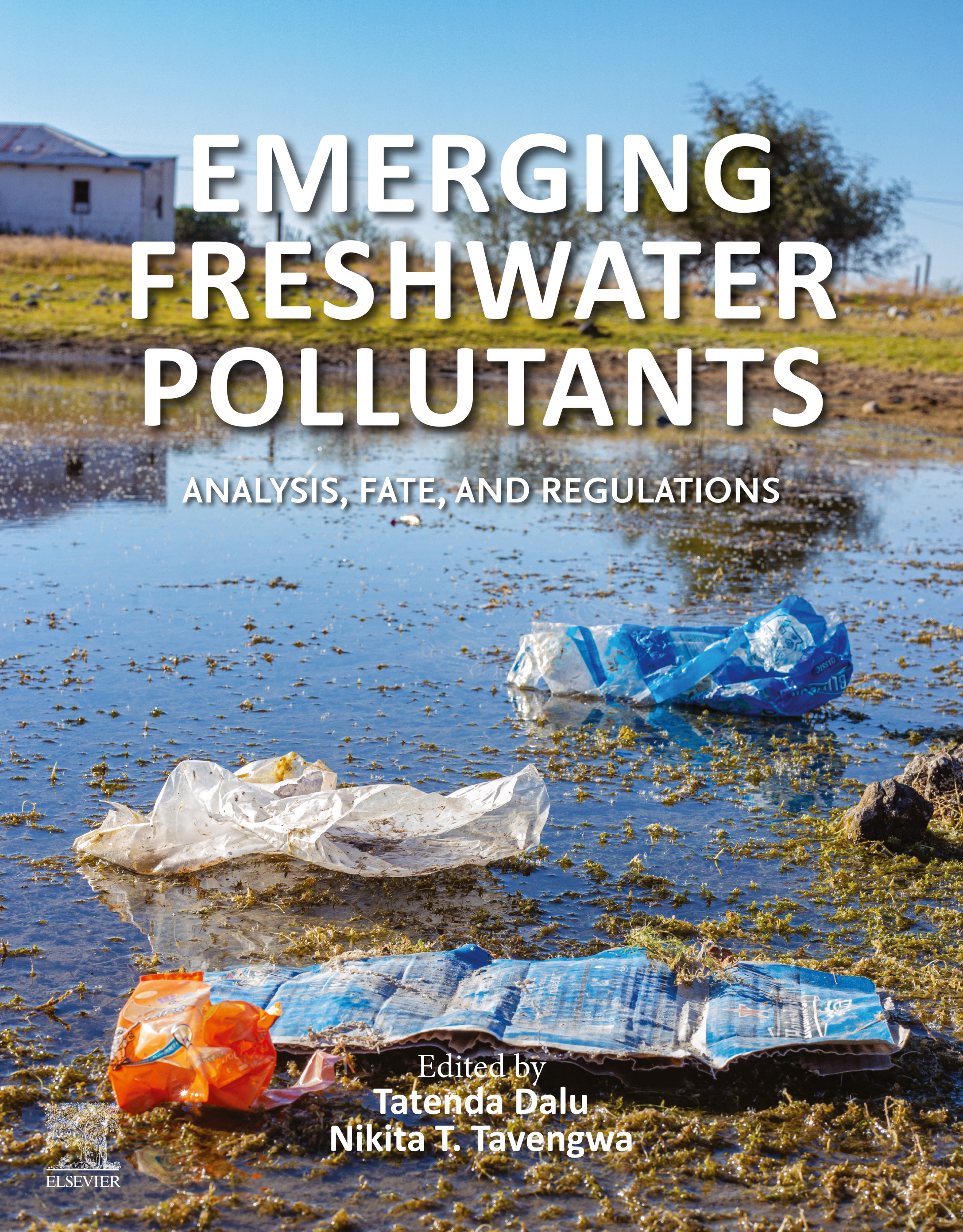

EMERGING FRESHWATER POLLUTANTS

ANALYSIS, FATE, AND REGULATIONS

Edited by
Tatenda Dalu
Nikita T. Tavengwa

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Analysis, Fate, and Regulations

Edited by

TATENDA DALU
School of Biology and Environmental Sciences, University of Mpumalanga, Nelspruit, South Africa; South African Institute for Aquatic Biodiversity, Makhanda, South Africa

NIKITA T. TAVENGWA
Department of Chemistry, University of Venda, Thohoyandou, South Africa

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1. Plastic polluted Khakhea Bray pan, South Africa (credit Chad Keates)

Back cover (from top)

1. Polluted Bloukrans River, Makhanda, South Africa (credit Tatenda Dalu)
2. Polluted Bloukrans River showing pollution forming due to bacterial activity, Makhanda, South Africa (credit Tatenda Dalu)
3. Fannie Masina collecting plankton samples from a pan in Khakhea Bray pan, South Africa (credit Chad Keates)
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6. Iron nanoparticles made from coffee extract (credit Nokwanda Ngema)

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Dedication

This book is dedicated to our spouses, Mwazvita Tapiwa Beatrice Dalu and Noleen Shamiso Tavengwa, including our daughters. They supported our efforts throughout the book editing process as we had to work long hours into the night and weekends to ensure the completion of the book.

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Contributors

R. Fanelwa Ajayi SensorLab, Chemistry Department, University of the Western Cape, Bellville, South Africa

Rana Al-Jaibachi Ecology and Evolutionary Biology, School of Biological Sciences, University of Reading, Reading, England, United Kingdom

Simone Barry SensorLab, Chemistry Department, University of the Western Cape, Bellville, South Africa

Taurai Bere Department of Freshwater and Fishery Science, Chinhoyi University of Technology, Chinhoyi, Zimbabwe

Amanda Callaghan Ecology and Evolutionary Biology, School of Biological Sciences, University of Reading, Reading, England, United Kingdom

Adroit T. Chakandinakira Lake Kariba Fisheries Research Institute, Zimbabwe Parks and Wildlife Management Authority, Kariba, Zimbabwe

Luke Chimuka Molecular Sciences Institute, School of Chemistry, University of Witwatersrand, Johannesburg, South Africa

Joseph Clokey Queensland Alliance for Environmental Health Sciences (QAEHS), The University of Queensland, Woolloongabba, QLD, Australia

Joyce Cristale School of Technology, University of Campinas—UNICAMP, Limeira, Sao Paulo State, Brazil

Ygor J.A.B. da Silva Departamento de Agronomia, UFRPE—Universidade Federal Rural de Pernambuco, Recife, Pernambuco, Brazil

Yuri J.A.B. da Silva Departamento de Agronomia, UFPI—Universidade Federal do Piauí, Bom Jesus, Piauí, Brazil

Tatenda Dalu School of Biology and Environmental Sciences, University of Mpumalanga, Nelspruit; South African Institute for Aquatic Biodiversity, Makhanda, South Africa

Jéssyca Ferreira de Medeiros Department of Analytical Chemistry, Institute of Chemistry, University of Campinas, Campinas, SP, Brazil

Eder de Vilhena Araújo Department of Analytical Chemistry, Institute of Chemistry, University of Campinas, Campinas, SP, Brazil

Simiso Dube Department of Chemistry, University of South Africa, Florida, South Africa

Juliana A. Galhardi Department of Chemistry, University of Montreal, Montreal, QC, Canada

Sara G. Gorji Queensland Alliance for Environmental Health Sciences (QAEHS), The University of Queensland, Woolloongabba, QLD, Australia

Leandro W. Hantao Department of Analytical Chemistry, Institute of Chemistry, University of Campinas, Campinas, SP, Brazil

Sayyed H. Hashemi Department of Marine Chemistry, Faculty of Marine Science, Chabahar Maritime University, Chabahar, Iran

Darryl W. Hawker Queensland Alliance for Environmental Health Sciences (QAEHS), The University of Queensland, Woolloongabba; Griffith School of Environment and Science, Griffith University, Nathan, QLD, Australia

Tatenda A. Kajau Institute for Nanotechnology and Water Sustainability, University of South Africa, Pretoria, South Africa

Sarit L. Kaserzon Queensland Alliance for Environmental Health Sciences (QAEHS), The University of Queensland, Woolloongabba, QLD, Australia

Massoud Kaykhaii Department of Chemistry, Faculty of Sciences, University of Sistan and Baluchestan, Zahedan, Iran

Temesgen G. Kebede Department of Chemistry, University of South Africa, Florida, South Africa

Sinegugu Khulu Molecular Sciences Institute, School of Chemistry, University of Witwatersrand, Johannesburg, South Africa

Isaac Kudu School of Chemistry and Physics, University of KwaZulu-Natal, Westville Campus, Durban, South Africa

Ramesh B. Kumar Center for Process Research and Innovation (CPRI), Dr. Reddy's Institute of Life Sciences, University of Hyderabad Campus, Hyderabad, Telangana, India

Karen Luko-Sulato Instituto de Geociências e Ciências Exatas, IGCE, UNESP—Universidade Estadual Paulista, Rio Claro, São Paulo, Brazil

Lawrence M. Madikizela Department of Chemistry, Durban University of Technology, Durban, South Africa

Tinotenda Mangadze School of Life Sciences, University of KwaZulu-Natal, Durban, South Africa

Geaneth P. Mashile Department of Chemical Sciences, University of Johannesburg, Johannesburg; Department of Science and Innovation-National Research Foundation South African Research Chair Initiative (DSI-NRF SARChI): Nanotechnology for Water, University of Johannesburg, Doornfontein, South Africa

Cassiana C. Montagner Department of Analytical Chemistry, Institute of Chemistry, University of Campinas, Campinas, SP, Brazil

Brenda Moodley School of Chemistry and Physics, University of KwaZulu-Natal, Westville Campus, Durban, South Africa

Babra Moyo Department of Chemistry; Department of Food Science and Technology, University of Venda, Thohoyandou, South Africa

Anele Mpupa Department of Chemical Sciences, University of Johannesburg, Johannesburg; Department of Science and Innovation-National Research Foundation South African Research Chair Initiative (DSI-NRF SARChI): Nanotechnology for Water, University of Johannesburg, Doornfontein, South Africa

Takalani Muluadzi Biotechnology Department, University of the Western Cape, Bellville, South Africa

Nívea C.G. Munin Department of Analytical Chemistry, Institute of Chemistry, University of Campinas, Campinas, SP; Institute of Exact Sciences and Technology, Federal University of Amazonas—UFAM, Itacoatiara, AM, Brazil

Herbert Musarurwa Department of Chemistry, University of Venda, Thohoyandou, South Africa

Tongayi Mwedzi Department of Wildlife Ecology and Conservation, Chinhoyi University of Technology, Chinhoyi, Zimbabwe

Somandla Ncube Department of Chemistry, University of South Africa, Florida, South Africa

Nzumbululo Ndou SensorLab, Chemistry Department, University of the Western Cape, Bellville, South Africa

Sol S. Nety Department of Chemistry, University of South Africa, Florida, South Africa

Nokwanda Ngema SensorLab, Chemistry Department, University of the Western Cape, Bellville, South Africa

Mathew M. Nindi Department of Chemistry, University of South Africa, Florida, South Africa

Mulisa Nkuna Biotechnology Department, University of the Western Cape, Bellville, South Africa

Azile Nqombolo Department of Chemical Sciences, University of Johannesburg, Johannesburg; Department of Science and Innovation-National Research Foundation South African Research Chair Initiative (DSI-NRF SARChI): Nanotechnology for Water, University of Johannesburg, Doornfontein, South Africa

Philiswa N. Nomngongo Department of Chemical Sciences, University of Johannesburg, Johannesburg; Department of Science and Innovation-National Research Foundation South African Research Chair Initiative (DSI-NRF SARChI): Nanotechnology for Water, University of Johannesburg, Doornfontein, South Africa

Sphamandla Nqunqa SensorLab, Chemistry Department, University of the Western Cape, Bellville, South Africa

Gershom M. Ntshani Department of Chemistry, School of Mathematics and Natural Science, University of Venda, Thohoyandou, South Africa

Srinivas Oruganti Center for Process Research and Innovation (CPRI), Dr. Reddy's Institute of Life Sciences, University of Hyderabad Campus, Hyderabad, Telangana, India

Vishalan Pillay School of Chemistry and Physics, University of KwaZulu-Natal, Westville Campus, Durban, South Africa

Tessia Rakgotho SensorLab, Chemistry Department, University of the Western Cape, Bellville, South Africa

Cornelius Rimayi Department of Water and Sanitation, Resource Quality Information Services, Pretoria, South Africa

Edmond Sanganyado Institution of Marine Science, Guangdong Provincial Laboratory of Marine Biotechnology, Shantou University, Shantou, Guangdong, China

Leandro M. Santos Instituto de Química, USP—Universidade de São Paulo, São Paulo, São Paulo, Brazil

Shirley K. Selahle Department of Chemical Sciences, University of Johannesburg, Johannesburg; Department of Science and Innovation-National Research Foundation South African Research Chair Initiative (DSI-NRF SARChI): Nanotechnology for Water, University of Johannesburg, Doornfontein, South Africa

Saikat Sen Center for Process Research and Innovation (CPRI), Dr. Reddy's Institute of Life Sciences, University of Hyderabad Campus, Hyderabad, Telangana, India

Nikita T. Tavengwa Department of Chemistry, School of Mathematics and Natural Science, University of Venda, Thohoyandou, South Africa

Velaphi Thipe Laboratório de Ecotoxicologia—Centro de Química e Meio Ambiente—Instituto de Pesquisas Energéticas e Nucleares (IPEN)—Comissão Nacional de Energia Nuclear—IPEN/CNEN-SP, São Paulo, Brazil

Rahul K. Varma Center for Process Research and Innovation (CPRI), Dr. Reddy's Institute of Life Sciences, University of Hyderabad Campus, Hyderabad, Telangana, India

Rory Verhagen Queensland Alliance for Environmental Health Sciences (QAEHS), The University of Queensland, Woolloongabba, QLD, Australia

B.C. Vizioli Department of Analytical Chemistry, Institute of Chemistry, University of Campinas, Campinas, SP, Brazil

Lauren N.M. Yabuki Institute of Geosciences and Exact Sciences (IGCE), Sao Paulo State University—UNESP), Rio Claro, SP, Brazil

Lewis D. Yardy Ecology and Evolutionary Biology, School of Biological Sciences, University of Reading, Reading, England, United Kingdom

Foreword

It is my pleasure to be invited to write this foreword for the book "Emerging Freshwater Pollutants: Analysis, Fate, and Regulations." The book has 20 chapters divided into the following three main themes:

- Monitoring techniques, current analytical approaches, and instrumental analyses
- Fate and occurrence of emerging pollutants in aquatic systems
- Management policies and legislations on emerging pollutants

Freshwater systems are currently experiencing a lot of pressure due to the diverse emerging pollutants being released into them. The situation is compounded by the fact that many countries of the world face a freshwater-scarce situation. This is being made worse by climate change, especially global warming. To understand the extent of freshwater pollution, modern techniques are used to extract the target compounds, and to study their transport and fate within aquatic systems.

This book gives practical detail of the principles and applications of the currently most widely used extraction techniques to study the presence and amounts, transport, and fate of freshwater pollutants. These techniques include liquid phase micro-extraction, solid-phase micro-extraction, and headspace miniaturization. These are written in a practical way for easy understanding to benefit even entry-level researchers who intend to use such techniques, as their principles are well-described in the relevant chapters.

Wastewater treatment plants are now seen as the major sources of some of these emerging freshwater pollutants. The book also gives a concise overview of the behavior of these emerging freshwater pollutants during the wastewater treatment process. Details of various emerging freshwater pollutants are discussed, including their sources, physical characteristics, transport, and fate. The physicochemical characteristics of pollutants often govern their transport and fate, including toxicity, in freshwater systems. Examples of such freshwater pollutants that are discussed include microplastics, pharmaceuticals and personnel care products, azo dyes, flame retardants, rear earth elements, antiretrovirals (ARVs), and disinfection by-products. All of the investigated model pollutants discussed in this book are emerging contaminants, meaning that they are rarely monitored in all environmental compartments, including freshwater systems.

To minimize the contamination of freshwater systems with emerging pollutants, besides the use of environmental remediation technologies, policy interventions are important by various national governments and international environmental regulatory bodies. Some of these policy documents are discussed, especially as to how they can effectively contribute to reducing the effects on freshwater systems by emerging pollutants. The book ends by giving insights into numerous challenges and future directions for freshwater research into emerging pollutants. Thus, for people in academia, research institutions, and entities, as well as environmental scientists interested in issues related to freshwater contamination by emerging pollutants, this book represents a practical guide and an important educational tool. It provides straightforward and concise information on issues related to scientific and management issues concerning freshwater emerging pollutants. It has been edited by two experienced scholars, Dr. Tatenda Dalu from the University of Mpumalanga and South African Institute for Aquatic Biodiversity, South Africa, and Dr. Nikita Tawanda Tavengwa from the University of Venda, South Africa. To date, the two editors have published a combined total of over 200 scientific articles in the fields of freshwater issues and analytical extractive techniques, respectively. It is the combination of their research fields that is reflected in this book that makes it a cutting-edge and synthesized reading. This book recognizes that water chemistry, emerging freshwater pollutants, and water policy management are interdependent disciplines. More so, noting that the lead authors for the 20 chapters are also respected researchers in their fields is a plus for this book.

Chimuka

Luke Chimuka (Professor in Environmental Analytical Chemistry)
School of Chemistry
University of the Witwatersrand
Johannesburg, South Africa

Acknowledgments

The reason why we wrote this book is highlighted in the Introduction of Ecology of Freshwaters 4th edition book by Brian Moss: "*Textbooks usually sound a bit pompous. It's in their nature as the factual 'text': that which has to be known. Yet some, at least, come from the passions of their authors wanting to pass on their enthusiasms, reflected in the facts. But the relative importance of facts changes as understanding grows and the facts only increase in number as time passes. A huge number appear in articles, books, and websites on almost everything, and although there is a lot of repetition, sometimes direct, sometimes just new examples of general principles, and sometimes recycling, by newer methods, of ideas that originated long ago, the amount is nonetheless daunting. Most of the scientific literature is written as if no one wants to communicate anything, anyway. The writing is pompous, self-serving, full of unnecessary jargon, and distinctly off-putting. Quite a lot of it is deceptive in that something is written as if it is an entirely new revelation when this is far from the case…. Not surprisingly the population, in general, cannot be much bothered with scientific findings. The positive side is that when one teases out the meaning, it is completely fascinating!*" This book on emerging freshwater pollutants is based on our numerous discussions with colleagues on the need to have a book focusing on emerging freshwater pollutants within the tropical region of the world which currently lacks such material and information. Therefore, the book presents a break of information from North America and Europe and mostly focuses on Africa, Asia (including the Middle East), and South America written by some of the leading and emerging scientists in their respective fields. Thus, the editors sincerely appreciate the contributions of every chapter author who helped ensure that this book project was a great success. We like to thank the different colleagues from around the world who reviewed chapters in this book: Edmond Sanganyado, Lawrence M. Madikizela, Rabelani Mudzielwana, Dumisani Khosa, Hamed O. Odountan, Herbert Musarurwa, Mphilisi Mahlambi, Babra Moyo, Linton Munyai, Cassiana C. Montagner, Bereki S. Batlokwa, George Mosotho, Luke Chimuka, Samuel Chigome, Ross N. Cuthbert, Holly A. Nel, B Ramesh Kumar, Philiswa Nomngongo, Danilo Russo, Kenneth Otieno K'oreje, Barbara Moyo, Herbet Musarurwa and Glynn Pindihama. We would also like to recognize the support from Louisa Munro, Danielle Mclean, Alexandra Ford, Christopher Hockaday, and Kumar Anbazhagan from Elsevier for their editorial support and help to transform the various manuscripts into a finished book product. Finally, to our caring, loving, supportive, and ever-patient spouses, Mwazvita Tapiwa Beatrice Dalu and Noleen Shamiso Tavengwa: our deepest gratitude for your encouragement when the times got rough are much appreciated and duly noted plus you didn't mind us working late into the night and during weekends. Our heartfelt thanks to you for the delicious meals while we were busy typing away from our laptops. It was a great comfort and relief to know that you were willing to provide household activities management while we completed our work.

CHAPTER

1

Introduction to emerging freshwater pollutants

Nikita T. Tavengwa and Tatenda Dalu

1.1 Introduction

Water, an essential source for life on Earth, is one of the most vulnerable environmental compartments; consequently, its pollution has become a matter of utmost interest and concern worldwide. This is as a result of the increase of anthropogenic activities (e.g., manufacturing, application of pesticides, herbicides and fertilizers, discharge or disposal of untreated waste), especially through the production and use of chemicals known as "emerging pollutants" and/or "contaminants of emerging concerns" (Tang et al., 2019). Emerging pollutants can be understood in a broad sense as any synthetic or naturally-occurring chemicals or any microorganisms that are not commonly monitored or regulated in the environment with potentially known or suspected adverse ecological and human health effects (Arguello-Pérez et al., 2019; Boxall, 2012). These emerging pollutants most of the time are not necessarily new chemicals but can be substances that have been present in the environment for a long time but whose presence and significance are only now being recognized. It is important to note that there is no internationally agreed definition for emerging contaminants or pollutants, and several definitions have been proposed (Boxall, 2012). These contaminants include mainly chemicals found in pharmaceuticals and personal care products (Madikizela et al., 2022, Chapter 10), pesticides (Montagner et al., 2022, Chapter 12), industrial and household products (Vizioli et al., 2022, Chapter 14), metals (Galhardi et al., 2022, Chapter 17), surfactants, industrial additives, and solvents (Cristale, 2022, Chapter 16; Hashemi and Kaykhaii, 2022, Chapter 15). Many of them are used and released continuously into the environment even in very low quantities and some may cause chronic toxicity, endocrine disruption in humans and aquatic wildlife, and the development of bacterial pathogen resistance. For example, direct pathways for pharmaceuticals, urban and industrial pollutants to reach groundwater include leaking sewers, discharge of wastewater treatment effluent (directly to ground or to surface water), landfill leachate, leaking storage tanks, and other discharges to the ground that bypass the soil zone, such as septic tanks (Stuart et al., 2012; Fig. 1.1).

