking water samples. Emerging contaminants such as pharmaceuticals, hormones, and industrial products were not detected in the samples. Caffeine, atrazine, and bisphenol were detected in all seven surface samples. The highest concentrations of caffeine and bisphenol A detected were 18.828 µg/L and 0.011 µg/L in a reservoir connected to the Rio Grande River. Machado et al. (2016) concluded that in both drinking and source waters, caffeine reached concentration values from a few ng/L to µg/L, depending on the region of collection. The detection frequency of caffeine in drinking water was higher than other values reported in the literature. Its widespread presence in samples of treated water (detected in 93% of samples) suggested the presence of domestic sewage in the source water, considering that caffeine is a compound of anthropogenic origin, exhibiting great residence time in the environment and low susceptibility to degradation. Caffeine can be proposed as an indicator of contamination by sewage (Campanha et al. 2015; Machado et al. 2016).

More recently, Montagner et al. (2019) summarized the results of 10 years of analyses carried out in the State of São Paulo that has one of the highest population densities in Brazil and intense agricultural and industrial activities. In this work, 58 compounds (9 hormones, 14 pharmaceuticals and personal care products, 8 industrial compounds, 17 pesticides and 10 illicit drugs) were determined in 708 samples between 2006 and 2015. Samples were collected in 13 cities in the State of São Paulo (drinking water), in 10 rivers (surface waters) and 4 reservoirs, and in 5 municipal wastewater treatment plants (wastewaters). The frequency of detection of each substance strongly varied among samples. The average concentration for the synthetic contraceptive 17- α -ethynylestradiol was 777 ng/L. The highest frequencies of detection in surface water were in the following order: caffeine (97%), atrazine (69%), triclosan (43%), estriol (31%), estrone (28%) and testosterone (13%). Caffeine levels varied from 19 to 127,000 ng/L, reflecting the differences between sampling points according to their anthropogenic impact, similar to the results reported by Campanha et al. (2015) in the Monjolinho River, the main water body of São Paulo. Bisphenol A was quantified in 145 samples in a wide range of concentrations, between 2 and 13,016 ng/L. Cocaine and its metabolite (benzoylecgonine) were detected in 53% (average concentration: 10 ng/L) and 84% (average concentration: 133 ng/L) of the samples, respectively. For drinking water (289 samples between 2007 and 2015), bisphenol A was the most frequently analyzed substance

(258 samples, average concentration 23 ng/L and a maximum concentration of 178 ng/L) followed by caffeine (231 samples, average concentration of 548 ng/L), testosterone (215 samples, average concentration of 3 ng/L), 4-n-nonylphenol (189 samples, average concentration of 114 ng/L), triclosan (186 samples with concentrations ranging from 2 to 37 ng/L), and atrazine (179 samples, average concentration of 36 ng/L). All hormones were analysed in more than 100 samples, but the frequencies of detection were between 0 and 4%, the maximum concentration being 125 ng/L for estriol. Other substances such as diethylphthalate and octylphenols were found in drinking water. From the 33 groundwater samples collected, the most prevalent substance was atrazine (86% of samples 6/7) followed by caffeine (55%, 17/31) and bisphenol A (50%, 16/32). Finally, a preliminary risk assessment for aquatic life protection identified potential risks for caffeine, paracetamol, diclofenac, 17- α -ethynylestradiol, 17- β -estradiol, estriol, estrone, testosterone, triclosan, 4-n-nonylphenol, bisphenol A, atrazine, azoxystrobin, carbendazim, fipronil, imidacloprid, malathion and tebuconazole. As expected, raw wastewaters had high levels of concentrations, with the highest values reported for caffeine, benzoylecgonine and cocaine. Peña-Guzmán et al. (2019) reported similar findings. However, even after treatment, some emerging contaminants were still detected at relatively high concentrations in the treated wastewaters. Montagner et al. (2019) suggested that the wastewater treatment technology used in São Paulo State (Brazil) was not effective for the elimination of most of the target compounds. Campanha et al. (2015) also indicated that the main source of emerging contaminants in the river was related to the discharges from wastewater treatment plants. Drinking water criteria were available only for 22 compounds of those studied by Montagner et al. (2019) and for those substances no adverse effects were expected at the concentrations found, except for 17- β -estradiol and atrazine. Montagner et al. (2019) concluded that, among the 58 studied contaminants, caffeine, estrone, 17- α -ethynylestradiol, 17- β -estradiol, bisphenol A, atrazine, carbendazim, fipronil, malathion and imidacloprid were underlined as substances of priority concern, due to the high frequency of detection above water quality criteria. Another important conclusion was the fact that caffeine and benzoylecgonine were pertinent anthropogenic indicators, especially for regions highly inhabited and with poor sanitation structure. Since the cocaine metabolite can persist in the aquatic environment even after 2 weeks from the discharge, this substance may be a reliable marker of contamination of surface water and also for drinking water.