The scientific knowledge and understanding of potential human and environmental health risks posed by emerging freshwater pollutants are still very scarce particularly within the developing world, as well as on their presence in water resources and wastewater and their pathways and accumulation in the environment (Sanganyando and Kajau, 2022). Data for emerging pollutants is often very scarce mostly due to detection methods that may be nonexistent or in the early stage of development for them to detect these pollutants in the natural environment. Most emerging pollutants are not regulated in environmental, water quality, and wastewater discharge regulations (Mashile et al., 2022; Sanganyando and Kajau, 2022, Chapter 7). Hence, there is an urgent need to strengthen scientific knowledge particularly with the developing world that is very much far lagging in terms of research, and adopt appropriate technical and policy approaches to monitor emerging pollutants in water resources and wastewater (Ajayi et al., 2022), assess their potential human health and environmental risks, and prevent and control their disposal to water resources and the environment (https://en.unesco.org/emergingpollutantsinwaterandwastewater). As alluded to in the abstract, these contaminants are discussed as separate chapters of this book; microplastics (Yardy et al., 2022, Chapter 9), pharmaceuticals and personal care products (Madikizela et al., 2022, Chapter 10), antibiotics (Ntshani and Tavengwa, 2022, Chapter 11), pesticides (Montagner et al., 2022), antiretrovirals

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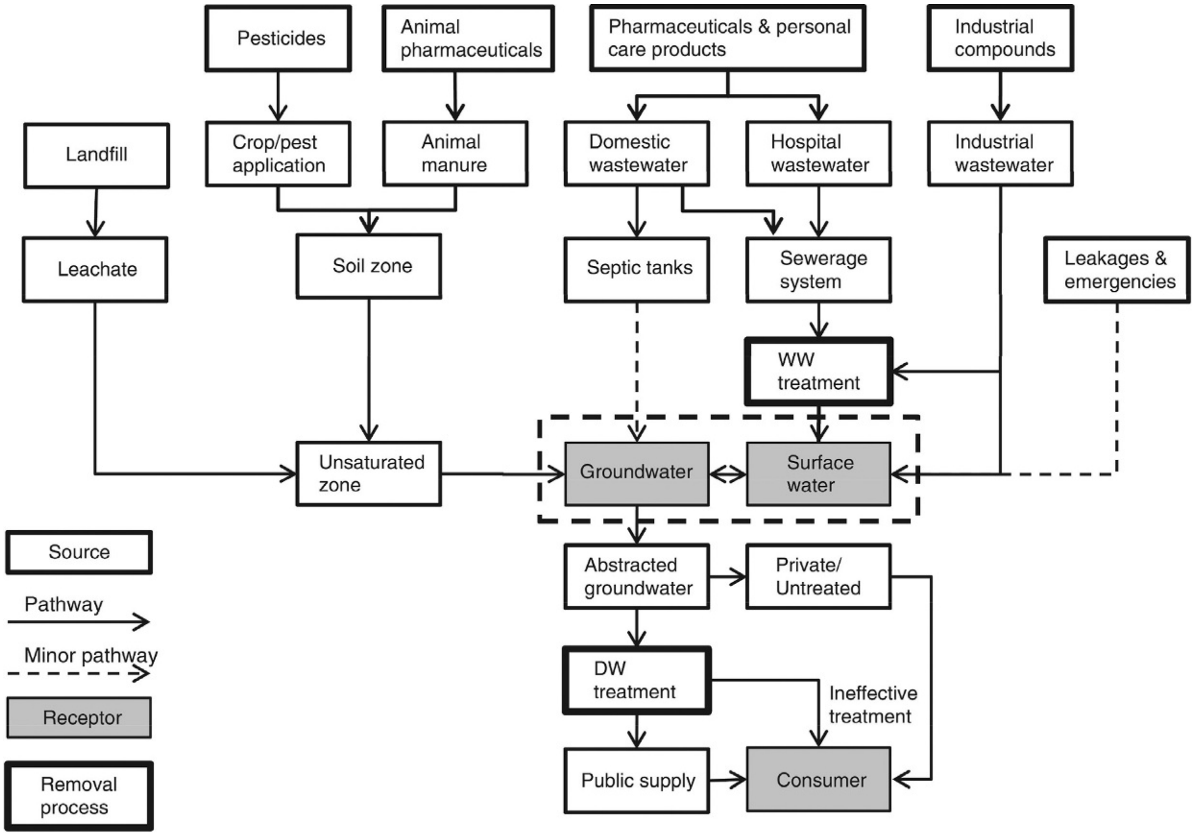

FIG. 1.1 Sources and pathways for emerging pollutants to reach various receptors *(in gray). Based on Stuart, M., Lapworth, D., Crane, E., Hart, A., 2012. Review of risk from potential emerging contaminants in UK groundwater. Sci. Total Environ. 416, 1–21.*

(Moodley et al., 2022, Chapter 13), disinfection by-products (Vizioli et al., 2022), azo dyes (Hashemi and Kaykhaii, 2022), flame retardants (Cristale, 2022), rare earth elements and radionuclides (Galhardi et al., 2022) and nanoparticles (Ajayi et al., 2022, Chapter 18). These classes of compounds are collectively known as emerging pollutants because they are not routinely monitored in all environmental compartments. More than 700 emerging pollutants have been categorized into 20 classes only in the European aquatic environment. There exists a gap in the knowledge on their fate, behaviors, and effects, as well as on treatment technologies for their efficient removal (Gogoi et al., 2018).

This book is intended as a practical guide and important educational tool to scientific and management issues concerning freshwater emerging pollutants within the tropical regions. It is written in the most practical terms which are easy to understand, with numerous relevant examples and case studies that cover complex scientific and management aspects of water quality assessments. It is demonstrated in this book that water chemistry, emerging freshwater pollutants, and management are interdependent disciplines.

1.2 The fate of emerging pollutants in aquatic systems

The distribution of pollutants to various environmental compartments is usually through leaching, agricultural runoffs, and air particulates (Schulz et al., 2020). This distribution results in their presence in surface water, groundwater, and wastewater treatment plants (WWTPs). Emerging pollutants can be discharged into any of the environmental compartments which include air, soil, and sediments. One major concern is when they are discharged into water bodies as most of them end up in aquatic systems. These compounds can even partition between the aqueous phase and the sediments. Some of them might end up accumulating in the food chain and cause various diseases. They have the potential to enter the environment and cause adverse ecological/human health effects (Geissen et al., 2015). The behavior of different emerging pollutants after their entry into the environment is very important. Their thermal stability and their partitioning behavior in different environmental compartments (e.g., water sediments, plants, and water) were thoroughly discussed, regarding their physicochemical properties (Sanganyando and Kajau, 2022). The effect of their stability and their intactness to environmental conditions such as exposure to sunlight (photosensitivity) was also discussed by the same authors.

1.3 Treatment in wastewater treatment plants

Most of the time, emerging pollutants from domestic, industrial, and agricultural activities end up in WWTPs. The mandate of these WWTPs is to treat (clean) water laden with potential harmful analytes such as emerging pollutants before discharged back into the environment. This is very important as it safeguards humans and aquatic animals. However, the efficiencies (Comparison of influent and effluent concentration) of WWTPs in developing countries have not been well documented in a single document. For example, WWTPs have been estimated to be one of the point sources of antibiotics (Ntshani and Tavengwa, 2022, Chapter 11). Tran et al. (2018) investigated 60 emerging contaminants in influent, treated effluent, sludge, and biosolids in WWTPs and found out that there was no 100% efficacy. All these issues pertaining to WWTPs are well articulated by Mashile et al. (2022, Chapter 8). Maximum allowable limits by international regulatory bodies and domestically the respective countries where these WWTPs are based are also presented.

1.4 Monitoring techniques

While the remediation, mitigation, and minimization of legacy pollutants is currently a challenging task, new substances are appearing as contaminants of emerging concern. There is therefore a need to monitor these emerging pollutants, which is one of the themes of this book. Monitoring and determination of emerging pollutants in freshwater systems start with sampling. The most commonly used sampling approach is grab sampling when sample representatives are collected and transported to laboratories where further treatment and analysis is done (Burke et al., 2016; Dong et al., 2016). However, there are several limitations to this commonly used approach which are discussed in detail by Mwedzi et al. (2022, Chapter 2) and Kaserzon et al. (2022, Chapter 3). Other researchers found it cheap to use the already existing biota which will have bioaccumulated the emerging pollutant of interest (Mangadze et al., 2019; Nhiwatiwa et al., 2017; Dalu et al., 2016; M'Erimba et al., 2014). A detailed study on biomonitoring is also given in this book by Mwedzi et al. (2022). These two important sampling techniques which are not grab sampling (Magi et al., 2018; Heidari et al., 2013), has a lot of disadvantages such as giving only the snapshot of the concentrations of emerging pollutants at that particular instance are discussed. On the contrary, passive sampling (Jones et al., 2019; Rimayi et al., 2019) and biomonitoring present concentrations that are averaged over extended periods of times, more than 14 days for passive sampling (Anderson et al., 2014) and the lifetime of the biota and flora organisms in the case of biomonitoring (Oduntan et al., 2016). Regardless of these glaring advantages, most reported sampling techniques are grab sampling since it is a traditional approach. Passive sampling and biomonitoring give more realistic episodic concentrations of analytes under study.

1.5 Laboratory sample pretreatment

After sampling and having the samples in the laboratory, sample treatment is done which includes filtration. Emerging pollutants are found in complex matrices such as sludge and sample pretreatment is required since samples cannot be directly analyzed on analytical instruments. Even in aqueous samples, some form of pretreatment such as filtration has to be done, especially for real samples. At times, physicochemical characterization has to be done such as sample pH, electrical conductivity, total dissolved solids, dissolved oxygen, and total suspended solids, especially when dealing with inorganic species (Matodzi et al., 2020). The overall sample preparation and preconcentration consume almost 95% of the work done in most analyses.

1.6 Analyte extractive techniques

Liquid-liquid extraction and solid-phase extraction are some of the traditional techniques used for isolation and achieving the preconcentration of analytes in the environment. Besides their effectiveness in the extraction of antibiotics, these techniques are associated with some setbacks such as the consumption of high content of organic solvents, expensive and inability to be automated (Khatibi et al., 2020). Thus, it is important to limit these downfalls and be compliant with green analytical chemistry. Depending on the physicochemical characteristics of the emerging pollutant, various other techniques for pretreatment are pursued such as solid-phase miniaturization techniques, liquid-phase miniaturization techniques, and headspace miniaturization techniques have been discussed comprehensively by Kaykhaii and Hashemi (2022, Chapter 4), Kebede et al. (2021, Chapter 5), and Kumar et al. (2022, Chapter 5), respectively. The aim of all these is to simultaneously isolate and preconcentrate the target analytes from the matrix (Dimpe and Nomngongo, 2016). Analytes that are present in trace level can be preconcentrated into small volumes of organic solvents to increase their concentration so that they will be detected with instruments with high detection like ultraviolet (UV) spectrometers. Emerging pollutants normally occur in low concentrations in aquatic environments and their concentrations vary with seasons (dilution effect). Their analysis at trace levels is difficult. Experienced researchers will normally do a preconcentration of them before instrumental analysis. This is a very crucial step in the analysis and determination of trace analytes. If this is not done, there won't be an instrumental response as this concentration will be below detection limits, hence the use of miniaturization discussed above. As concluded by Ntshani and Tavengwa (2022), these miniaturization techniques have more advantages over conventional extraction techniques.

1.7 Management policies and legislations on emerging pollutants

There is a need to have policies and intervention methods to control these emerging pollutants. The need to establish maximum allowable limits is especially important as it is noted that most treatments in WWTPs have poor recoveries of organic pollutants, and large volumes of new emerging analytes are being discharged into water bodies. In this section of the book, governmental legislation regarding institutions and companies which discharge wastewaters with high concentrations of emerging pollutants is discussed by Sanganyando (2021, Chapter 19). In this section, intervention methods to control emerging pollutants and policy formulations are also discussed.

1.8 Conclusion

Some of the challenges posed by emerging pollutants are very diverse not only to freshwater environments but other different habitats such as air, plants, microorganisms, humans, and soil. These emerging pollutants have created research opportunities, but also increase the onus on us to try to manage the impacts that they cause. The problems associated with these emerging pollutants are difficult to deal with in prospect, but by tracking what we know now from the developing world and developing strategies to cope and mitigate impacts, we can chart a course to a future we desire. New strategies are implemented to minimize materials and solvents in laboratories and to develop on-site capabilities and in vivo applications, microextraction techniques have been developed. Lastly, a concluding insightful chapter which ties up all the chapters concerning challenges and future trends of the analysis of emerging pollutants is presented by Tavengwa et al. (2022, Chapter 20). This book demonstrates that these emerging pollutants continuously produce new and urgent challenges to the water and other ecosystems, particularly human health (Fig. 1.2).

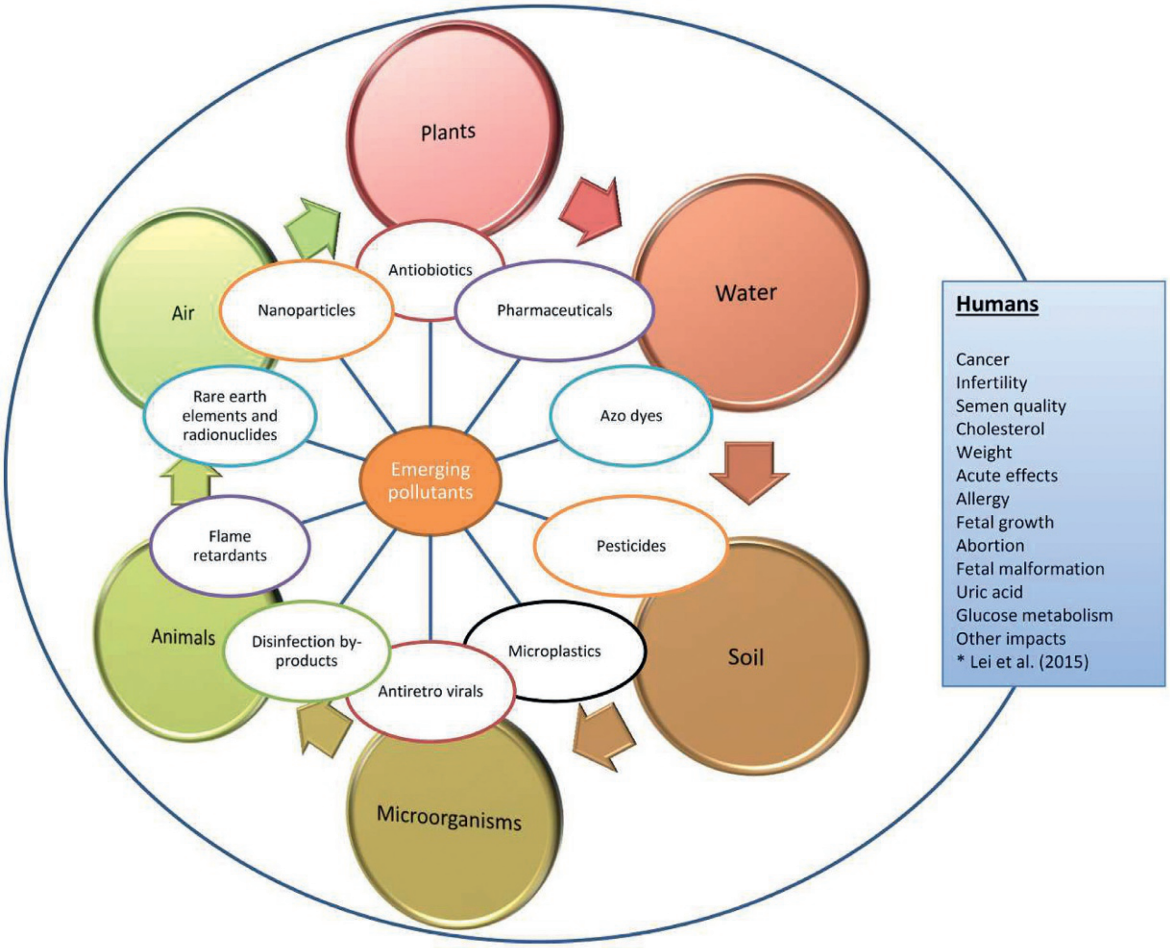

FIG. 1.2 The impact of emerging pollutants acts on soil, air, water, animals, plants, microorganisms, and humans, and exposure to emerging pollutants has potential adverse effects (Lei et al., 2015).

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PART 1

Monitoring techniques, current analytical approaches, and instrumental analyses

CHAPTER

2

Stream biomonitoring: The role of diatoms, macroinvertebrates, and fish

Tongayi Mwedzi, Tinotenda Mangadze, Adroit T. Chakandinakira, and Taurai Bere

2.1 Introduction to biomonitoring

High population densities and multiplicity of industrial and agricultural activities expose most hydrographic basins to heavy and rising environmental impacts especially to pollution by domestic and industrial waste residues (Salomoni et al., 2006; see Tavengwa and Dalu, 2022, chapter 1). This increasing anthropogenic influence on lotic environments that parallels civilization has captured public interest because of the consequent deterioration of water quality, health problems, pest plants and animals, and other problems (Bere, 2007). Several techniques have been employed to assess the ecological integrity of lotic systems; chief among which is biological monitoring.

Aquatic biological monitoring (or biomonitoring) is the use of biotic components to assess changes in the condition of the rivers, lakes, and wetlands (Cairns and Pratt, 1993; Dallas, 1995; Li et al., 2010). Aquatic organisms are good indicators of the condition of the freshwater ecosystems as they are permanently present in water and assessment based on them integrates cumulative effects of changes in the physical and chemical constituents of the water body (Rosenberg and Resh, 1993). Biomonitoring is fast and cost-effective in assessing the effects of environmental stressors on aquatic ecosystems (Bere and Tundisi, 2010; Mangadze et al., 2019). The organisms used in biomonitoring are referred to as bioindicators. Periphyton, fish, and macroinvertebrates are the frequently used bioindicators in lotic systems globally (Bonada et al., 2006; Siziba et al., 2017). Each of these bioindicators has distinct advantages in terms of their sensitivity to different stressors, ability to indicate short- and long-term impacts, taxonomic needs, and sampling equipment requirements (Table 2.1) (Resh, 2007).

Biomonitoring is more established and has a long history in developed (mainly temperate regions) than in developing countries (mainly tropical regions) (Mezgebu, 2020). Biomonitoring in developed countries, therefore, tends to have a long tradition in the approaches used e.g., countries in Eastern Europe have used the Saprobien approach for at least a century (Resh, 2007). Developing countries on the other hand often modify and adopt sampling techniques and indices from developed countries (Bere et al., 2014; Mangadze et al., 2019). In many cases, these transfers are from different geographic regions i.e., temperate to tropical e.g., North America to India (Sivaramakrishnan et al., 1996), the United Kingdom (UK) to Thailand (Mustow 2002). This poses reliability and validity challenges as biomonitoring indices are usually developed based on species assemblages and associated environmental sensitivities within their respective regions (Ochieng et al., 2019). Furthermore, some taxa occur differently (in terms of diversity, abundance, and sometimes the niche they occupy) in different regions. For example, Plecoptera has low diversity in the tropics but high in temperate regions, shredders are rare in the tropics but common in the temperate regions (Mwedzi et al., 2016, 2020; Masese and Raburu, 2017).

Biomonitoring in developing countries is limited by incomplete taxonomical resolution and seldom known sensitivities of many tropical taxa, lack of research funding and priorities, lack of legislation (or lack of implementation), lack of clear political regional policies, and incomplete knowledge on how tropical rivers function (Resh, 2007; Odountan et al., 2018; Mangadze et al., 2019; Mezgebu, 2020). In most cases, there is no biomonitoring supportive decision-making process and there is little state support for research (Mezgebu, 2020). The objective of this chapter is to provide the history, current efforts, challenges, and future direction of biomonitoring with a special focus on

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TABLE 2.1 Advantages and challenges associated with different biotic groups used in aquatic biomonitoring.

Organism	Advantages	Challenges
Diatoms	• High species diversity • Pollution tolerances are well documented in books, webs, and articles. • Useful and quick indicators of eutrophication and increases in turbidity. • Easy and quick to collect (scraping, pipetting, using corers for soft sediments and sand). • Artificial substrates can be used. • Preservation of the siliceous cell wall (paleolimnological applications) and integrative power variable depending on the species	• Taxonomic identification is challenging, hence data collected by non-specialists is not reliable. • There are sampling and enumeration problems with certain groups. • Background life-history information is often lacking for many species • Not very useful for severe organic or fecal pollution. • Poorly sensitive to habitat disturbances • Results obtained are usually difficult to interpret into values meaningful to the general public. • The applicability of diatom indices across geographical regions differs yet most indices are used internationally despite the need for indices to be unique for a region.
Macro-invertebrates	• Many sedentary species can indicate effects at the site of sampling. • Whole communities can respond to change. • Long-lived species can indicate integrated pollution effects over time. • Qualitative sampling is easy. • Simple sampling equipment. • Good taxonomic keys.	• They are difficult and time-consuming to sample, sort, and identify • Quantitative sampling is difficult. • background life-history information is often lacking for many species • The substrate type is important when sampling. • Species may drift in moving waters. • Knowledge of life cycles is necessary to interpret the absence of species. • Results obtained are usually difficult to interpret into values meaningful to the general public. • Ecological status evaluations do not take into consideration the presence of new non-native species in their calculations
Fish	• Methods are well developed. • Immediate physiological effects can be obvious. • Can indicate food chain effects. • Ease of identification.	• Fish are highly mobile- they may migrate to avoid disturbance/pollution. • Sampling gear can be very selective • Seasonal time scales, • Relative tolerance of fish to substances chemically harmful, • Requires more manpower for field sampling. • The lack of ecological and life-history information makes the development of IBI difficult • A high degree of omnivory • Shifts in food items consumed by a given species is often determined by the habitat where the fish occur making assignations to trophic groups difficult and probable species extinctions in the rivers and streams caused by introduced species.

developing countries (which are largely tropical). The chapter also provides a practical guide of how the most commonly used bioindicators i.e., diatoms, macroinvertebrates, and fish can be used in biomonitoring.

2.2 History of aquatic biomonitoring

The idea of using biota as indicators of environmental condition started with Kolkwitz and Marsson (1902, 1908, 1909) who developed the saprobic system in rivers as a measure of the degree of contamination. The term "saprobic system" was derived from the word saprobia which refers to the dependence of an organism on decomposing substances. It used the presence and/or absence of different aquatic taxa particularly bacteria, algae, protozoans, and rotifers to ascertain the degree of contamination by organic pollution primarily sewage (Rolauffs et al., 2004; Monaghan and Soares, 2012). Different organisms (identified at species level) were therefore assigned "saprobic values" based on their pollution tolerance. Values ranged from zero to eight with higher values being for those organisms which are tolerant to pollution.

The saprobic system was criticized for prescribing subjective pollution tolerance limits for organisms, intensive sampling, and non-applicability of the saprobic values to other geographic locations and other types of pollution, e.g., inorganic and radioactivity (Metcalfe, 1989). Hence ecological studies shifted their focus to biodiversity indices (e.g., Shannon-Wiener diversity index) which use components of community structure (richness, evenness, and abundance) to describe the response of a community to the quality of its environment.

Biodiversity indices were favored for their quantitative and dimensionless nature, independence of sample size, and the fact that they lend themselves to statistical analysis (Metcalfe, 1989). In this approach, less disturbed environments are expected to be characterized by a high species diversity and richness. Species diversity is expected to decrease in stressed environments as sensitive organisms are lost. However, biodiversity indices tend to have varying values depending on the taxonomic resolution used (e.g., species or genetic diversity). Furthermore, individual species are reduced to anonymous numbers disregarding pollution tolerances (Chutter, 1972). For these reasons modern indices were developed which combined the indicator value concept with the biodiversity of different selected groups (Li et al., 2010).

The ecological indices commonly used to evaluate river health broadly fall into three groups; biotic, multivariate, and multimetric indices. Biotic indices evaluate river health based only on organisms' tolerance to pollution e.g., the Hilsenhof Biotic Index, Biological Monitoring Working Party (BMWP) scoring system, fish species biotic index, etc. Individual taxa are assigned sensitivity weightings to environmental characteristics such as organic pollution. The values for all taxa in a sample are then summed or averaged. Biotic indices have the advantage of being simple and rapid, measuring only one disturbance (e.g., organic pollution tolerance). However, organisms usually do not respond to only one disturbance as stressors do not occur in isolation (Mwedzi et al., 2017). Furthermore, biotic indices are unlikely to be universally applicable as indicator organisms vary from region to region (Taylor et al., 2007a; Rimet, 2012; Bere et al., 2014; Mangadze et al., 2019). For that reason, multimetric and multivariate statistical approaches are being considered for the rapid bioassessment of river ecosystems (Rosenberg and Resh, 1993; Stevenson and Smol, 2003; Mueller et al., 2014). These approaches are a more objective way of identifying groups of reference sites with which monitoring sites can be compared (Mangadze et al., 2016).

The multimetric approach combines several variables associated with structural and functional attributes of a biological community (e.g., number of families, functional feeding groups, life history strategies, pollution tolerance, etc.) into a single index e.g., the index of biotic integrity (IBI). This provides a broader understanding of assemblage responses to different stressors. Furthermore, unlike any other ecological index, multi-metric indices can identify the cause of degradation. They are therefore the most recommended ecological indices (Fierro et al., 2017).

Multivariate indices use statistical analysis to infer relationships between faunal patterns and environmental stressors. This includes ordination analysis (e.g., Principal components analysis, canonical correspondence analysis, etc.) and clustering analysis (e.g., hierarchical clustering, multidimensional scaling, etc.). The most advanced multivariate indices are predictive and compare the observed with the expected faunal patterns in the absence of environmental stress (Bird and Day, 2010; López-López and Sedeño-Díaz, 2015). Examples include the River InVertebrate Prediction And Classification System (RIVPACS) and the Australian River Assessment System (AusRivAS). Predictive modeling approaches are cheaper and provide a holistic assessment of anthropogenic effects on rivers. While multivariate indices offer a higher predictive power compared to other indices, they were not developed to find patterns and therefore do not establish impacts.

2.3 Practical guide to biomonitoring

2.3.1 Diatoms

2.3.1.1 The use of diatoms in biomonitoring

Diatoms (Bacillariophyceae) are unique microscopic unicellular micro-organisms, found in all aquatic biotypes, and play a vital role in the food web structure of aquatic ecosystems as they are the chief primary producers in these ecosystems (Smucker and Vis, 2011; Dalu and Froneman, 2016; Kock et al., 2019; Pajunen et al., 2020; Dalu et al., 2020). Diatom species have a cosmopolitan nature, shortest generation times, and quick response to environmental perturbations (Stevenson et al., 2010). Unlike animal components of an ecosystem (e.g., macroinvertebrates and fish), diatom species have specific optima and tolerance ranges for nutrients as well as pH and have therefore been used successfully in studies of monitoring eutrophication, organic and metal pollution in streams (e.g., Bellinger et al., 2006; Potapova and Charles, 2007; Pandey and Bergey, 2016). Diatoms constitute an extremely diverse phylum (approximately 100,000 species) (Guiry, 2012; Mann and Vanormelingen, 2013). A large number of taxa allows redundancies of information in the data sets and increases the assurance of environmental inferences (Ovaskainen and Soininen, 2011). Therefore, many diatom-based biotic indices have been developed worldwide on species-specific sensitivities, or tolerances to infer specific environmental conditions in lotic systems and to estimate the status of river ecosystems (Li et al., 2010). These indices have universal applicability since they are based on the ecology of widely distributed or cosmopolitan taxa. However, due to the scarcity of information on ecological preferences and tolerances of diatoms in developing countries, diatom-based biotic indices developed in Europe are often applied to assess ecological conditions in tropical context (Bere et al., 2014). Nonetheless, floristic and faunal differences among regions may contribute to differences in the water quality characteristics of rivers and may lead to variation in diatom taxa composition (Taylor et al., 2007a; Bere et al., 2014; Mangadze et al., 2019). Different regions may also have endemic diatom species, therefore there is a need for the development of region-specific diatom indices (Harding and Taylor, 2011).

Diatoms were first used to assess water quality conditions in freshwater habitats by Kolkwitz and Marsson (1908). Their study demonstrated the potential and robustness of diatoms that could enable their use to monitor river quality. They developed the saprobe system (the Saprobity index) which is based on the classification of diatom taxa according to the resistance, sensitivity, or indifference to pollution (e.g., Lange-Bertalot, 1979). These saprobe systems led to the direct development of numeric biotic indices. For example, in Austria, this method has been the basis of a diatom index that is the only index routinely applied on a national scale in Europe (Prygiel et al., 1999). After these first approaches, the use of indices to assess water quality was also attempted by Zelinka and Marvan (1961), Slàdeček (1973, 1986), Coste and Leynaud (1974), and Descy (1979).

Coste and Leynaud (1974), developed the diatom-based stream quality assessment which targets water quality parameters such as phosphorus, nitrogen, biological oxygen demand (BOD), and chemical oxygen demand (COD). These parameters, varying at different scales in time and space, can impact diatom assemblages differently. In France, Coste (in CEMAGREF, 1982) proposed an index known as the Specific Pollution Sensitivity Index (SPI), which is based on 189 surveys conducted from the year 1977 to 1980 at the Rhône- Méditerranée-Corse basin national monitoring network. The index has been updated since 1982 to incorporate changes in taxonomy and new knowledge of diatom ecology. Several studies have showen that the SPI index is the most widely used in Europe and water quality class boundaries have been set by several authors for rivers in Sweden, Finland, Belgium, and France (Prygiel and Coste, 2000; Eloranta and Soininen, 2002). Currently, in South Africa, the South African Diatom Index (SADI), a modified version of the Specific Pollution Sensitivity Index (SPI) which includes indicator and tolerance values for South African endemic species is being employed (Harding and Taylor, 2011).

Following the SPI, other indices were also developed, e.g., the Generic Diatom Index (GDI; Coste and Ayphassorho, 1991); Artoise-Picardie Diatom Index (APDI; Prygiel et al., 1996) was proposed (Coste and Ayphassorho, 1991); Biological Diatom Index (BDI; Lenoir and Coste, 1996) and Eutrophication/Pollution Index (EPI; Dell'Uomo, 1996). However, principal components analysis of data collected from the Artois-Picardie Region of France indicated a stronger correlation between most of these diatom indices and variables associated with organic pollution compared to eutrophication (Prygiel and Coste, 1993). This prompted the first attempts to develop a purpose-designed index to monitor eutrophication in rivers, the Trophic Diatom Index (TDI; Kelly and Whitton, 1995). This TDI index uses 86 epilithic diatom taxa (species and/or genus level) and each taxon is given a sensitivity value (1–5) and an indicator value (1–3). The final result of the TDI value ranges from 1 (very low nutrient levels) to 5 (very high nutrient levels).

In addition to these diatom-based auto ecological indices, other multimetric indices such as Metzmeier's diatom index of biotic integrity have also been developed in the United States of America (Kentucky Division of Water, 1993). This index includes taxa richness, Shannon diversity (Shannon and Weaver, 1949), the pollution tolerance index (Lange-Bertalot, 1979), and the proportion of species sensitive to pollution. Other studies in Europe (Barbour et al., 1999; Karr and Chu, 1999; Hering et al., 2006a) have also proved these multimetric indices as effective tools for assessing lotic systems, lakes, and wetlands at varying geographic scales (Delgado et al., 2010).

2.3.2 Diatoms' sampling protocols

The need to monitor water quality has led to the development of standardized sampling protocols for diatoms since the end of the nineties (Kelly and Whitton, 1998; Afnor, 2007; Morin et al., 2016). Two Rapid Bioassessment Protocols are commonly used for diatom sampling. The first approach involves the assessment of species composition and/or biomass performed in the laboratory. The second approach involves a field-based rapid survey of diatom biomass and coarse-level taxonomic composition. These two approaches are discussed briefly below.

2.3.2.1 *Laboratory-based approach*

Field sampling procedures and sampling habitats

Benthic diatoms occur in four major and distinct habitats: (1) attached to macrophytic plants supporting the epiphyton; (2) gravel, bedrock, and stone surfaces supporting the epilithon; (3) sand surfaces supporting the epipsammon and (4) the epipelon, mobile taxa growing among deposited inorganic and organic sediment particles (Round, 1991). Differences in species composition of diatoms among these habitats are often evident as changes in color and texture of the diatom biofilms (Bahls et al., 2018). For this bioassessment protocol, multihabitat sampling or single habitat sampling may be used. However, many studies have shown that multihabitat sampling provides a more complete assessment of all taxa at a site, which potentially is a better characterization of biodiversity and bio integrity than assemblages from targeted habitats (Stevenson and Smol, 2003; Taylor and Cocquyt, 2016). Diatom samples are collected from all available substrates and habitats to form one composite sample, which is proportionally representative of the periphyton assemblage in the sampling area. The diatom suspension will be fixed with ethanol or 4% buffered formalin to a final concentration of 20% by volume. (APHA, 1995) (refer to Box 2.1 for all field equipment for diatom sampling). The techniques for the collection of diatoms in the different habitat types are described in the table below (Table 2.2).

Although many scientists prefer sampling natural substrates whenever possible to reduce field time and improve the ecological applicability of the information, artificial substrata can also be used to assess benthic diatom assemblages (Wojtal and Sobczyk, 2012). These include typically uniform substrata (e.g., glass slides, clay tiles, acrylic, or wooden dowels) that can be used across many water body types (streams, rivers, wetlands, lakes). Artificial substrates are placed in aquatic habitats and colonized over a period of time. Some of the advantages of using artificial substrates include; decreased habitat disruption; substantially improved sampling precision and reduced effects of small-scale habitat variations that inevitably exist in relation to natural substrata (Lane et al., 2003; Wojtal and Sobczyk, 2012). However, artificial substrates are time-consuming and require more attention during collection. Moreover, they have the risk of being vandalized by non-scientific people or loss of the artificial substrates from unforeseen events like floods (Bere and Tundisi, 2010; Morin et al., 2016). For that reason, many large national and state programs in Europe have chosen to sample natural substrata (e.g., Hering et al., 2006a; Johnson et al., 2006).

Laboratory procedures: Diatom preparation, identification, and counts

Diatom samples have to be cleaned through sedimentation (removing mineral debris) and oxidation (removing organic matter) before they can be identified. This is done to improve conditions for observation of the morphological elements (e.g., the shape and number of chromatophores and the shape and type of colony formation) in the

BOX 2.1

FIELD AND LABORATORY EQUIPMENT FOR DIATOM SAMPLING, PROCESSING, AND IDENTIFICATION (STEVENSON AND BAHLS, 1999).

Field equipment for diatom sampling–natural substrates

- Wide-mouth sampling bottle ~100 mL.
- Preservative [ethanol (final concentration of 20% by volume) or 4% buffered formalin (APHA, 1995)]
- Turkey baster; useful for collecting sediment samples.
- Pencil and labels, ethanol does not dissolve pencil markings.
- Forceps for picking up filamentous algae and detritus.
- Water-proof marking pen.
- Plastic Pasteur-pipette are useful for collecting small amounts of sediment.
- Toothbrushes for scrubbing solid substrata.
- Knife for cutting the stems of aquatic vegetation
- White plastic tray with a lip
- Fine-mesh plankton net. (<10 μm)

Laboratory equipment for diatom processing and identification

- Micro-pipette 1 mL with disposable tips
- Glass and plastic Pasteur-pipettes (2–3 mL)
- Forceps
- Microscope slides
- Coverslips
- Diatom mountant
- 10 mL plastic graduated centrifuge tube
- 15 mL glass test tube
- 4 mL glass sample storage bottles with a rubber seal inside the cap
- Waterproof fine marking pen
- Heat-resistant glass beaker ~100 mL
- Watch glass.

TABLE 2.2 Summary of collection techniques for diatoms in different habitat types.

Substrate type	Collection technique
Hard substrates (removable) e.g., stones, gravel, cobble, and woody debris	Randomly collect the representative substrates along each sampling stretch; brush or scrape representative area of diatoms from the surface and rinse into a sample jar.
Soft removable substrates e.g., macrophytes (submerged/emergent), mosses, and macroalgae	Select different species of plants. Put a portion of the plant in a sample container with some distilled water. Shake it vigorously and rub it gently to remove the resulting diatom suspension. Remove the plant from the sample container.
Large substrates (not removable) e.g., logs, boulders, roots, bedrock	Place PVC pipe with a neoprene collar at one end on the substrate so that the collar is sealed against the substrate. Brush or scrape algae in the pipe with a toothbrush or scraper. Remove the diatom suspension from the pipe with a pipette
Sediments e.g., sand, clay/silt, fine particulate organic matter	Invert petri dish over sediments. Trap sediments in a petri dish by inserting spatula under the dish. Remove sediments from the stream and rinse into a sampling container. Diatom samples from depositional habitats can also be collected with spoons, forceps, or pipette.

Adapted from Kentucky DEP Kentucky Division of Water, 1993. Methods for Assessing Biological Integrity of Surface Waters. Kentucky Natural Resources and Environmental Protection Cabinet, Frankfort, Kentucky, 139; Bahls L.L., 1993. Periphyton Bioassessment Methods for Montana Streams. Water Quality Bureau, Department of Health and Environmental Services Helena, MT.

microscope (Hasle and Fryxell, 1970). The detailed methods for diatom cleaning have been summarized by APHA (1995) and Taylor et al. (2007b). After cleaning, valves are mounted in a resin (Naphrax) or another high refractive index medium to make permanent slides. Diatoms are then counted and identified using a light microscope (1000 × magnification) (see Box 2.1 for all laboratory equipment needed for diatom processing and identification). The abundances of all observed taxa are expressed as relative counts. The diatoms will be identified to the lowest possible taxonomic level using the best available keys (e.g., Krammer and Lange-Bertalot, 1986; Taylor et al., 2007b).

However, diatom species-level identifications can be difficult because of their tremendous diversity and the increasing interest in taxonomy leading to the description of numerous new species and incessant taxonomic arrangements (Rimet, 2012). Zampella et al. (2007) also highlighted that the great diversity of diatom species and identification difficulties limit their use in routine monitoring and identification mistakes are numerous at the species level. Conversely, other studies have highlighted that it is necessary to have precise determination for a good environmental assessment (e.g., Ponader and Potapova, 2007). Nonetheless, investigations in sub-tropical rivers in Taiwan showed that identification of diatoms at genus level gave similar results as species level in assessing the effects of river regulation (Wu and Kow, 2002). The application of higher taxonomic level identification should not be indiscriminate, as it depends on physicochemical parameters and the study region (Chen et al., 2016).

2.3.2.2 Field-based rapid periphyton survey-viewing bucket survey method

This approach is a semi-quantitative rapid periphyton survey of algal biomass and taxonomic composition (Box 2.2). The advantages of this approach are that it reduces field and laboratory time; it can easily be employed in all sampling programs and enables rapid assessment of algal biomass over larger spatial scales than substrate sampling and laboratory analysis. This technique (i.e., processing done in the field) allows visual characterization of algal type, percentage cover, filament length, and periphyton mat thickness along multiple transects in streams (Stevenson and Bahls, 1999). Secchi-disc transparency is also a semi-quantitative approach for assessing plankton biomass in lakes (Wetzel and Likens, 1991). Coarse-level taxonomic characterization of communities is also possible with this technique; thus they require little taxonomic expertise (Stevenson and Bahls, 1999).

2.4 Macroinvertebrates

2.4.1 The use of aquatic macroinvertebrates in biomonitoring

Aquatic macroinvertebrates are water-dwelling invertebrates with a body size greater than 5 mm (Ochieng et al., 2020). Their communities perform a variety of functions including accelerating detrital decomposition, transferring energy between primary producers and consumers, and translocation of nutrients from upstream to downstream river sections (Wallace and Webster 1996). Macroinvertebrates are the most widely used bioindicators (both in developed and developing countries) because they have a well-known life history and ecology (Rosenberg and Resh, 1993; Resh, BOX 2.2

FIELD-BASED RAPID PERIPHYTON SURVEY (BARBOUR ET AL., 1999; STEVENSON AND BAHLS, 1999).

At least three transects are established across a habitat being sampled (e.g., riffle or run, with water clarity such that algal accumulation can be observed readily and characterized). Three locations along each transect will be selected (e.g., right bank, middle, and left bank). At each selected sample location, a viewing bucket (≥0.5 m diameter) containing a grid of 50 dot grid ($7 \times 7 + 1$), is immersed into the water. At each of these nine locations, the viewing bucket is submerged so that the diatoms are visible through the clear bottom of the bucket. Algal biomass is roughly characterized by counting the dots that occur over macroalgae and by measuring the length and thickness of algal accumulation. If different types of algae are present (e.g., diatoms, blue-green algae, or other microalgae), each type is assessed separately. After the visual assessment is completed, statistically characterize the mean density and the average percent cover by each type of algae.

Field equipment

- Viewing bucket with a 50-dot grid
- meter stick
- pencil
- Rapid Periphyton Survey Field Sheet

2007). Furthermore, macroinvertebrates are ubiquitous, diverse (with a wide range of feeding habits and pollution tolerances), have long life spans (integrating short and long-term effects of environmental variations), have different sensitivities in their life stages, and rapidly recover from repeated sampling (and hence easily generate a lot of data for effective biomonitoring) (Rosenberg and Resh, 1993; Ochieng et al., 2020). Moreover, in the presence of well-developed taxonomic keys, macroinvertebrates are relatively easy to identify and their sampling protocols involve simple equipment (e.g., kick net) (Ochieng et al., 2020).

The Trent Biotic Index (TBI) (Woodiwiss, 1964) developed in the UK; is seen as the origin of most modern macroinvertebrate biotic indices. The TBI used two main aspects of benthic communities; i.e., biological richness and the presence of some key groups (with different levels of tolerance to environmental degradation). The index ranged from zero (polluted condition) to ten (clean waters). However, being the first index of its kind, it was criticized for being insensitive and providing erroneous results. It was modified to different indices in different countries e.g., the Indice Biotique in France (in 1968), Chandler's score in Scotland (in 1970), Chuttter's Biotic index in South Africa (in 1972), Extended Biotic Index in the UK (in 1978) (Dallas, 1995), Hilsenhoffs Biotic Index (in 1977) and Family-level Biotic Index (in 1987) in the United States (Li et al., 2010).