Caldas et al. (2019) studied the presence of 33 pesticides in surface and drinking water in Southern Brazil (data of four-year monitoring; 48 samples) and reported that 30 substances were identified and quantified, whereas four compounds (tebuconazole, atrazine, azoxystrobin, clomazone) were identified in more than half of the samples. Five class of pesticides, *i.e.*, triazines, triazoles, carbamates, strobilurins and imidazolinones, were identified. Among them, the herbicide atrazine was the most frequently detected pesticide, with concentrations ranging from 0.005 μ g/L to 0.049 μ g/L in drinking water and from 0.005 μ g/L to 0.037 μ g/L in surface water. In this study, atrazine was identified as a priority substance amongst those that pose a significant risk to the aquatic environment. The authors hypothesized a relationship

with agricultural activities because atrazine is widely used in Brazil as a weed-killer in the cultivation of crops (rice, soybeans, sugarcane, corn). Other pesticides detected in the whole 4-year monitoring period were the fungicide azoxystrobin (concentrations ranging from 0.041 $\mu\text{g/L}$ to 0.233 $\mu\text{g/L}$ and from 0.1 $\mu\text{g/L}$ to 0.192 $\mu\text{g/L}$ in surface and drinking water, respectively), the herbicide clomazone (identified in more than 50% of the samples at concentrations up to 0.164 $\mu\text{g/L}$) and the triazole molecules such as cyproconazole, difenoconazole, epoxiconazole, propiconazole and tebuconazole (identified in more than 80% of the samples at concentrations up to 0.46 $\mu\text{g/L}$). Triazole substances are used not only as fungicides in agriculture and as biocides but also as antifungal agents in human and veterinary pharmaceuticals. Caldas et al. (2019) concluded that the concentrations detected (ranging from 0.004 to 1 $\mu\text{g/L}$) were of the same order of magnitude as those detected in other regions of Brazil. The concentrations of the target pesticides detected in drinking water in the city of Rio Grande were below the limits established by the Brazilian legislation and by the World Health Organization. However, considering the values established by the European Union for individual pesticides in drinking water of 0.1 $\mu\text{g/L}$, the maximum values detected for some pesticides (*e.g.*, azoxystrobin, cyproconazole, clomazone, quinclorac and tebuconazole) exceeded this limit.

Numerous Brazilian studies come to the conclusion that, in many Brazilian regions that suffer from poor sanitary conditions, there is an urgent need to study the occurrence of emerging contaminants in natural waters. Those reports show the importance of continuous monitoring of this type of substances and other water parameters for proper water management. The use of pesticides should be minimized, and if necessary, agricultural practices should be modified. Another important action should focus on improving the treatment processes applied in the municipal wastewater treatment plants (Sodré et al. 2018; Montagner et al. 2019; Peña-Guzmán et al. 2019; Caldas et al. 2019; Starling et al. 2019).

In conclusion, the extent of industrial pollution is not yet well known in Latin America, as discharges are poorly monitored and rarely aggregated at the national level. Although some domestic and industrial wastewater is treated on-site, few data are available and aggregated for national and regional assessments, unlike in Europe. Many countries lack the capacity to collect and analyze the data needed for a comprehensive assessment. Reliable monitoring of water quality is nevertheless essential to guide investment priorities. It is also important for assessing the status of aquatic ecosystems and the need to protect and/or restore them.

1.6 Conclusion

Emerging substances are a diverse group of chemical and biological agents, which possible consequent health and ecological effects are of increasing concern. Many chemical substances are non-biodegradable or refractory, toxic or carcinogenic, some are regulated, and others have been banned for several years but are still found in the environment. As described in this chapter, emerging substances are present in

water resources around the world, from all the 5 continents, with specific examples given from China, Portugal, Mexico, Colombia and Brazil, raising concerns for human health and the environment. The list of substances and products is exceptionally long: pesticides, pharmaceuticals, hormones and steroids, cosmetics, personal care products, illicit drugs, surfactants, cleaning products, industrial formulations and chemicals, food additives, food packaging, metalloids, rare earth elements, nanomaterials, microplastics and pathogens. Due to insufficient chemical treatment abatement, the discharge of effluents from municipal wastewater treatment plants is an important route for the appearance of chemical substances in the aquatic environment. One of the levers for action concerns the improvement of the operation of wastewater treatment plants, such as, for example, the installation of tertiary treatment systems in order to move towards zero pollution discharge. However, attention must be paid to all sources of water pollution, such as those resulting from the intensive use of pesticides.

We are all both concerned and worried about water pollution. The multifaceted pollution resulting from our lifestyles and consumption patterns and the worrying synergies that can occur in wastewater due to the multiplicity of pollutants (pathogens, emerging substances, metals, etc.) are major threats to this vital element that is water, with consequences also for the environment and human health. However, the behavior of emerging substances in the environment and their effects on all living organisms remain largely unknown. We must (continue) to mobilize to protect this resource.

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