The Biological Monitoring Working Party protocol (BMWP) (Hellawell, 1986) evolved from Chandler's score and assumed particular importance. In this method, taxonomic identification was easier, because it was performed at the family level (Bo et al., 2017). In developing countries, modification of the BMWP led to several indices including the development of the South African Scoring System (SASS) (Chutter, 1994, 1998) and the Ethiopian Biotic scoring system (ETHbios) (Aschalew and Moog, 2015). Several southern African countries have subsequently modified and standardized the SASS protocol e.g., to Namibian Scoring System in Namibia, Okavango Assessment System in Botswana, and Zambian Invertebrate Scoring System in Zambia (Aschalew and Moog, 2015; Mangadze et al., 2019).

Given that differences in ecoregions lead to a wide array of habitat types, there are significant differences between sampling protocols and tools used across the globe (Bonada et al., 2006). This is expected as different habitat types will require different assessment methods and different bio criteria. However, the use of different tools and techniques (e.g., mesh size, time of collection, range of habitat type sampled) introduces bias making the comparison between biotic indices challenging (Brown, 2001). Universally consistent sampling and processing techniques are important in addressing global issues such as climate change. Even though biomonitoring programs following standard methods could aid international data sharing and interpretation, internationally accepted standard methods for collecting and processing benthic macroinvertebrate samples do not exist as yet (Buss et al., 2015). However, there have been efforts to develop standardized protocols in Europe since the introduction of the European Water Framework Directive in 2000.

The development and testing of an integrated Assessment system for the ecological Quality of streams and rivers throughout Europe using benthic Macroinvertebrates (AQEM) project and Standardization of River Classifications: Framework method for calibrating different biological survey results against ecological quality classifications to be developed for the Water Framework Directive (STAR), the project have facilitated the development of the AQEM/STAR (Haase et al., 2004) and modified AQEM/STAR (MAS) protocols respectively (Clarke et al., 2006). While great efforts have been made in developing the AQEM/STAR and MAS protocols in Europe, most European Union countries have retained their methods that they have used for decades. There is greater potential for easier adoption of standardized regional protocols in geographic regions without a long history of comprehensive biomonitoring, such as Asia, Latin America, and Africa as new protocols are more acceptable among communities who do not have a history with their biomonitoring protocol (Buss et al., 2015). These countries will not have to deal with issues of national pride, prejudice, etc. (Resh, 2007). However, such political regional policies (like the European Water Framework Directive) are lacking in developing countries and would be a good starting point if regional protocols are to be developed. There is a general lack of regional collaboration to improve biomonitoring tools among stakeholders and governments of developing countries (Mangadze et al., 2019).

2.4.2 Macroinvertebrate sampling tools

Several different tools have been developed for collecting macroinvertebrate assemblages; e.g., grab nets, stovepipe coring devices, substrate Hess samplers, Surber samplers, and kick nets, (Fig. 2.1) (Merritt et al., 2008; Elias et al., 2014). Coring and dredging devices are used when sampling soft sediments or in deep waters where sampling has to be done from a boat.

Surber and Hess samplers are generally used in shallow streams (i.e., less than 15 cm depth) with small substrata (i.e., sand, gravel, and very small cobble) (Buss and Borges, 2008). Kick nets are preferred in front of Surbers or Hess samplers especially when the substratum is large (Bonada et al., 2006). Kick nets are the tools of choice in rivers with fast flowing riffles (>50 cm/s), typical of third to sixth-order rivers (Hauer and Resh, 2017). In the case of kick nets, macroinvertebrates are generally collected by disturbing bottom sediments and catching organisms swept into the net

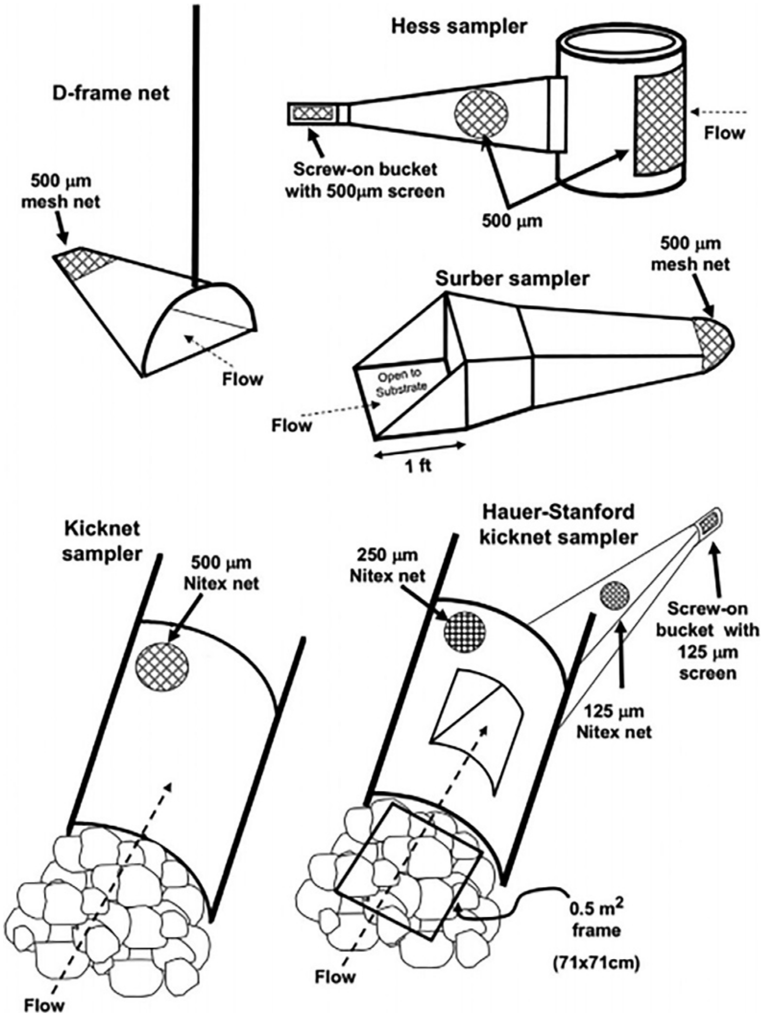

FIG. 2.1 Illustration of some of the most common macroinvertebrate sampling devices. *Adapted from Hauer, F.R., Resh, V.H., 2017. Macroinvertebrates. In: Gore, J.A., Banning, J. (Eds.) Methods in Stream Ecology. Elsevier.*

downstream of the disturbance. The major limitation of kick nets is the fact that they rapidly fill with material clogging the net and resulting in back welling (Hauer and Resh, 2017).

Ideal mesh size is the one with favorable cost/ effectiveness ratio, in which sample processing time is reduced and the sample is representative of the macroinvertebrate fauna at the site. A range of sizes (from 200 to 1000 μm) has been used worldwide (Bonada et al., 2006). The standardization normative recommends a mesh size of 500 μm in Europe (AENOR, 1995). This is also the most commonly used mesh size in the United States of America (Bonada et al., 2006). In Africa, a kick net (Fig. 2.2) with a mesh size of 1000 μm is commonly used following the recommendations of the SASS protocol from which other Southern African protocols have been derived. Generally, literature recommends a mesh size of approximately 500 μm as it is the most cost-effective retaining the most macroinvertebrate genera per unit of effort despite losing smaller specimens and earlier instars that are often difficult to identify accurately (Bonada et al., 2006; Buss et al., 2015).

2.4.3 Macroinvertebrates' sampling habitats

The habitats to be sampled in a macroinvertebrate biomonitoring exercise varies among sampling protocols. A single sample from the "most productive habitat" is usually recommended (Bonada et al., 2006). Riffles or stones generally seem to be the most productive habitat for macroinvertebrates and are thus emphasized in different protocols. However, anthropogenic impacts can be specific to a particular habitat, and/or sometimes the most productive habitat is not evident. Consequently, other protocols emphasize sampling all available habitats (Bonada et al., 2006; Blocksom et al., 2008; Buss et al., 2015). In that sense, a multihabitat protocol integrating all habitats, as in SASS5 (Dickens and Graham, 2002) (Box 2.3) is desirable (Bonada et al., 2006). The SASS5 protocol is highlighted here as it is the most used protocol in Africa and the index from which most African protocols are derived.

2.4.4 Sample processing and identification of macroinvertebrates

Separating invertebrates from detritus and other debris and identifying them are the most time-consuming components of invertebrate-based monitoring studies. Sample sorting may be done in the field (Fig. 2.3) or samples can be collected and preserved for later processing in the laboratory. Field sorting saves time, allows easy location of moving live organisms (e.g., the stick-dwelling caddies), and reduces human exposure to preservatives such as formaldehyde (ethanol is usually a better alternative). However, field sorting can be biased toward selecting large, active, or conspicuous organisms and may not be practicable for large aquatic systems such as the Congo River. Some protocols e.g., SASS emphasizes field sorting and returning the samples to the river after identification and enumeration while as in other protocols e.g., the European Union's AQEM/STAR, sorting is done completely in the laboratory and requires that a defined subsample is taken before sorting (Haase et al., 2004).

Identifying samples to species-level improves the sensitivity of biomonitoring, especially to subtle impacts (Campbell, 2002). However, identification to species level can be costly (in terms of time and money) and is usually

FIG. 2.2 Picture of South African Scoring System kick net during sampling, mesh size 1000 μm on a 30-cm square frame with stout handle. *Manyame river, Zimbabwe (Photo Credit: Tongayi Mwedzi).*

BOX 2.3

THE SOUTH AFRICAN SCORING SYSTEM VERSION 5 (SASS5) PROTOCOL.

A kick net of 30 × 30 cm and 1000 μm (1 mm) mesh size is used in three different biotopes : stones (both in and out of current); vegetation (both marginal and aquatic); and gravel, sand, and mud (GSM). For stones in current, kick sampling is performed for 2 min or 5 min if the stones are difficult to move. For stones out of the current, kick sampling is performed for 1 min. For the marginal vegetation, the net is pushed vigorously over a total length of 2 m, spread over one or more locations in different flow velocities. For aquatic vegetation, the net is pushed repeatedly over an area of approximately one square meter. Gravel, sand, and mud are stirred by scraping with the feet (for approximately 1 min), while continuously sweeping the net over the disturbed area to catch dislodged biota. All collected material separated by biotope is poured into three different trays. Taxa are sorted and identified for 15 min in the field or until no new taxa have been seen after 5 min of sorting. Identification is at the family level except for Hydropsychidae and Baetidae which are identified to species level (these families have pollution tolerant and intolerant species). Approximately 1 min is assigned to hand-picking/noting specimens that may have been missed by the sampling procedure e.g., snails and fast-moving pond skaters. Each macroinvertebrate taxon is awarded a score (from 1 to 15) in increasing order of the sensitivity to the water quality changes. The final SASS5 score is calculated by summing the predetermined taxa tolerance values of all macroinvertebrates within a particular sample. The Average Score Per Taxon (ASPT) is calculated by dividing the total SASS5 score by the number of taxa.

FIG. 2.3 Sorting and identification of macroinvertebrates in the field. *Photo credit: Tongayi Mwedzi.*

difficult due to taxonomic training required (Campbell, 2002; Bonada et al., 2006). Resources and taxonomic expertise are often limiting in developing countries and hence family level is often the only option for bioassessment (Ochieng et al., 2019). Other authors have argued that while species-level identification implies better precision in reporting the state of the aquatic environment, in most cases the general patterns reported at the family level usually convey similar information (Bowman and Bailey, 1997; Nielsen et al., 1998). Hence, various biotic indices identify samples at a family level making the process uncomplicated and cost-effective e.g., the BMWP and SASS5 (Hewlett, 2000). The limitation remains that of taxonomy field guides as in many cases the guides developed in temperate regions are being used in tropical regions. There is a need to develop local taxonomic guides (particularly in developing countries) based on species assemblages of the region.

2.5 Fish

2.5.1 Biomonitoring using fish

The use of fish in the biomonitoring of water quality dates back to the 1970s (Karr, 1981; Harris, 1995). Fish communities are valuable components of the freshwater ecosystems as they are on the top of the aquatic food web (Barbour et al., 1999). Fishes possess a suite of advantages, which make them good indicators of water quality e.g. they live in water all their life; have a long lifespan (about 2–10 years), and can reflect both long-term (several years) and current water quality and are less affected by natural microhabitat differences (López-López and Sedeño-Díaz, 2015, Raburu and Masese, 2012). More importantly, fish can easily be used to evaluate the societal costs of degradation as their economic and aesthetic values are well known. This makes it easy to use citizen science in which case taxa with societal and economic values must be targeted to involve local communities in data collection.

Biomonitoring using fish entails the collection of fish for the assessment of the quality of a site based on species presence (Karr, 1981; Culp et al., 2011) as well as tissue collection from fish samples for toxicological evaluation (Shailaja and D′Silva, 2003). Behavioral and physiological (cardiac and respiratory rates) responses of fish can also be used to indicate contamination (Morgan, 1978; Ma et al., 2010; Kuklina et al., 2013).

2.5.2 Collection of fish species samples

It is important to note that many countries require a permit for the collection of fish samples. As such researchers must consult the relevant authorities. The collection of fish samples can be done from different aquatic environments ranging from streams to rivers. Many gear types (active and passive) can be routinely used to sample fish, however, the most commonly used collection methods in freshwater habitats are electrofishing equipment, seine, fyke, and gill nets. The type of gear used is generally dependent on the size of the water body.

2.5.2.1 *Active fishing gear*

Electrofishing can be used in a wide range of habitats where safe wading or boating is possible. Electrofishing is considered the most effective method for capturing moderate to large-size fish, but when negative uncontrollable impacts are seen, its use should be severely restricted (Snyder, 2003). Seines and portable electro fishers are generally used in smaller streams. Catch efficiency is dependent on the conductivity and temperature of the habitat. Mortality rates with DC are low although spinal injuries are common in large fish (Portt et al., 2006). Seining cannot be used in habitats with a lot of macrophytes and stumps, in fast currents, or deep water. Fish mortalities can occur especially when the catch is being processed and the fish are subject to the stress of capture (Bayley and Herendeen, 2000; Portt et al., 2006).

2.5.2.2 *Passive fishing gear*

Fyke nets are used in habitats with water that is deeper than the height of the net as this helps maintain the shape of the frame of the net. Fish survival is high in fyke nets although larger fish tend to prey on small fish inside these nets (Mccombie and Berst, 1969; Portt et al., 2006). Gill nets can be used in most habitats with depths that allow the mesh to be extended between the float and lead lines and where the current is not strong (Portt et al., 2006). Gill nets however cannot be set in habitats with emergent and floating vegetation, and other obstructions near the surface. Gill nets can be set over any substrate but when the substrate is very uneven, catch efficiency is reduced. Net color, light, and turbidity also affect catch efficiency (Jester, 1973; Portt et al., 2006). Physical injury during retention and removal can also occur. While mortality is typically high, it varies with species and how the fish are wedged to the net. While all types of fish sampling gear are generally considered selective and their use depends on the sampling time and other environmental variables such as temperature and environmental features (Mcinerny and Cross, 2000), electrofishing has become the preferred method for collecting stream fishes, especially for IBI purposes.

Sampling should be done quantitatively and should also be standardized to reduce sampling error (Masese et al., 2013). Fish samples are laboratory frozen in dry ice and stored in a freezer until prepared for analysis (Schmitt et al., 1990). Species identification can be done in the field or laboratory with the help of relevant regional taxonomic guides such as Skelton (2012) and Bell-Cross and Minshull (1988) in the case of Zimbabwe.

2.5.3 Fish indices

Ecological indicators for fish were historically based on parameters associated with individual species. As a result, they did not fully represent the entire biological community of organisms present (Niemi and McDonald, 2004). Karr (1981) described a multimetric index- IBI based on fish assemblages. It was after the formation of this multimetric index, that similar indices were been developed for benthic macroinvertebrates and periphyton (Hering et al., 2006b).

Several studies have shown that the Index of Biotic Integrity (IBI) is widely used to assess stream health based on fish and can be modified to suit different ecological regions and fish communities in the world (Harris, 1995; Ganasan and Hughes, 1998; Zhu and Chang, 2008). Many IBIs have therefore been developed and are currently available for different regions and river basins. The IBI uses a combination of key metrics that have demonstrated a response to human influence. Each metric is scored in comparison to the values of the regions' least impaired streams (Karr, 1981). It is based on 12 criteria, including such metrics as the number of native species, the relative abundance of tolerant and intolerant species, and the percent of the fish in the sample that show evidence of disease or parasites. The sample site is given a rating of very poor, poor, fair, good, or excellent based on the IBI score (Karr, 1986).

2.5.4 Other fish biomonitoring techniques

Tissue samples of flesh and other parts such as the liver and kidney of fish can also be taken for analysis for trace metals (Lee et al., 2019). Fish dissection can either be carried out in the field or laboratory. Tissue samples are freeze-dried, weighed and microwave acid digested, and metal concentrations are determined using an atomic absorption spectrophotometer (Swales et al., 1998). The presence of microplastics in water systems can also be assessed using fish as they enter fish using different pathways such as ingestion and/or through the gill and skin and cause negative effects that include intestinal damage and inflammation. The whole fish or parts of it such as the gills or guts are collected and used to assess the intake of microplastics by fish (Su et al., 2019).

Real-time monitoring of water quality can also be done using fish by observing their behavioral and physiological responses (Kuklina et al., 2013). Acoustic monitoring (Conti et al., 2006), Vision-based real-time monitoring (Chew et al., 2009), and Ethovision (Noldus et al., 2001) are some of the methods used to observe aquatic organisms and evaluating the environment in which they exist (Kuklina et al., 2013).

2.6 Recommendations

While biomonitoring has increased in importance because of the human-induced deterioration in water quality, a lot of challenges still need to be addressed particularly in developing countries as highlighted in this chapter. The deficiency in taxonomic identification skills and later on the taxonomic keys themselves is undoubtedly a big challenge in developing countries. There is a need to develop local identification guides, especially for diatoms and macroinvertebrates using species assemblages of the region. This necessitates sampling surveys of local assemblages, identifying them at the genus and species level and establishing their sensitivity and response to various stressors. Also, there have been advances in the use of molecular genetics in taxonomy and in identifying species all over the world (Ochieng et al., 2019; Mezgebu, 2020). This makes identification faster and more accurate. Furthermore, any life stage or remains of the organism can be used in the process (Li et al., 2010). Developing countries should also consider applying these tools in enhancing taxonomic resolutions.

Developed countries usually have legal and policy framework which clearly articulates aquatic ecosystem monitoring and diligently enforce their environmental laws (Mezgebu, 2020). While environmental regulations are increasingly being codified into law in developing countries, the problem remains that of enforcement. International funding agencies and aid organizations should assist by increasing pressure to require enforcement as was done in West African countries (Burkina Faso, Ghana, Ivory Coast, Guinea, Senegal, Niger, Mali, Benin, Togo, Sierra Leone, and Guinea Bissau) in a biomonitoring program that sought to address possible impacts of insecticide application in the control of Onchocerciasis (River blindness) (Resh, 2007).

Funding for biomonitoring programs is a problem in many developing countries. In many cases, aid agreements are often influenced by political policies. Developing countries must engage in multiple-country biomonitoring programs which can more easily receive funding from international agencies (Resh, 2007). They must take advantage of these multiple-country biomonitoring programs to develop ecoregion-based indices that are reliable and clearly show the status of ecosystem health in that ecoregion.

As indicated in this chapter, biomonitoring is a cheap and easy tool, easily reflecting the impact of pollution and other stressors on freshwater. Developing countries, therefore, stand to benefit if it is well developed in their regions. As a matter of course, developing countries should channel resources toward tackling these challenges particularly, training of skilled labor and acquiring and maintaining the necessary tools for biomonitoring. There is also a need to leverage citizen science networks. This is an attainable goal when taxa with societal and economic values (particularly fish) are used in biomonitoring. However, the key challenge will be on how to maintain continuity and more importantly quality control in these voluntary and unregulated bodies (Jackson et al., 2016). This falls under the section on monitoring techniques, current analytical approaches, and instrumental analyses with other chapters e.g., Kaserzon et al. (2022), Kaykhaii and Hashemi (2022), Kebede et al. (2021), Kumar et al. (2022) aims to understand how emerging freshwater pollutants are analyzed or detected within aquatic ecosystems.

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CHAPTER

3

Monitoring techniques–Grab and passive sampling

Darryl W. Hawker, Joseph Clokey, Sara G. Gorji, Rory Verhagen, and Sarit L. Kaserzon

3.1 Introduction

Emerging freshwater pollutants are, by definition, not regulated or not commonly regulated (Pal et al., 2010; see Tavengwa and Dalu, 2022, Chapter 1). Their presence in freshwater resources is often unrecognized despite known or suspected adverse environmental and human health effects. Risks and hazards need to be properly assessed and appropriate technical and policy approaches employed to ensure good quality water. Current understanding of sources together with environmental fate and behavior is often inadequate. Even trace levels of these pollutants may have significant adverse consequences on biota and environmental systems (Pal et al., 2010). Therefore, reliable monitoring of freshwater resources is crucial. Sampling techniques need to ensure that samples collected contain sufficient analyte for subsequent analysis, are representative of the source water, and that spatial and temporal variations are accounted for if required. Ideally, the cost of sampling programs should be as small as possible while still meeting their objectives. Sampling techniques may be subdivided into active and passive. The former comprises grab sampling at high or low temporal resolution, composite sampling, and continuous or discrete water sampling with autosamplers (PaSOC, 2020). The latter includes a range of monitoring techniques, typically employing receiving phases that allow the sorption of compounds of interest in situ.

3.2 Grab sampling techniques in freshwater monitoring

In monitoring emerging pollutants by grab sampling techniques, the method and equipment chosen should consider the objectives of the monitoring program, local conditions, the safety of operation, and acceptability of the method.

3.2.1 Compatibility of container and equipment material with water samples

The materials used in water sample containers should be compatible with water samples themselves and should not affect the sample chemistry. The container can affect the chemistry of a water sample since it can either adsorb some of the sample's components or be a source of contamination (Batley, 1989).

The equipment utilized for water sampling consists of different combinations of materials, but the components that are in contact with the sample should be composed of the most inert material. Plastics, metals, glass, and ceramics are the materials typically used in water-sampling equipment (Table 3.1). Within each material group, the chemical reactivity of the material depends on the manufacturing process, chemical composition, and physical configuration.

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TABLE 3.1 Generally appropriate materials for use in water-sampling equipment: organic analytes (Wilde et al., 2014).

Material	General guideline
Plastics	
Fluorocarbon polymers e.g., Teflon®, Kynar®, and Tefzel®	Generally appropriate for use, some organics might be adsorbed (Not appropriate for sampling per and polyfluorinated compounds)
Silicone	Not appropriate for use
Polyethylene (linear)	Appropriate for use in some cases
Polyvinyl chloride (PVC)	Not appropriate for use
Polypropylene	Appropriate for use in some cases
Nylon	Not appropriate for use
Metals	
Stainless steel, 316-grade (SS 316)	Generally appropriate for use, but not appropriate if corrosion is evident
Other metals: brass, iron, copper, aluminum, and galvanized and carbon steels	Generally appropriate for use, frequently used for chlorofluorocarbons (CFCs). Not appropriate if corroded
Glass	
Borosilicate glass (laboratory grade)	Generally appropriate for use

Within the plastics group, fluorocarbon polymers are less reactive towards water and dissolved pollutants than other plastics such as polyethylene. Within the metals group, stainless steel 316-grade (SS 316) is less reactive than galvanized steel, brass, and iron (Table 3.1). Generally, any metal or plastic material is less reactive if the surface of the material is more polished and more rigid.

Containers can be a source of contamination and should be cleaned and prepared appropriately before sampling (Wilde et al., 2014). Cleaning methods differ between laboratories. The most common method is acid washing of containers and then rinsing them with deionized water. For example, some laboratories soak sample containers in 10% nitric acid overnight and rinse them with deionized water.

3.2.2 Sample preservation and storage

After sample collection, it is important to make sure that no significant change occurs in sample composition. There are various preservation techniques to prevent physical, biological, and chemical changes. Usually, to retard these changes, chemical additives (e.g., ethanol, glutaraldehyde, glyoxal, zinc acetate, and thiosulfate) are used, or samples refrigerated at 4°C or frozen. Elimination of biological activity occurs at -40°C and below, so cooling to 4°C or freezing at > -10°C only reduces the biological activity. Some sample preservation techniques to delay biological, chemical, and physical changes are shown in Fig. 3.1.

3.2.3 Sample collection techniques

Sampling collection techniques can be divided into two categories viz. integrative (composite samples) and discrete (spot grab samples). Sample collection methods include manual or automatic sampling. Spot grab sampling is one of the most popular sampling techniques (Facchi et al., 2007; Directive, 2000). It is usually done by filling a sample container (0.5–1 L) at a single time point and is only a snapshot of the level of compounds at that particular time (Hageman et al., 2019; Vrana et al., 2005). Grab sampling is suitable to confirm the presence of a pollutant with the analytical results representative of the water body if it is well mixed and concentrations stable with time. Sufficient volume must also be collected to ensure pollutants can be quantified during analysis. This is particularly important for contaminants at trace levels (Valenzuela et al., 2020). The technique is not suitable for situations where pollutant concentrations are subject to fluctuation such as in many rivers, streams, and reservoirs (Table 3.2; Bernard et al., 2019; Bundschuh et al., 2014). Composite sampling can be a useful strategy to overcome spatial and/or temporal concentration variation.

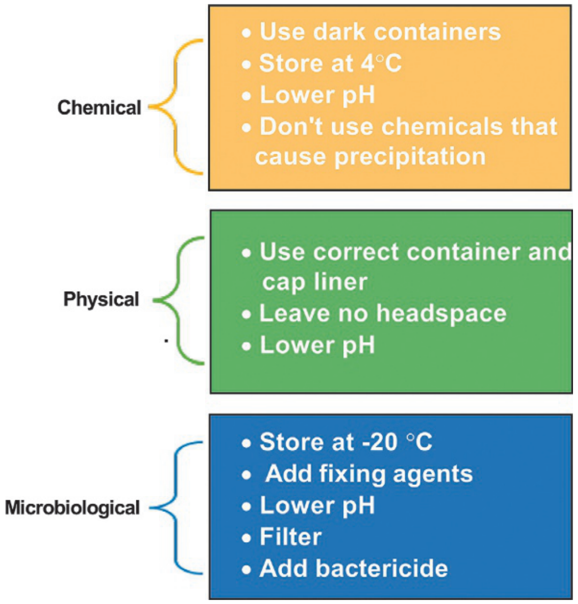

FIG. 3.1 Pre-treatment techniques to delay chemical, physical, and microbial changes in water samples.

TABLE 3.2 Comparisons of grab spot, flow-proportional, and time-proportional sampling methods.

Sampling method	Description	Equipment	Advantages	Disadvantages	References
Grab spot	The sample is collected at a single time point	Bottle	Easy and cheap to perform An accurate picture of analytes at one single time point	A single snapshot. Can fail to detect trace elements. Does not reflect different conditions such as rainfall	Facchi et al. (2007); Mills et al. (2007); Valenzuela et al. (2020); Xing et al. (2013)
Time-proportional	Constant volume of sample is collected at desired times	Autosampler	More representative of the general exposure compared to spot sampling	Can be costly. Can under or overestimate the exposure pattern over long periods when flow varies	Mills et al. (2007); Bundschuh et al. (2014); Ort et al. (2010)
Flow-proportional	Volume proportional to the flow rate is collected at constant time intervals	Automated sampler (adjustable volume of sample proportional to the flow rate)	More representative of the general exposure compared to spot sampling. Can capture the peak concentration of analytes	Can be costly. No data on the exposure pattern of constantly introduced analytes	Bundschuh et al. (2014)

Composite samples are prepared by combining a series of discrete spot grab samples taken over a specific period or flow volume (Ort et al., 2010). In this approach, the concentration in the composite sample is equal to the average concentration during the sampling course (Facchi et al., 2007). Composites samples can be subdivided into two categories, time-proportional and flow-proportional. In time-proportional sampling, a constant volume of sample is collected at defined time intervals e.g., 100 mL every 15 min over 24 h. In contrast, a flow-proportional composite sample represents varying volumes of water proportional to flow rate collected at constant time intervals (Facchi et al., 2007). Automatic samplers are usually used for collecting composite samples (Ort et al., 2010).

It is important to recognize that grab sampling will provide total (i.e., dissolved plus sorbed) concentrations of emerging contaminants unless filtered whereas passive sampling discussed below targets the dissolved fraction. In addition, the act of grab sampling may disturb spatial heterogeneity e.g., stratification whereas passive sampling does not, except during deployment itself (PaSOC, 2020).

3.3 Passive samplers—Background and theory

Passive samplers accumulate emerging contaminants by diffusive transfer from ambient water to a receiving phase. The receiving phase can be a solvent or a solid sorbent (Vrana et al., 2005). This transfer occurs as a result of a difference in chemical potentials of the contaminant in these two phases. Passive samplers themselves can consist of a single phase e.g. polyethylene (PE), silicone, polyether sulfone (PES), or two or more phases (Salim and Górecki, 2019; Chepchirchir et al., 2020). Two-phase samplers for example typically comprise a permeable, uptake limiting membrane and a receiving phase. Examples include semi-permeable membrane devices (SPMDs) with the triglyceride triolein enclosed in a lay-flat PE tube and the Polar Organic Chemical Integrative Sampler (POCIS) consisting of a solid phase sorbent sandwiched between two microporous membranes (Alvarez et al., 2007).

3.3.1 Single-phase passive samplers

Single-phase passive samplers are conceptually simple, and their uptake and accumulation of contaminants are also relatively easy to model. Multiphase samplers are also often regarded as single-phase samplers for modeling accumulation, with only the uptake-limiting phase considered. From Fick's First Law of diffusion in one dimension, contaminant mass flux (J; e.g., mol h^{-1}) may be related to the negative of the chemical potential gradient between phases (μ; e.g., J mol^{-1}) by

$$J \propto -(\mu_W - \mu_S) \tag{3.1}$$

where μ_w and μ_S are the contaminant's chemical potential in water and the sampler phase respectively. Chemical potential can be related to concentration (C; e.g., mol m^{-3} or mol kg^{-1}), so that inter-phase mass flux may be expressed as

$$J = k_O A \rho_S (C_W K_{SW} - C_S) \tag{3.2}$$

where k_O is an overall mass transfer coefficient for contaminant flux between water and the sampler (e.g., m h^{-1}), K_{SW} the equilibrium partition coefficient of a contaminant between the sampler phase and water (e.g., m^3 kg^{-1}), ρ_S the density of the sampler material, and A the interfacial area between sampler and water. This treatment assumes local equilibrium of the contaminant at the water-sampler interface and that there exist linear concentration gradients in boundary layers on either side of this interface (Fig. 3.2.). The inclusion of the partition coefficient is a point of difference with the familiar intra-phase version of Fick's First Law. Thompson et al. (2015) have observed that Fickian concentration gradients may not be linear and provide an analytical solution for coupled diffusion processes in the boundary layers as a function of time, based on Fick's Second Law. The solutions are relatively complex however and most models assume linear gradients.

A simple concentration difference is sufficient for intra-phase diffusion but is not satisfactory for describing inter-phase diffusion. The overall mass transfer coefficient in Equation 3.2 can be regarded as the reciprocal of the overall resistance to inter-phase chemical transfer that in turn is the sum of the individual resistances in the boundary layers.

$$\begin{aligned} \frac{1}{k_O} &= \frac{K_{SW}\rho_S}{k_W} + \frac{1}{k_S} \\ &= \frac{K_{SW}\rho_S\delta_W}{B_W} + \frac{\delta_S}{B_S} \end{aligned} \tag{3.3}$$

Here, B_W and B_S are the diffusion coefficients or diffusivities (e.g., m^2 h^{-1}) of an emerging contaminant in water and the sampler medium respectively, with δ_W and δ_S the distances over which diffusion occurs, usually taken to be the boundary layer thicknesses. This expression may be simplified if resistance to diffusive transfer lies primarily in either the water or sampler phases.

From Eq. (3.2), one-dimensional inter-phase mass flux may be expressed as a differential equation

$$J = \frac{m_S dC_S}{dt} = k_O A \rho_S (C_W K_{SW} - C_S) \Rightarrow \frac{dC_S}{dt} = \frac{k_O A}{V_S}(C_W K_{SW} - C_S) \tag{3.4}$$

$$\Rightarrow \frac{dC_S}{dt} = \frac{k_O A}{V_S} C_W K_{SW} - \frac{k_O A}{V_S} C_S \tag{3.5}$$

with V_S being the volume of the sampler (e.g., m^3) and m_S its mass (e.g., kg). This expression can be related to the familiar expressions for sampler accumulation involving uptake and loss rate constants (k_U; e.g., m^3 kg^{-1} h^{-1} and k_L; h^{-1} respectively) (Eqs. 3.6–3.8) and shows the relationship between mass transfer coefficients and rate constants.

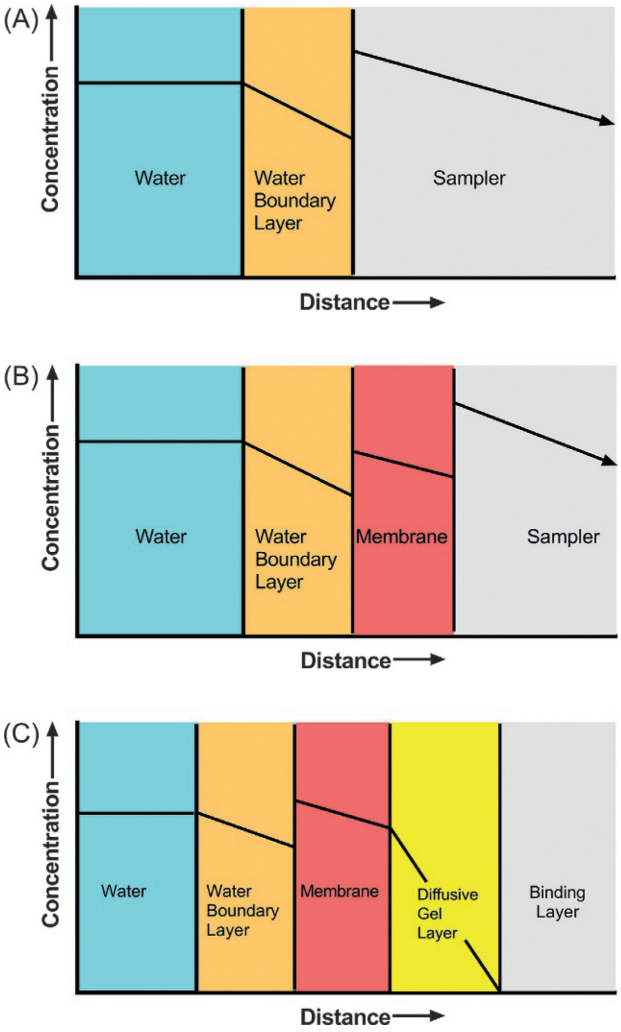

FIG. 3.2 Contaminant concentration profiles for (A) a one-phase sampler, e.g., PE strip; (B) a multi-phase sampler, e.g., POCIS; and (C) a diffusive gradient in thin-film (DGT).

In addition, it explicitly shows why first-order uptake rate constants generally do not have units of reciprocal time in this context when the concentration in the sampler is on a mass basis and that in the water on a volume basis (Bartkow et al., 2005).

$$\begin{aligned} \frac{dC_S}{dt} &= k_U C_W - k_L C_S \\ \Rightarrow k_U &= \frac{k_O A K_{SW}}{V_S} \text{ and } k_L = \frac{k_O A}{V_S} \end{aligned} \tag{3.6}$$

Integration of Eq. (3.4) under conditions of no contaminant in the sampler at initial deployment and a constant concentration of the contaminant in the water enables C_S to be related to deployment time (Fig. 3.3).

$$C_S = \frac{k_U}{k_L} C_W \left(1 - e^{-k_L t}\right) \tag{3.7}$$

$$= K_{SW} C_W \left(1 - e^{-k_L t}\right) \tag{3.8}$$

Initially, there is little contaminant present in the passive sampler, so the loss rate is negligible, and the sampler then acts as an infinite sink. Given such an approximation, Eq. (3.6) can be simplified to

$$\frac{dC_S}{dt} = k_U C_W \Rightarrow C_S = k_U C_W t \tag{3.9}$$

so that a plot of C_S vs deployment time should be linear and pass through the origin with a slope of $k_U C_W$. The passive sampler is then regarded as operating in a linear mode or regime (Fig. 3.3) (Taylor et al., 2020). In many

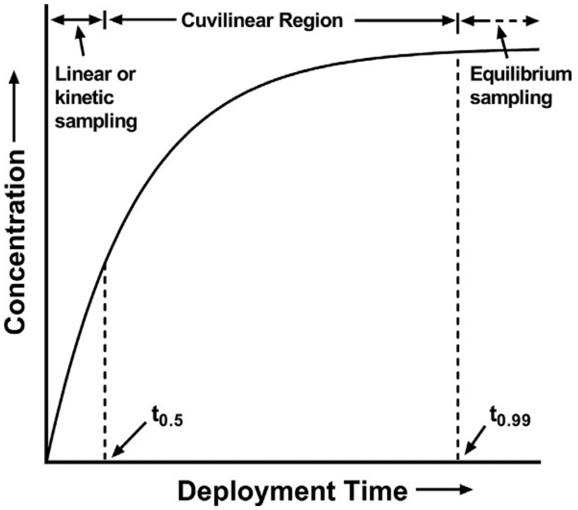

FIG. 3.3 Temporal accumulation profile of passive samplers exposed to a constant contaminant concentration, showing regions for linear or kinetic sampling, the curvilinear region, and the region where equilibrium sampling occurs.

cases, the contaminant amount in the sampler (N_S) is plotted against deployment times (Kaserzon et al., 2019; Mckay et al., 2020).

$$N_S = m_S k_U C_W t = R_S C_W t \tag{3.10}$$

with the product of m_S and $\boldsymbol{k_U}$ being termed the sampling rate ($\boldsymbol{R_S}$; e.g., $m^3\ h^{-1}$) (Booij et al., 2007; Morin et al., 2013; Salim and Górecki, 2019; De Weert et al., 2020; Jeong et al., 2020; Taylor et al., 2020; Valenzuela et al., 2020). This parameter is used to characterize the performance of a passive sampler in sampling a particular contaminant since it can be interpreted as the apparent volume of water that the sampler clears of a contaminant in a given time (Booij et al., 2007). Huckins et al. (2006) note that the only difference between $\boldsymbol{k_U}$ and $\boldsymbol{R_S}$ is that the latter is not normalized to a unit mass or volume of the sampler and that the group $\boldsymbol{R_S t}$ provides a link with classical batch extraction techniques because it represents an extracted fluid volume. The duration of the linear region is often arbitrarily taken to be the time it takes the sampler to reach 50% of its equilibrium concentration of the contaminant i.e., $t_{0.5}$ (Huckins et al., 2006; Vrana et al., 2005). This duration is given by

$$\boldsymbol{t_{0.5}} = \frac{-\boldsymbol{ln}\mathbf{0.5}}{\boldsymbol{k_L}} = \frac{\mathbf{0.693}}{\boldsymbol{k_L}} = \frac{0.693 m_S K_{SW}}{R_S} \tag{3.11}$$

At equilibrium $\frac{dC_S}{dt} = \mathbf{0}$, and from Eq. (3.6),

$$\frac{\boldsymbol{C_{S(Eq)}}}{\boldsymbol{C_{W(Eq)}}} = \frac{\boldsymbol{k_U}}{\boldsymbol{k_L}} = \boldsymbol{K_{SW}} \tag{3.12}$$

The exponential term in the uptake expression means that in theory, it takes an infinite deployment time to attain equilibrium. Practical attainment of equilibrium is generally taken as sampler concentrations reaching 99% of their true equilibrium value (Bartkow et al., 2005; Kaserzon et al., 2011). The finite time for this is

$$t_{Eq} = \frac{-\boldsymbol{ln}\mathbf{0.01}}{\boldsymbol{k_L}} = \frac{\mathbf{4.605}}{\boldsymbol{k_L}} = \frac{4.605 m_S K_{SW}}{R_S} \tag{3.13}$$

For deployment times of t_{Eq} or greater, the sampler is regarded as operating in the equilibrium mode or regime.

The purpose of a passive sampler is to enable the estimation of the aqueous concentration of an emerging contaminant from its concentration in the sampler.

In the kinetic mode, aqueous concentrations can be derived from the slope of plots of C_S or N_S versus time. The inherent error in derived aqueous concentrations, expressed as percent relative error (%$\boldsymbol{\delta}$), in assuming linear uptake at $t_{0.5}$ can be quantified as

$$
\begin{aligned}
\%\delta = 100\left|\frac{C_W - \frac{C_S}{k_U t}}{C_W}\right| &= \left|\frac{C_W - \left(\frac{1}{k_L t}\right) C_W\left(1 - e^{-k_L t}\right)}{C_W}\right| \\
&= 100\left[1 - \frac{\left(1 - e^{-k_L t}\right)}{k_L t}\right] \\
&= 100\left[1 + \frac{\left(1 - e^{\ln(1-0.5)}\right)}{\ln(1-0.5)}\right] \\
&= 100\left[1 + \frac{0.5}{\ln(1-0.5)}\right]
\end{aligned}
\tag{3.14}
$$

It is immediately apparent that the error is independent of C_W, analyte, and sampler type or composition since $\%\delta$ is simply a function of the fraction of equilibrium attained. This means that if the extent of linearity is chosen as $t_{0.5}$, and the ambient aqueous concentration is constant, a concentration derived from a kinetic passive sampler at this deployment time will underestimate the true concentration by 27.9%. Alternatively, if the upper bound of the linear uptake phase is taken to be $t_{0.25}$ (Harner et al., 2003), then $\%\delta = 13.1\%$.

A more accurate method for samplers in the linear or curvilinear modes of uptake is from Eq. (3.15).

$$
C_W = \frac{C_S}{K_{SW}\left(1 - e^{-k_L t}\right)} \tag{3.15}
$$

$$
= \frac{C_S}{K_{SW}\left(1 - e^{-\frac{R_S t}{K_{SW} m_S}}\right)} \tag{3.16}
$$

As well as the concentration in the sampler, it is necessary to know K_{SW}, $R_{S,}$ and the mass of the sampler phase. For samplers operating in the equilibrium mode, aqueous concentrations are derived from the ratio of the sampler concentration and K_{SW}.

These derivations of aqueous concentration above are not applicable if aqueous concentrations are not constant with time (Hawker, 2010). For samplers operating in the kinetic mode, if C_W is varying,

$$
\int_0^{C_S} dC_S = \frac{R_S}{m_S}\int_0^t C_W dt \tag{3.17}
$$

$$
\Rightarrow C_S = \frac{R_S}{m_S}\overline{C_W} \tag{3.18}
$$

where, $\overline{C_W}$ is the time-weighted average (TWA) of the aqueous concentration during the deployment period (Booij et al., 2007; Salim and Górecki, 2019). Details such as concentration maxima, minima, and variance or whether the variation is not random cannot be obtained with this approach.

3.3.2 Multi-phase passive samplers

Many passive samplers are more complex than a single phase. Taylor et al. (2020) recently observed that Chemcatcher©, POCIS, and the o-DGT (DGT sampler for organic contaminants) were the predominant multi-phase samplers used for polar pesticides. The former comprises a Teflon body housing a receiving phase in the form of a disk with sorbent particles e.g., C-18, in an inert polymeric matrix (Charriau et al., 2016; Taylor et al., 2019; Valenzuela et al., 2020). The device is also often equipped with a diffusion membrane (generally polystyrene, low-density PE, or PES) to reduce the contaminant's sampling rate and extend the duration of kinetic sampling. The choice of sorbent and membrane depends on the nature of the analyte. In POCIS, the sorbent is sandwiched between two diffusion membranes, typically PES or Teflon (Harman et al., 2012; Morin et al., 2018; Jeong et al., 2020). Accumulation of emerging contaminants by these devices involves diffusive transfer through three phases viz. a quiescent water boundary layer, a membrane, and the receiving phase. In terms of mass transfer and diffusion coefficients, and considering diffusion through the membrane occurs via water-filled pores

$$\frac{1}{k_O}=\frac{K_{SW}\rho_s}{k_W}+\frac{K_{SM}}{k_M}+\frac{1}{k_S} \tag{3.19}$$

$$=\frac{K_{SW}\rho_S\delta_W}{B_W}+\frac{K_{SM}\delta_M}{B_M}+\frac{\delta_S}{B_S} \tag{3.20}$$

where K_{SM}, k_M, B_M, ρ_M, and δ_M represent the contaminant's sorbent/membrane partition coefficient, mass transfer coefficient and diffusion coefficient in the membrane, together with membrane density and thickness respectively. Other passive sampling devices that can be considered similarly include the microporous PE tube sampler and a ceramic dosimeter. The former has been deployed with TiO_2/agarose, anion exchange or hydrophilic-lipophilic balanced sorbent for the sampling of glyphosate and aminomethyl phosphonic acid, PFASs and illicit drugs and PPCPs respectively (Fauvelle et al., 2017; Kaserzon et al., 2019; Mckay et al., 2020). The latter comprises a ceramic tube as a diffusion-limiting barrier enclosing an ion exchange resin (Bopp et al., 2005).

Three-phase or compartment models involving simultaneous linear differential equations have been derived to separately describe contaminant concentrations in the water boundary layer, membrane, and receiving phases with time for SPMDs, POCIS, and Chemcatcher© devices (Gale, 1998; Vermeirssen et al., 2012). Although only numerical solutions are accessible, such approaches have successfully described lag times in the appearance of contaminants in the receiving phase or sorbent after deployment due to significant accumulation in the membrane and/or restricted diffusion through the membrane (Vermeirssen et al., 2012). Factors affecting diffusion through porous membranes include the membrane porosity (ϵ), tortuosity (τ), and the compound's membrane/water partition coefficient K_{MW}. Incorporating these factors, the overall mass transfer coefficient may be represented by (Fauvelle et al., 2017)

$$\frac{1}{k_O}=\frac{K_{SW}\rho_S\delta_W}{B_W}+\frac{K_{SM}\tau^2\delta_M}{\varepsilon B_W}+\frac{\delta_S}{B_S} \tag{3.21}$$

A more complete description involves parallel membrane transfer by water-filled pore and the polymer phase itself (Kaserzon et al., 2019)

$$\frac{1}{k_O}=\frac{K_{SW}\rho_S\delta_W}{B_W}+\frac{K_{MW}\rho_M K_{SM}\tau^2\delta_M}{\varepsilon B_W K_{SM}+(1-\varepsilon)B_M\tau^2 K_{SW}\rho_S}+\frac{\delta_S}{B_S} \tag{3.22}$$

The lag-time for transit of a porous membrane is given by (Crank, 1979; Booij et al., 2007; Shackelford and Moore, 2013; Endo et al., 2019)

$$t=\frac{\delta_M^2(\varepsilon+K_{MW}\rho_M)\tau^2}{\varepsilon B_W} \tag{3.23}$$

and delays of the order of hours to days before accumulation in the sorbent begins have been observed for POCIS (Morin et al., 2013) and Chemcatcher© (Vermeirssen et al., 2012) for example, depending on the contaminant and membrane properties e.g. pore size, ambient conditions.

The three-phase model approach does not always predict passive sampler accumulation satisfactorily. With POCIS, (Morin et al., 2013, 2018) attribute this to an initial rapid sorption process in the sorbent, followed by slower sorption, possibly due to heterogeneity of sorbent composition or varying pore sizes. The pharmaceutical version of POCIS comprises three different sorbents. Inherent in the three-phase model approaches outlined is the assumption that all phases, exclusive of their respective boundary layers, are well mixed at all times and that ambient water concentrations are constant. These assumptions are not always valid and Endo et al. (2019) argue that three-phase models lack a solid mechanistic basis. They propose a dynamic model where transient diffusion through the water-filled membrane pores for example is given by

$$\frac{\partial C_W}{\partial t}=\frac{B_W\varepsilon}{(\varepsilon+K_{SW}\rho_S)\tau^2}\frac{\partial^2 C_W}{\partial x^2} \tag{3.24}$$

This has shown good fidelity with membrane and sorbent concentrations of selected herbicides and pharmaceuticals. Regarding aqueous concentrations that vary with time, Mutzner et al. (2019) investigated how accurate TWA water concentrations derived from Chemcatcher© were when deployed in sewer overflows and rivers. They found relatively short duration events or spikes resulted in a smaller error and that other factors such as analytical error and inaccurate or inappropriate sampler calibration have a similar or higher impact. Juntunen et al. (2020) propose a model with mass transfer coefficients and a parameter describing contaminant bonding to the receiving phase allowed to vary with time to accommodate ambient fluctuations. Salim and Górecki (2019) conclude that dynamic models are more complex but provide mechanistic understanding through simplified models are desirable for most users.

Diffusive gradient in thin-film (DGT) samplers comprise a membrane overlaying a diffusive hydrogel layer underneath which is a binding layer where the emerging organic contaminant e.g., PFASs and antibiotics (Guibal et al., 2017; Guan et al., 2018; Li et al., 2019) is irreversibly sorbed. They rely on diffusion to establish a concentration gradient between a surrounding water boundary layer and the base of the diffusive hydrogel layer (Fig. 3.2.). DGT samplers are therefore best described by a three-phase (viz., diffusive hydrogel layer (G), membrane filter (F), and water boundary layer (W)) model. Re-arranging Fick's First Law and expanding the mass flux term affords an expression relating the TWA concentration during the deployment time (t) to the amount accumulated on the binding layer of the sampler (N_S), the interfacial area with ambient water (A), and diffusion coefficients and path lengths in the transited phases (Davison and Zhang, 2012).

$$\overline{C_W} = \frac{N_S}{At}\left(\frac{\delta_G}{B_G} + \frac{\delta_F}{B_F} + \frac{\delta_W}{B_W}\right) \tag{3.25}$$

It is generally considered that $B_G = B_F$ and in addition, the water boundary layer is often ignored since the thickness of the diffusive hydrogel layer is thicker than that of the water boundary layer, except when the ambient water is relatively quiescent (Guan et al., 2018).

3.3.3 Calibration

To successfully relate measured contaminant sampler concentrations to TWA levels in the water, expressions such as Eqs. 3.5, 3.10, and 3.20 show that knowledge of the magnitude of mass transfer coefficients and sampling rates and hence diffusion coefficients, phase or layer thicknesses, and various partition coefficients are necessary. Since these vary with the contaminant and environmental site-specific factors such as temperature and flow rate of water, calibration of passive samplers is required (Taylor et al., 2019, 2020; Vrana et al., 2016). Some calibration e.g., determination of partition coefficients can be performed in the laboratory provided prevailing temperature and water quality details such as ionic strength are similar to those in the deployment (Berho et al., 2017; Kaserzon et al., 2012, 2013). From the Stokes-Einstein equation, diffusion coefficients are a function of temperature, phase viscosity, and molecular size. While some diffusion path lengths will be known from the sampler configuration, that of the water boundary layer depends on hydrodynamics at the sampling site and even if a relationship between flow rate and sampling rate has been established, the flow rate must be determined in situ. Co-deployed flow rate monitors are an obvious means while alternatives include passive flow monitors (PFMs) comprising materials such as gypsum and alabaster whose temporal mass loss due to dissolution can be related to flow rate (O'Brien et al., 2012; Booij et al., 2017). A similar strategy is employed in SorbiCell samplers that rely on advective water movement rather than diffusion (Rozemeijer et al., 2010).

For absorption-based samplers that demonstrate isotropic exchange e.g., SPMDs (Harman and Booij, 2014) where loss rate constants are related to uptake rate constants for a given compound (Huckins et al., 2002), performance reference compounds (PRCs) offer a means of in-situ calibration. PRCs are compounds with similar characteristics to contaminants of interest e.g., labeled analytes, that are chromatographically distinct and ideally, do not occur in water at the deployment site. They are spiked into the sampler before deployment and their loss rate constant is determined from simple first-order kinetics.

$$k_L = -\frac{ln\left(\frac{C}{C_O}\right)}{t} \tag{3.26}$$

The principle is that loss rate constants of PRCs are affected by the same factors that govern uptake rates of relevant contaminants. As a consequence, contaminant sampling rates may be obtained from

$$R_S = k_L K_{SW} m_S \tag{3.27}$$

The use of PRCs with adsorption-based samplers such as POCIS has met with little success because of incomplete mechanistic understanding of the operation of these samplers (Harman et al., 2011, 2012). However, there is also some evidence of anisotropic behavior with PRCs in ostensibly absorption-based samplers i.e., PES and silicone rubber samplers (Chepchirchir et al., 2020; Allan and Jenssen, 2019). With the latter, this was attributed to the deposition of suspended particulate matter enhancing PRC loss, but inhibiting contaminant uptake.

3.4 Passive sampling of non-polar chemicals of emerging concern

Passive sampling techniques designed for a wide range of non-polar organic contaminants have been developed and used since the early 1990s. The predominant samplers of use include SPMDs (Huckins et al., 1990), low- or high-density polyethylene (LDPE/HDPE) strip samplers (Adams et al., 2007; Booij et al., 1998; Müller et al., 2001), silicone (e.g. PDMS) strip samplers (Huckins et al., 1999; Prest et al., 1995; Booij and Van Drooge, 2001; Booij et al., 2002; Richardson et al., 2002), and Chemcatcher© (Kingston et al., 2000) (Table A1 in the Appendix).

Samplers for hydrophobic contaminants typically have a relatively large surface area that is advantageous for sampling large volumes of water (e.g., hundreds of liters over several weeks of deployment) (Interstate Technology & Regulatory Council, 2005; Kot et al., 2000; Stuer-Lauridsen, 2005; Vrana et al., 2005). This allows for an adequate concentration of emerging contaminants that are often found in trace levels in freshwater environments. An advantage of these devices is that non-polar chemicals are pre-concentrated before extraction in the laboratory. This can save efforts normally associated with laborious liquid-liquid extraction or solid-phase extractions of large volumes of water, to obtain sufficient material for analysis of the compounds of interest. Some samplers (e.g., PDMS) have been attractive to users due to the relatively low cost of the component material (Kwon et al., 2007; Ter Laak et al., 2008; Rusina, 2009). Other advantages include their capacity to act as in situ proxies for bioaccumulation of contaminants in aquatic organisms (such as bivalves (Smedes, 2007)) and fish (Rusina et al., 2017).

Derivation of water concentration estimates from passive samplers for non-polar contaminants is performed through the use of chemical and sampler specific sampling rates (R_s) and partition coefficients which are generally available in the literature, especially for the commonly monitored persistent organic pollutants (POPs) (Smedes and Booij, 2012; Booij et al., 2016; Rusina et al., 2010). Sampling kinetics are generally faster at greater external flow rates and higher temperatures and therefore should be considered when using these devices. As described in a previous section of this Chapter, methods for correcting for the influences of flow velocity and temperature on sampling performance with non-polar chemicals of emerging concern include PRCs (Huckins et al., 2002) and co-deployed PFMs (O'Brien et al., 2009).

Passive samplers such as those comprising PDMS, PE as well as Chemcatcher© (typically containing a polystyrene-divinylbenzene sorbent) have proven effective for targeting a range of non-polar bioaccumulative legacy compounds such as those regulated by the Stockholm Convention (UNEP, 2001) (i.e., chlorinated pesticides and solvents (e.g., DDT), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and brominated flame retardants (PBDEs)).

More recently these passive samplers have been used in combination with High Resolution Mass Spectrometry (HRMS) and suspect screening approaches to identify chemicals of emerging concern in freshwaters such as UV filters, halogenated, brominated, organophosphate and musk compounds, synthetic steroids, pharmaceuticals, food additives, plasticizers and pesticides and endogenous metabolites excreted from fish (Peijnenburg et al., 2014; Allan et al., 2008; Zhang and Davison, 2000; Jordan et al., 2013; Verhagen et al., 2019). Table A1 lists the types of passive samplers used for various non-polar organic contaminants in water systems and the type of compounds they have been used to monitor and detect in aquatic systems. It is not likely that one tool would be sufficient for a wide range of chemicals of concern, therefore a combination of methods may be required, depending on the needs and requirements of the monitoring campaign and specific sites investigated.

3.5 Passive sampling of Inorganic metals and nutrients

Passive samplers have been used to monitor species of metals and nutrients in aquatic environments. The most widely used samplers for this application are the DGT device (Peijnenburg et al., 2014) and Chemcatcher© (Allan et al., 2008). These samplers accumulate a labile fraction of metals by diffusion and can provide representative bioavailable metal concentrations. Regardless of the technique used, diffusion coefficients of the model species have to be determined individually to make accurate measurements of the concentration of the labile species (Zhang and Davison, 2000). The speciation of metals sampled will be influenced by the relative difference in diffusion coefficients together with the relative difference in affinity towards the receiving phase used.

A similar sampler configuration has been applied for the sampling of nutrients such as phosphate and nitrate. In these samplers, a cartridge with an adsorbent to collect P and N forms has been utilized (O'Brien et al., 2009; Jordan et al., 2013) and techniques such as the previously mentioned PFM (O'Brien et al., 2009) or the use of a known mass of salt whose dissolution rate is proportional to flow rates through the sampler have been used (Jordan et al., 2013) (Table A1).

3.6 Passive sampling of polar chemicals of emerging concern

Polar chemicals are chemicals with relatively high solubility in water due to the presence of one or more polar functional groups and also their molecular shape, resulting in a separation of charge (i.e., dipole moment) (Alvarez et al., 2007). Different studies define a polar chemical by their low *n*-octanol-water partition coefficient (K_{OW}) e.g., <log K_{OW} of 3.0. However, what the cut-off or threshold K_{OW} for polar chemicals is, is a subjective choice.

Passive samplers have been used extensively over the past three decades to measure the concentrations of both organic and inorganic chemicals (Mills et al., 2010; Vrana et al., 2005; Lohmann et al., 2017; Lohmann and Muir, 2010; Huckins et al., 1990; Booij et al., 2016). While earlier studies have focused on non-polar chemicals, there are currently four passive samplers principally used to measure polar chemicals in the aquatic environment viz. the POCIS, DGT, Chemcatcher©, and microporous polyethylene tubes (MPTs) (Fig. 3.4.). All samplers have the same basic configuration of a receiving phase located behind a diffusive membrane (Gong et al., 2018).

Each of those samplers has been used to measure a broad range of chemicals. Among these chemicals is a group referred to as Chemicals of Emerging Concern (CECs) which are often polar, have not been studied thoroughly, are not covered by any existing water quality regulations, and could potentially have toxic effects in the aquatic environment (Bletsou et al., 2015). The term "Emerging" however can be misleading, as some chemicals may have existed for decades in low concentration and only in recent years detected due to advances in analytical and sampling techniques. The CECs group covers a variety of polar chemicals including pharmaceuticals, hormones, pesticides, flame retardants, plasticizers, fragrances, endocrine-disrupting chemicals, surfactants, per- and polyfluorinated compounds, and industrial agents (Sauvé and Desrosiers, 2014).

3.6.1 Pharmaceuticals, personal care products, and pesticides

Most passive sampler water monitoring studies focus on pharmaceuticals and personal care products (PPCPs) and pesticides (see Madikizela et al., 2022, Chapter 10). PPCPs are defined by their usage for personal health or cosmetic purposes. Pesticides are mainly used in agriculture to protect crops but there is increasing usage in the domestic and industrial sectors. Due to their wide usage, their persistent or pseudo persistent nature, and the fact that many are still unregulated (Archer et al., 2017) they are ubiquitous in the aquatic environment (Dhodapkar and Gandhi, 2019). PPCPs mainly find their way into the environment via wastewater treatment plant (WWTP) effluent discharge whereas pesticides mainly find their way into the aquatic environment via soil and groundwater (Stuart et al., 2012) and members of both groups can cause adverse health effects to aquatic organisms and humans (Gerbersdorf et al., 2015).

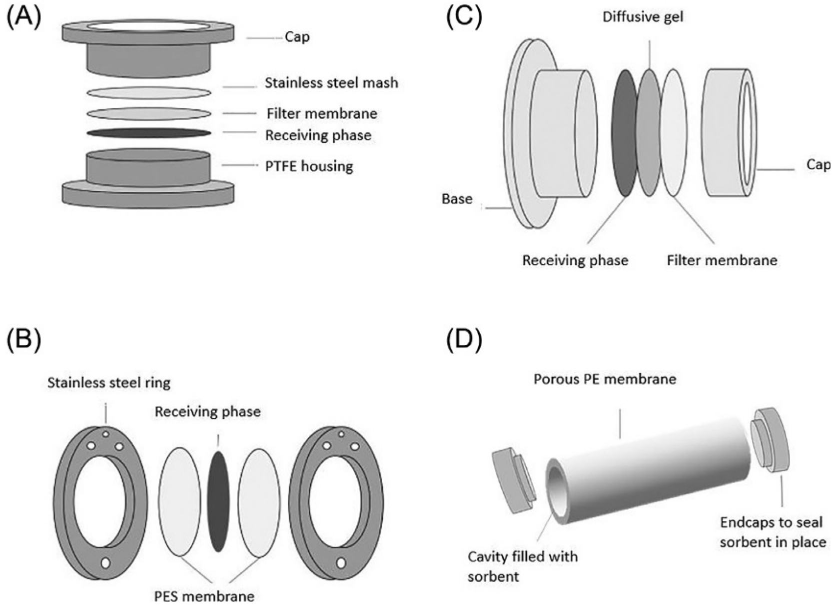

FIG. 3.4 Configurations of (A) Chemcatcher©, (B) POCIS, (C) o-DGT, and (D) MPT passive samplers. *Adapted from Gong, X., Li, K., Wu, C., Wang, L., Sun, H., 2018. Passive sampling for monitoring polar organic pollutants in water by three typical samplers. Trends Environ. Anal. Chem. 17, 23-33.*

PPCPs and pesticides comprise a large chemical class with a broad range of chemical properties such as log K_{OW}, net charge, diffusion coefficients, and partition coefficients. Many different passive samplers have been used to sample PPCPs and pesticides in the aquatic environment. Most studies in the literature use the Chemcatcher© and the POCIS which are similar in construction. Their main difference is their exposure surface, with the Chemcatcher© having an exposed surface of 15.2 cm^2 compared to typically 45.8 cm^2 for the POCIS. Another difference is the nature of their receiving phase, with the Chemcatcher© using sorbent disks as a receiving phase made of polystyrene-divinylbenzene reversed-phase copolymer (SDB-XC), or a similar polymeric structure but functionalized with sulfonic acid moieties (SDB-RPS). The latter disk with cation-exchange sites can adsorb polar and ionizable chemicals due to multiple binding mechanisms including van der Waals interactions and hydrogen bonding. More recently an hydrophilic-lipophilic balance (HLB) disk has been brought onto the market (Petrie et al., 2016). Both the SDB and HLB polymers with their mixed-mode interactions are therefore suitable for polar chemicals. In contrast, the POCIS uses loose sorbent (typically around 200 mg) including anion and cation exchange sorbents as well as HLB but in theory, any sorbent can be used. However, studies have shown that the loose sorbent in the POCIS can end up being compressed in the bottom which affects the sampling rates (Vermeirssen et al., 2012; Booij et al., 2020; Gravell et al., 2020). Because POCIS uses loose sorbent, the POCIS can only be deployed with a membrane (e.g., PES) to cover the sorbent whereas the Chemcatcher©, a disk, can be deployed without the membrane. These membranes are used as a barrier to slow down chemical uptake and filter out particles.

Studies show when comparing Chemcatcher© with SDB-XC and SDB-RPS disks, better uptake is found with the SDB-RPS, especially for ionizable pesticides and PPCPs and chemicals with a lower log K_{OW} (Kaserzon et al., 2014; Vermeirssen et al., 2009). For the SDB-XC sorbent disk, slightly better recoveries for nonionized herbicides and better uptake of chemicals with higher log K_{OW} were observed (Vermeirssen et al., 2009). A calibration study assessing 22 chemicals (PPCPs and pesticides) with log K_{OW} ranging from -2.6 to 3.8 found kinetic or non-linear uptake for 21 of these chemicals after 25 days, concluding the sampler is feasible to be used for deriving TWA concentrations (Vermeirssen et al., 2013). The SDB-RPS sampler is so versatile that (Moschet et al., 2015) investigated the uptake of 322 micropollutants (log K_{OW} -3 to 5) including neutral, cationic, zwitterionic, and anionic species. In total 204 chemicals were detected on the sampler. Overall a good correlation was found between the concentration in the water and the mass accumulated on the passive sampler, especially for chemicals that had less fluctuating water concentrations. For some pesticides where there was a poor correlation between the measured concentration and the mass in the sampler, concentrations were dynamic due to factors such as runoff events caused by rainfall. Extra caution is needed when interpreting data from chemicals released with inconsistent patterns (Moschet et al., 2015).

More recently, the utility of Chemcatcher© equipped with an HLB disk has been investigated (Petrie et al., 2016). This sorbent is potentially a good option to sample a broad range of polar chemicals since it has been extensively studied in the context of extraction of water samples with SPE (Petrie et al., 2016). However, studies have shown that HLB sorbent is inadequate for sampling some cationic drugs or anionic chemicals such as ibuprofen (Rimayi et al., 2019). To overcome this, Townsend et al. (2018) have employed an anion-exchange disk as a passive sampler receiving phase for acidic herbicides with linear uptake observed for 14 days.

POCIS has been calibrated and used extensively to quantify PPCPs and pesticide levels in the freshwater aquatic environment and more recently to assist in studies to assess chemical toxicity to organisms (e.g., (Taylor et al., 2020)). There are two principal standardized POCIS configurations commercially available i.e., the Pharma-POCIS and Pest-POCIS to measure pharmaceuticals and pesticides respectively. The Pest-POCIS comprises a sorbent mixture containing polystyrene-divinylbenzene similar to the Chemcatcher© together with a carbonaceous material (originally Ambersorb 1500), whereas the Pharma-POCIS uses HLB as the receiving phase (Alvarez et al., 2004). The Pharma-POCIS is more heavily used as it retains not only polar pharmaceuticals but also non-ionic detergents, hormones, and pesticides, and the carbonaceous sorbent in the Pest-POCIS binds so strongly to some pharmaceuticals that extraction is nearly impossible (Alvarez et al., 2004; Morin et al., 2013). Morin et al. (2013) used the Pharma-POCIS but found negligible accumulation of ionized chemicals. Other ion exchange sorbents like weak anion exchange (WAX) and MCX were suggested, however, there was no improvement in performance compared with the Pharma-POCIS (Li et al., 2011). Acidic chemicals and highly hydrophilic ones are problematic when they reach equilibrium or have no sorption affinity due to limited van der Waals interactions (Bäuerlein et al., 2012). Promising uptake patterns with the accumulation of acidic pesticides using a mixed-mode cation exchange sorbent MAX sorbent have been observed, however, due to Coulombic interaction, competition with other anions might occur (Bäuerlein et al., 2012; Fauvelle et al., 2012).

Most o-DGT studies have been focusing on the sampling of pharmaceuticals and pesticides (Guibal et al., 2017). Different sorbents have been investigated as receiving phases to measure PPCPs and pesticide concentrations in water including HLB, XAD18, Sepra ZT, XDA-1, MCX, and MAX (Chen et al., 2018; Challis et al., 2016; Challis et al., 2018a; Stroski et al., 2018). Stroski et al. (2018) optimized the o-DGT to sample the potentially difficult anionic pesticides. They found that overall HLB was the more reliable receiving phase compared to the anion exchange sorbent MAX except for the chemical ioxynil. For PPCPs the most used receiving phase is the cross-linked polystyrene XAD18 (Chen et al., 2018). The second most used binding phase is HLB (Challis et al., 2018b; Stroski et al., 2018).

In a recent study by Hageman et al. (2019) the MPT sampler was used in combination with the POCIS and o-DGT to measure pesticides in New Zealand streams. Overall, more chemicals were detected in the POCIS compared to the other two samplers, which highlights the advantageous higher sampling rate of the POCIS. The sampler could have been deployed for a longer period, however, the POCIS might reach equilibrium meaning no TWA can be calculated. For the o-DGT sampler, a longer deployment can cause degradation of the diffusive gel (Challis et al., 2018a; Stroski et al., 2018). The concentration calculated for imidacloprid, atrazine, and 2,4-D were comparable for all three samplers, indicating the feasibility of the more novel o-DGT and MPT samplers for the analysis of pesticides in the aquatic environment.

3.6.2 Per- and polyfluoroalkyl substances

In the last two decades, the monitoring and occurrence of per- and polyfluoroalkyl substances (PFASs) in the aquatic environment have increased as they have been recognized as important emerging contaminants. They are widespread due to their persistence, bioaccumulation potential, and relatively high aqueous solubility (Lai et al., 2019; Ahrens, 2011). There are over 3000 PFAS chemical formulations with aqueous film-forming foams (AFFFs) containing between 200 and 300 different PFASs (Wang et al., 2017b). The first passive sampler used for monitoring PFASs in surface water was a modified POCIS. Results were promising with a range of PFASs retained using the weak anion exchanger Strata XAW as a receiving phase. However, even with a smaller surface area (i.e., 16 cm^2 compared to 41 cm^2 for the traditional POCIS) half time to equilibrium was reached between the 2.4 and 13 days for PFOS and PFOA respectively (Kaserzon et al., 2012). As a result, the sampler could only be deployed for a relatively short period while staying in kinetic mode. As expected, sampling rates of PFAS using the POCIS were affected by flow (Kaserzon et al., 2013), making it difficult to use sampling rates obtained in laboratory studies, instead of needing specific in situ sampling rates.

Nevertheless, passive sampling of PFAS is currently primarily done using the POCIS, and different studies have investigated various sorbents such as HLB, WAX, and the Pest-POCIS (Gobelius et al., 2019; Li et al., 2016; Fedorova et al., 2013). Wang et al. (2017a) regarded the receiving phase available for the carboxylic and sulfonic acids to be limited and testing an immobilized ionic liquid (IIL) as a receiving phase. The IIL showed linear uptake for 21 days, in contrast to HLB that became curvilinear after 7 days (Chung et al., 2017). Studies have also used o-DGT or the MPT passive sampler for PFASs using sorbent phases such as XAD18, HLB, and Strata X-AW, with results showing longer half times to equilibrium and little effect of flow on sampling rates (Guan et al., 2018; Urík and Vrana, 2019).

3.6.3 Other polar emerging contaminants

Due to its broad applicability, the POCIS has been used to monitor a wide range of other polar chemicals including UV-Filters such as the benzophenone-type UV-filters (Fent et al., 2010), organophosphate flame retardants including tripropyl phosphate, and tris (2-chloroethyl) phosphate (Yang et al., 2017) as well as hormones, synthetic steroids and illicit drugs (Creusot et al., 2014; Fedorova et al., 2014; Jacquet et al., 2012).

The applicability of the o-DGT sampler to monitor illicit drugs (Guo et al., 2017; Zhang et al., 2018), endocrine-disrupting chemicals (Chen et al., 2018), industrial chemicals such as nitro-chlorobenzene compounds (Zhang et al., 2019) and organophosphorus flame retardants (Zou et al., 2018) has been investigated and resulted in the derivation of sampling rates and well-calibrated samplers. The Chemcatcher has also recently been applied to monitor vulcanizers associated with tire wear particles in drinking water dams (Rauert et al., 2020).

The combination of advanced High-Resolution Mass Spectrometry (HRMS) suspect screening approaches together with passive sampling techniques for polar organic contaminants (e.g., Polar Organic Chemical Integrative Sampler (POCIS) and Chemcatcher) are increasingly being applied to increase the range of compounds that can be detected in water systems. Studies have reported the identification of compounds such as synthetic steroids, pharmaceuticals, food additives, plasticizers, and pesticides using this approach (Allan et al., 2013; Chung et al., 2017).

3.7 Quality assurance—Quality control

Quality assurance and quality control (QA and QC) are terms often associated with laboratory analysis, but they are also important in monitoring and sampling. QA in this context refers to documented procedures and protocols developed to ensure the monitoring program produces results of known precision and bias. QC represents the operational activities that validate the collected data and check whether there is any bias, sample contamination, or loss of contaminant (D.E.S., 2020).

Factors to consider with QC of grab sampling include the number of samples to collect and the use of procedural, laboratory, and field blanks. Multiple samples are necessary to derive statistical measures and confidence intervals and it allows testing for significant differences between data for spatial variance and non-compliance with any regulations. A minimum of three samples is required for these purposes. Blanks enable any sources of contamination to be identified during the sampling procedure or subsequent transportation, preservation, and storage. Blank water should be ultra-pure Milli-Q water or water shown to have no contamination present. Types of blanks include container blanks to assess contamination associated with sample containers themselves or any preservation process. Transport blanks identify contamination arising from transport from the field while field blanks are necessary to check for contamination arising during the collection itself. The use of blanks is good basic sampling practice, but especially important when sampling emerging contaminants at trace or ultra-trace levels (D.E.S., 2020).

The use of blanks is also important with passive samplers to ensure confidence in derived results. The deployment of replicate passive samplers enables statistical measures of variance to be calculated in the same way as multiple grab samples. The ISO Standard *Guidance on passive sampling in surface waters* (I.S.O., 2011) outlines important considerations for quality control during use, deployment, and analysis of passive sampling tools. Calibration of passive samplers is essential since the flow rate of water over the external surface of many passive samplers affects sampling rates. Accurate determination of flow rates and knowledge of the relationship between flow rate and contaminant sampling rate reduces variability from this source (D.E.S., 2018).

3.8 Application of sampling techniques to water quality guidelines

Of the 148 chemical hazards in drinking water defined by the World Health Organization (WHO) 107 are organic (WHO, 2021). These guidelines refer only to water for drinking and are not derived based on ecological impacts. As a baseline WHO's guidelines can be interpreted and implemented inconsistently with sampling and analysis referred to as "it is not essential to use standard methods, the methods used must be properly validated (WHO, 2021). Each jurisdiction will have its lists of priority pollutants, methods for data acquisition, and recourse for breaches. This is exemplified in the differences between the EU's water framework directive (WFD) and US EPA's clean water act (CWA). Both look to improve water quality but the CWA looks at point-source pollution and the WFD at river basin management, meaning the CWA requires more supplementary regulations but less ambitious resource allocation (Steele et al., 2008). These are two very mature environmental policies in developed regions, but they are not easily compared with one another. These differences will only be accentuated when looking at other nations and regions.

Priority lists are generally short compared with the number of identified chemicals in a jurisdiction and the number introduced to the market annually (Llanos et al., 2019); the EU's water framework directive identifies 20 priority substances and 13 priority hazardous substances (Parliament, 2008), this is in contrast to the EU's ECHA (REACH) chemical database (European Chemicals Agency, 2020), which contains 10,000s of substances (Fig. 3.5.). With such a small proportion of existing chemicals being actively monitored, vital information on the status of freshwater resources may be missing.

Legislative inconsistency is particularly exacerbated when dealing with emerging contaminants. By their very nature, emerging contaminants are poorly categorized and reliant on definitions that may differ from one jurisdiction to the next. The NORMAN network's definition "A substance that has been detected in the environment, but which is currently not included in routine monitoring programs and whose fate, behavior and (eco)toxicological effects are not well understood" (N.O.R.M.A.N., 2012) can be interpreted differently based on the term "not well understood". This interpretation is challenging; does a substance require chronic human exposure understanding or is acute macroinvertebrate toxicology sufficient for example?

The issue of legislative inconsistency is important if a pollutant is measured or prioritized in one country but not another. Is it then categorized as an emerging contaminant or not? A contemporary high profile example is glyphosate whose use is allowed in the EU until 2022 (Parliament, 2017), still allowed in the US (USEPA, 2009) and Australia (A.P.

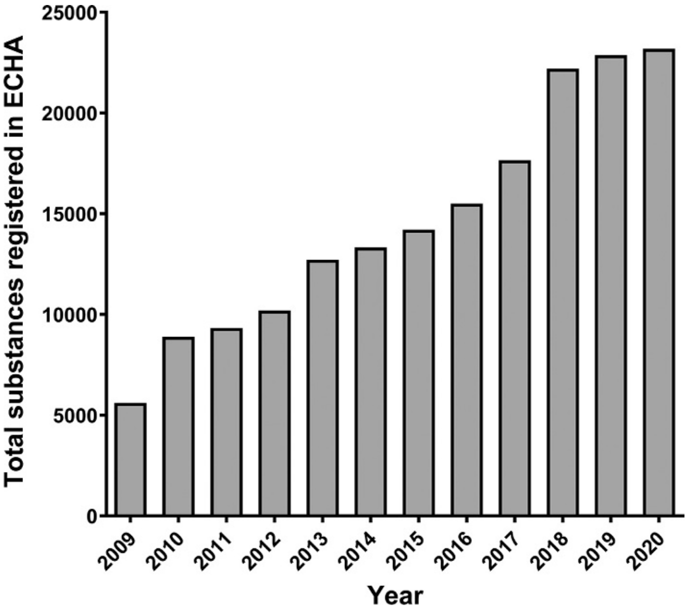

FIG. 3.5 Total number of substances registered in the ECHA database by year. *Data from European Chemicals Agency, 2020. REACH Registration Statistics. ECHA. https://echa.europa.eu/registration-statistics-infograph# (Accessed September 2020).*

V.M.A., 2017) and "either restricted or banned in approximately 20 countries" (Meftaul et al., 2020). The status of glyphosate as an emerging contaminant or a regular contaminant is uncertain.

The constantly growing chemical lists and ever-mutating legislation on water contaminants worldwide are inevitable and unlikely to become streamlined in the foreseeable future, negating the possibility of a single policy-based solution to tackling emerging contaminants in the international context.

If the international scientific community wishes to align its detection efforts to provide greater comparative data and trans boundary approaches, it will not be found in legislatures deciding which compounds are priorities. An alternative approach is to ensure that any data collected is as wide-ranging: as chemically, temporally, and spatially as possible and shared internationally. With broad-ranged data, non-priority compounds can be analyzed in addition to existing suites, or retroactively analyzed as necessities change as proposed in Tröger et al. (2018).

Collecting this broad data requires both the analytical capability to detect a wide range of compounds along with samples that are representative of spatial-temporal heterogeneity. Efforts to this effect have begun with international collaborations such as via the NORMAN network and other research organizations (Alygizakis et al., 2018).

3.8.1 Chemical variation

The chemical space of emerging contaminants is vast, incorporating ionic, polar, bioavailable, concentration, and just about any other variation possible. This ensures sampling is just as complex with individual methods capable of detecting and quantifying all emerging contaminants unlikely to be found. Rather, combinations of sampling methods and analytical developments will need to be taken advantage of if any comprehensive data is to be achieved.

Targeted analysis and suspect screening are a simple way of determining the presence and concentrations of regulated chemicals enabling comparisons with relevant guidelines and regulations, and actions to be taken where required. This procedure does not, however, easily indicate the presence of other compounds that may be toxicologically relevant. Non-target analysis (e.g. the use of High-Resolution Mass Spectrometry (HRMS)) offers the opportunity of detecting prioritized and non-prioritized contaminants (Schymanski et al., 2015), tentatively identifying unexpected pollutants (Gago-Ferrero et al., 2015), and preserving the entire sample's data (Gosetti et al., 2016). Application of the growing developments of non-target screening to samples would contribute greatly to international comparisons when combined with data sharing incentives and platforms.

3.8.2 Temporal variation

Grab sampling, despite being the predominant sampling method, suffers greatly from being a snapshot in time (Chen et al., 2020; Valenzuela et al., 2020). This 'snapshot' is entirely dependent on the frequency and timing of sampling programs, which are often ill-defined or occasional (Table 3.3).

TABLE 3.3 Sampling type and frequency of sampling for various water quality guidelines or legislations.

Legislation	Sampling type	Frequency	Legislation
WFD	Unspecified	Every 3 months	European Community (2000)
CWA major facilities	Unspecified	Once per 2 years	USEPA (2014)
CWA minor facilities	Unspecified	Once per 5 years	USEPA (2014)
South Africa	Unspecified		Department of Water Affairs and Forestry (1996)
Queensland, Australia	Composite, grab, and passive sampling	Sampling may be required every hour, day, week, fortnight, month, or possibly only once a year	D.E.S. (2018)
India	Unspecified	Other contaminants once per year	Bhardwaj (2005)
Argentina	Unspecified	All provinces set their own codes	OECD (2019)

Passive sampling and auto-sampling provide greater temporal generalizability than 'snapshot sampling' methods (i.e. grab/spot, sediment, biota) (Chepchirchir et al., 2017; Lai et al., 2019; Madrid and Zayas, 2007; Taylor et al., 2019; Vrana et al., 2005; Zhou, 2008). By accumulating contaminants over time, the TWA provided by auto and passive sampling ensure that acute peaks of pollution such as those from illegal dumping, storm runoff (Hitchcock, 2020), or other unaccounted peaks can be more representative in the data.

3.8.3 Spatial variation

Spatially diverse data acquisitions require increased resources since more samples need to be collected from wider-ranging areas necessitating greater financial, logistical, and human inputs. To ensure that regions with less intensive environmental legislation can acquire the same data, it is important to address sample collection as a holistic international effort rather than promote solutions that are developed in regions with advanced environmental legislation such as the WFD and CWA and the access to required resources and technologies. To this end, solutions should be simple to implement, with samples that are simple to analyze, easy to store, easy to transport, and cost-effective.

Spatial variation is best addressed through a combination of grab and passive sampling at this time. Grab sampling will ensure complete analysis of the sample at a given time and maybe easier to extract and analyze where there are limited analytical resources. By also using passive samplers, there is greater ease of transport and storage, which could be used to facilitate international analysis and collaboration.

3.8.4 Overall applicability

To provide a comprehensive, international alignment of emerging contaminant sampling strategy, the two primary considerations espoused by Ferreira et al. (2007) are that "(1) transitional and coastal water sampling stations within each river basin district are sufficient in number; and (2) observations are frequent enough to provide an assessment of the overall water status." These two factors, when addressed, can be used to overcome the innate differences in requirements for different legislatures, redirecting focus from a few contaminants to the inclusive future strategies necessary for future water conditions (Altenburger et al., 2019).

Factor 1 (sufficient sampling sites geographically) is addressed by ensuring sampling is relatively cheap and easy, and samples can be transported for both sampling and analysis. Factor 2 (sufficiently frequent samples) can be tackled by either a dramatic increase in the number of samples taken or by implementing time integrative sampling. Both factors 1 and 2 can be addressed through the use of passive sampling: deployments can be on the scale of months, deployments are generally simple due to the lack of active components, sizes of samples are generally small, meaning they can be transported cross-boundary as they are not water and storage over years has proven possible. With the development of new phases and tackling problematic compounds, passive sampling may continue to allow a better international understanding of emerging contaminants.

When this is combined with improvements to non-target analysis and data-sharing platforms the community will be able to take a more proactive approach to discourse, ensuring legislation reflects the environment rather than sampling merely reflecting the legislation.

3.9 Current limitations and opportunities with grab and passive sampling

While widely used, there are some limitations in grab sampling methods of emerging contaminants that should be recognized. Fig. 3.6. depicts past, present, and future trends in grab and passive sampling methods for emerging organic contaminants with associated limitations and opportunities. Spot grab sampling represents a single snapshot of the concentration of these analytes. Therefore, inconsistencies in results from sampling in waterbodies displaying spatial and temporal heterogeneity make the approach unsuitable for temporal trend studies for example (Xing et al., 2013). Composite sampling such as time-proportional sampling can be used to increase the frequency of sampling but this approach may miss the maximum concentrations of contaminants and cannot provide a representative sample for hydrographic variation in streams (Xing et al., 2013). These issues require a large number of samples which increases the cost of sampling and analysis (Xing et al., 2013). In addition to the need for large water volumes to determine the concentration of trace compounds, the stability of analytes before analysis is important. During grab sampling, compounds may degrade on the transportation of bottles from sampling sites to the laboratory (Valenzuela et al., 2020).

For passive samplers in general, lack of calibration or the absence of necessary calibration details e.g., diffusion coefficients and partition constants represent a potential limitation on their effective use. A common problem with Chemcatcher© and POCIS samplers for example is the effect of external flow over the sampler surface on the sampling rate. This cannot be assessed with PRCs because there is no true isotropic behavior with either sampler as hysteresis occurs with pollutant adsorption on the sorbent (Greenwood et al., 2007; Harman et al., 2011). The sensitivity to flow is caused by the WBL, which for both the Chemcatcher© and POCIS generally control the uptake of a chemical (Alvarez et al., 2007). The o-DGT sampler in contrast utilizes a relatively thick diffusive membrane restricting chemical uptake in such a way that uptake is largely independent of flow. Most o-DGT studies have focused on the sampling of pharmaceuticals and pesticides (Guibal et al., 2017). However, derivation of TWA concentrations requires knowledge of diffusion coefficients of analytes in the diffusive hydrogel layer (Eq. 3.25). The DGT technique was originally developed for metal ions and complexes (Scally et al., 2006). While diffusion coefficients for these are readily available (DGTResearch, 2020), relevant data for organic emerging contaminants is currently comparatively scarce although Urík et al. (2020) have recently published data for polar organic compounds in agarose hydrogel.

A practical issue with the deployment of passive samplers for extended periods is biofouling. Bacteria and resident flora and fauna can form biofilms on exposed surfaces potentially impeding uptake and accumulation of emerging contaminants, with this effect increasing over time. For modeling of mass transport, (Booij et al., 2007) have treated this biofilm as a stagnant water layer with dispersed organic matter (analogous to sediment). Remedial strategies include the use of PRCs and PES membranes that seem less susceptible to biofouling than PE for example (Vrana et al., 2005).

Regarding particular emerging contaminants, existing sampling phases employed may not be suitable for certain chemicals of concern. For example, one problematic pesticide to sample is glyphosate due to its ionic characteristics. Glyphosate cannot be sampled using standard POCIS or Chemcatcher configurations. However, studies have shown that titanium dioxide (TiO_2) is an efficient receiving phase to sequester anionic chemicals like glyphosate (Turner et al., 2012; Bennett et al., 2010). Fauvelle et al. (2015) adapted the o-DGT by using TiO_2 as the receiving phase with successful uptake of both glyphosate and its metabolite aminomethyl phosphonic acid (AMPA). The authors however

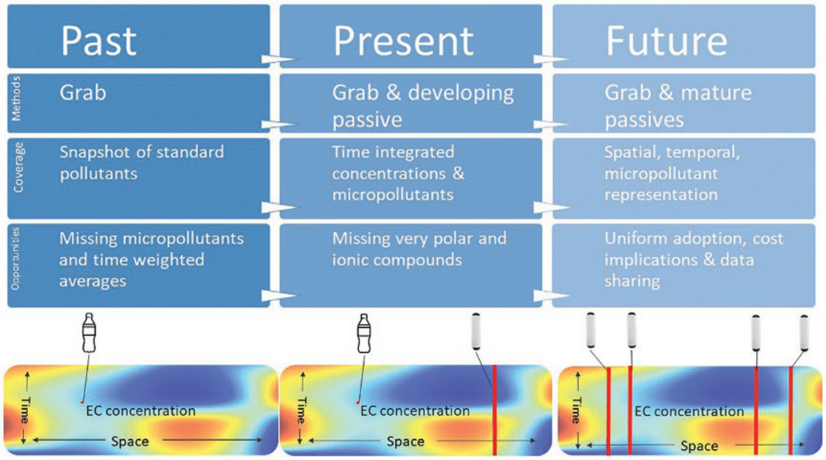

FIG. 3.6 A summary of past, present, and future trends in sampling methods for emerging organic contaminants with associated limitations and opportunities.

questioned the sensitivity and applicability due to the relatively low sampling rate (Fauvelle et al., 2015). To address this issue they developed and applied a passive sampler using microporous polyethylene as a diffusion membrane and found an increase in sampling rate by a factor of 2 in the laboratory and effective in situ deployment (Fauvelle et al., 2017).

Notwithstanding these limitations, passive sampling does offer some novel and important opportunities for sampling emerging contaminants. One reason those passive samplers may not be able to accumulate some of these compounds is a lack of binding affinity to the sorbents employed. A recent study developed a novel sampler utilizing water as a receiving phase to measure very polar chemicals in wastewater influent (Verhagen et al., 2020). This design might be applicable to measure chemicals in other aquatic environments for emerging contaminants that have not been successfully sampled previously by more traditional passive sampling configurations. Furthermore, the range of sorbents or receiving phases is increasing with advances in Materials Chemistry. Molecularly imprinted polymers (MIPs) for example are polymers formed with deliberate cavities based on a molecular template bound either covalently or non-covalently to the polymer framework during polymerization. Subsequent removal of the template leaves binding sites complementary in size and shape to the original molecular template. In this way, MIPs can be very specific sorbents for emerging contaminants (Kueseng et al., 2009). This strategy has been exploited to sample for glyphosate and AMPA (Berho et al., 2017) and PFASs (Cao et al., 2018) in a POCIS as well as antibiotics, 4-chlorophenol, and brominated flame-retardants (Tetrabromobisphenol A) in an o-DGT sampler (Cui et al., 2020; Feng et al., 2019; Dong et al., 2014). MIPs are specific for particular sorbates and may not be useful when monitoring a suite of contaminants or when a wide screening or preliminary reconnaissance of an unknown suite is undertaken.

Charcoal-based passive samplers have been used to measure chemicals such as bisphenols and *N*-nitrosodimethylamine (Kaserzon et al., 2011; Zheng et al., 2015). Carbon nanotubes offer promise in such situations as a versatile sorbent characterized by a large surface area and high sorption efficiency (Godlewska et al., 2020). Multi-wall carbon nanotubes have been employed in a POCIS configuration to successfully sample a range of pharmaceuticals, phenolics, and hormones (Jakubus et al., 2017). The combination of advanced High-Resolution Mass Spectrometry (HRMS) suspect screening approaches together with grab and passive sampling techniques involving novel sorbents for polar analytes increases the range of emerging freshwater contaminants that can be monitored.

Overall, to enable wider use of passive sampling approaches, there needs to be further development of samplers e.g. POCIS for polar compounds, given that calibration by PRCs is not applicable (Harman et al., 2011, 2012). In general, there is a lack of rigorous theoretical understanding of how samplers operate and a dearth of calibration data, especially for emerging pollutants that needs to be overcome. Integration of passive sampling with toxicity bioassays would facilitate improved monitoring programs from chemical and toxicological viewpoints (Vrana, 2008), given TWA concentrations from kinetic mode samplers are more relevant to aquatic organism exposure than grab sampling since only dissolved phase analytes are accumulated by passive samplers (Altenburger et al., 2019). This chapter falls under the section analyses with other chapters e.g. Mwedzi et al. (2022); Kaykhaii and Hashemi (2022), Kebede et al. (2021), Kumar et al. (2022) that aim to understand how emerging freshwater pollutants are analyzed or detected within aquatic ecosystems.

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CHAPTER

4

Miniaturized solid phase extraction

Massoud Kaykhaii and Sayyed H. Hashemi

4.1 Overview

Toxic pollutants originating from human activities, such as fuel combustion and industrialization are continuing to be introduced to the environment (see Tavengwa and Dalu, 2022, Chapter 1). Any assessment of efficiency of environmental protection policy requires the availability of relevant and reliable data on concentrations of pollutants in the environment. As a result, one of the major tasks of an analytical chemist is monitoring trace amounts of these pollutants, which include organic, inorganic, radioactive species, and biomolecules. Accordingly, analytical methods are needed to determine traces of heavy metals, anions, and organic compounds that range from simple aromatic cyclic structures to larger molecular weight compounds. So, these methods necessitate the usage of many materials and solvents, thus in many cases producing poisonous remnants. The number of the samples needed to be analyzed over the last decade has also grown rapidly. On the other hand, in recent years, the interest and attention of the scientific chemistry community in the development of green methods and techniques have increased significantly. This means that while by precise detection of pollutants, analytical chemistry tries to help prevent environment pollution, at the same time analytical methodologies produce harmful wastes that create risks for operators and damage the environment. Therefore, the concept of green analytical chemistry (GAC) was proposed as important criterion to reduce the amount of solvents and reagents employed to create environmentally friendly analytical chemistry methodologies. To achieve GAC, it is necessary to find out what part of a chemical analysis is the most critical section of the method in this regard. It has been proven that 80% of the time of analysis and most of the chemicals and reagents are used on sample preparation and collection step of the analytical protocol. This part is also representative of most errors that occur in chemical analysis. Clearly, any mistake occurring in collecting and processing a sample could lead to a substantial error in the final result regardless of the excellent performance of the analytical instrument. So, to minimize the amount of the chemicals, it would be necessary to scale down sample size and number of samples which also enables in-field measurements through solid-state portable analytical devices (Koohkan et al., 2020). In turn, this feature necessitates miniaturization of methods, including sample preparation steps. Miniaturization also minimizes waste generation, minimizes the use of energy, reduces the cost of analysis, and increases simplicity and the safety of the operator.

Although chemical instrumentation, such as sensors and micro-devices, microscopy, chromatography, and spectroscopy have undergone exceptional improvement in sensitivity, sample preparation step (whose goal is enrichment, cleanup, and signal enhancement) still plays an important role in identifying and measuring various analytes before their introduction to analytical instruments. That is because matrices of most samples are complex and the amount of the analytes in samples are lower than the limit of detection (LOD) of the instruments. Liquid–liquid extraction (LLE) has been widely used for extracting water contaminants since the early nineteenth century. In LLE, the sample and extracting phase are both liquids. The two liquid phases must be immiscible. The LLE is time-consuming, tedious, imprecise, and insensitive, and because of consuming large amounts of toxic and expensive solvents, it is very dangerous for health and the environment. Furthermore, LLE is unable to extract polar analytes. To overcome these problems, solid-phase extraction (SPE) was introduced in 1951 by the pioneer work of Braus et al. (1951). Many decades of research effort resulted in wide acceptance of this sample handling technique and also in growing interest of both

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analysts and manufacturers. SPE is more effective than LLE and it is easier to achieve higher extraction efficiencies by applying reduced volumes of eluents. SPE does not need the phase separation needed for LLE and deletes errors associated by variable or inaccurately determined extract volumes. However, like any other extraction technique, there are some drawbacks in SPE also. These include the possibility of low recovery because of interaction between sorbent and sample matrix, need for doing multiple steps, low reproducibility due to differences between different batches of a solid sorbent, sorbent bed clogging (especially in cartridges) by suspended particles of sample, and for special extracting phases, it is more expensive than LLE.

To overcome such disadvantages, miniaturization of solid-phase extraction was introduced. These miniaturized methods allow sampling and (almost) solventless extraction of trace amounts of analytes from just a few mL of complex samples. At the same time, analytes are enriched, and in many cases, they can be directly delivered to the analytical instrument. Since the introduction of solid-phase micro-extraction (SPME) as the first solventless micro-extraction technique in the 1990s, many other variants have been introduced, and these include micro-solid phase extraction (μSPE), stir-bar sorptive extraction (SBSE), and micro-extraction with packed sorbent (MEPS). The present chapter focuses briefly on describing these miniaturized SPE methods and their applications on emerging pollutants in freshwater. In all of these techniques, no extraction solvent is required; rather, a stationary phase is used to adsorb the analyte from the sample solution. Application of these micro-solid phase extraction techniques for water analysis enabled faster analysis with better accuracy and precision and less solvent consumption.

4.2 Solid-phase extraction

The SPE is a fully-developed sample preparation technique that is widely used for the extraction of analytes of a liquid sample, while they are pre-concentrated and cleaned up at the same time. Even though the first trials to do sample preparation using a solid sorption material (carbon filters) were published almost 70 years ago, this technique was expanded in the early 80s as many researchers were focused on it due to the need to decrease organic solvent usage in laboratories.

The SPE can be performed on cartridges or disks. Due to low reproducibility, and low capacity, the application of disks is less common these days and most SPE experiments are applying cartridges. Cartridge SPE is essentially a four-step process as depicted in Fig. 1. In the first step, wetting and conditioning of the sorbent is performed. The sorbent must be wetted and conditioned with a solvent or buffer similar to the sample solvent. This ensures an appropriate contact between the analytes and the sorbent material. In the second step which is loading the sample step, the sample is passed through the solid sorbent by gravity, pumping, or aspiration by vacuum. Target analytes will be exhaustively retained by the sorbent, and ideally, most of the matrix compounds will pass through the solid sorbent without being retained. Thus, pre-concentration of analytes and purification of the sample is achieved in this step. Washing of the sorbent with a solvent that cannot dissolve analytes will eliminate matrix compounds retained in the solid sorbent without displacing the analytes (third step). Target analytes are eluted from the solid sorbent by using the minimum solvent volume in the final step. Therefore, it is easy to achieve a high extraction efficiency of the analyte by using reduced volumes of elution solvents. In the last two decades, this sample handling technique became the method of choice in many analytical applications and it has been gradually included in standard methods of analysis.

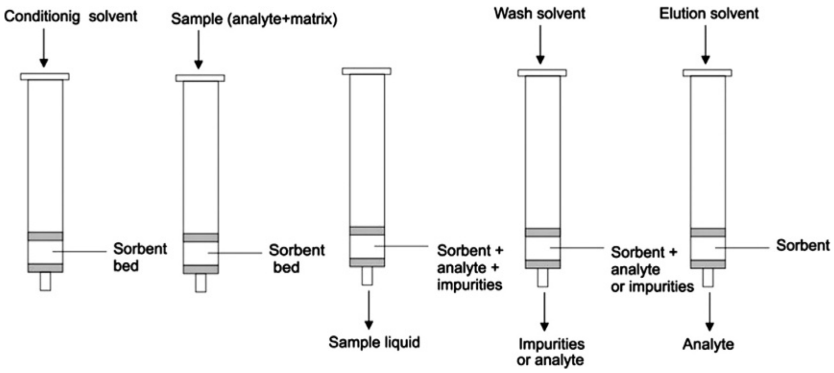

FIG. 1 Schematic of SPE procedure (Żwir-Ferenc and Biziuk, 2006).

4.3 Miniaturization of solid-phase extraction

Miniaturization methods are of increasing interest in analyte screening research and they lead to decreases in analysis time, the amount of solvent or enzyme required, and the consumption of reagents. Reduction in the quantity of biological and chemical reagents and samples used per assay enable higher throughput assays because of massive parallelization and multiplex detection modes and subsequently promulgates the creation of novel protocols by easier handling techniques. Miniaturized SPE (mini-SPE) has been used for pre-concentration and extraction of different analytes and it has many advantages such as low solvent consumption, low consumption of adsorbent, time efficiency, ease of operation, and versatility (Hashemi et al., 2019a, 2020a,b; Hashemi and Keykha, 2019). This advantages led to the invention of miniaturized modes of SPE such as SPME, SBSE, μSPE, and MEPS.

4.3.1 Solid-phase micro-extraction

Solid-phase microextraction (SPME) was developed in response to the need for rapid sample preparation in the extraction of organic compounds from both water and air (Pawliszyn, 1999). The first commercial SPME device was introduced by Supelco (Bellefonte, PA) in 1993. It is based on a fused silica fiber that is externally coated with a thin film of an appropriate polymeric stationary phase that acts as the extraction medium (Fig. 2). There are two major types of extraction modes in SPME: headspace SPME (HS-SPME) and direct immersion SPME (DI-SPME). The DI mode can only be used for non-solid samples (Kaykhaii and Linford, 2017). After enrichment and separation, fiber is thermally desorbed in the injector of GC. The detection limit of the method for volatile organic compounds is generally $<50\,\text{ng}\,\text{L}^{-1}$. Fiber coatings play a vital role in the extraction and desorption of analytes in SPME, therefore

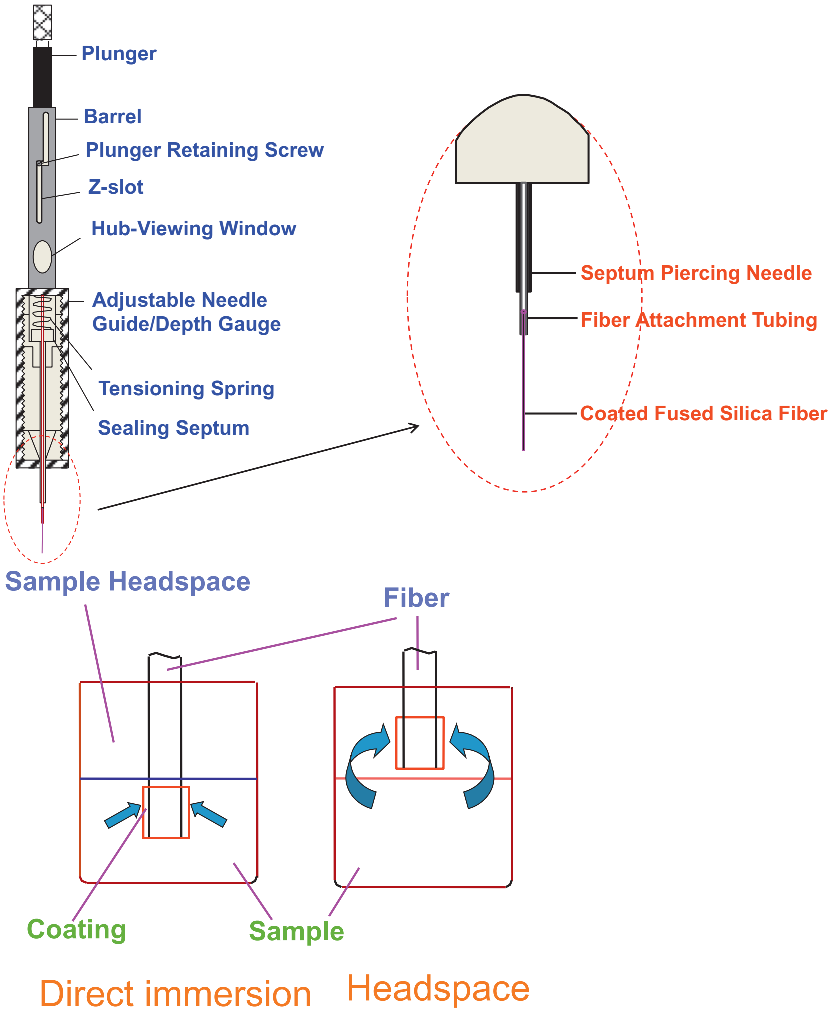

FIG. 2 The setting and modes of SPME (Lord and Pawliszyn, 2000)

many efforts have been done to design more selective coatings, especially for compounds with higher polarities. These include nanorods, nanoparticles, functionalized silica, mesoporous silica nanoparticles, Al_2O_3, carbon-based nanoparticles, graphene, conducting polymers, and metal-organic frameworks (MOFs) (Roychowdhury et al., 2020).

Another SPME mode is a coated capillary or needle, which is called the in-tube method. In-tube SPME uses open tubular capillary columns for compound retention. The mode can overcome some disadvantages related to using fiber SPME, including fragility, low sorption capacity, and bleeding of thick film coatings of fiber. In-tube SPME can be applied in dynamic mode, where analytes transfer actively by pumping the sample inside the tube. By applying longer tubes and an increased amount of adsorbent, it can be expected to increase sensitivity (Lord and Pawliszyn, 2000).

From the first days of its invention, SPME was used for preconcentration and enrichment of pollutants from freshwater samples in different modes with a variety of extracting phases. A graphene oxide-reinforced hollow fiber SPME was used by Darvishnejad et al. (2020) for the extraction of organophosphorus pesticides such as diazinon and chlorpyrifos in agricultural water samples from Babolsar of Iran. Measured diazinon and chlorpyrifos were found to be 3.1 and 4.3 $\mu g\,L^{-1}$, respectively. The instrument used was high-performance liquid chromatography-ultraviolet detection (HPLC-UV). Styrene and poly (ethylene glycol) diacrylate, as SPME coating was employed for the enrichment of pharmaceuticals from water samples, including two Pearl River water and one South Seawater samples (China); however, no pharmaceuticals were quantified. Using HPLC coupled to tandem mass spectrometry, LODs reported in the range of 1.7–11.7 $ng\,L^{-1}$ (Wang et al., 2020). A covalent organic framework modified graphitic carbon nitride, for polycyclic aromatic hydrocarbons (PAHs) SPME from river, rain, and lake water samples was used by Zang et al. (2020). The concentration of the analytes which was determined by gas chromatography–mass spectrometric detection (GC–MS) showed that 0.20 and 0.21 $\mu g\,L^{-1}$ of naphthalene are present in a local river and lake waters, and 0.19, 0.17, and 0.16 $\mu g\,L^{-1}$ of acenaphthene were detected out in the river water, lake water, and rainwater, respectively. Pyrocatechol violet impregnated magnetic graphene oxide coating was used for copper ion extraction from the tap, seawater, and mineral waters of Turkey. Flame atomic absorption detection showed that there is, no Cu in these samples. Reported LOD was 4.0 $\mu g\,L^{-1}$ (Ozkantar et al., 2020). A novel process for preparing porous SPME coatings by the sputtering of silicon onto silica fibers was suggested by Diwan et al. (2016). They applied this fiber for the detection of mixtures of alcohols, aldehydes, amines, and esters in water samples with LODs as low as 29 $ng\,L^{-1}$. Some very recent coatings of SPME fibers are reported based on carbon dots. For instance, Wu and his colleagues (Wu et al., 2020a,b) used SPME with this type of coating for the preconcentration of phthalate esters in Yangtze River water samples (China). They found that the concentrations of these compounds are between 2.09 and 5.32 $\mu g\,L^{-1}$. SPME using carbon nanomaterials supported on steel threads was also used to pre-concentrate and extract pesticides from the São Francisco River basin in Brazil and Chinampas in Mexico City. The concentration range of the analytes were 0.014 to 24.506 $\mu g\,L^{-1}$, determined by gas chromatography coupled to mass spectrometry (GC–MS) (Valenzuela et al., 2020). Some earlier attempts were performed to extract anions from water samples, employing SPME. As an example, Kaykhaii et al. (2020) used a functionalized latex nanoparticle coating for trace analysis of inorganic anions in real water samples. An ion chromatography was employed for the detection of the anions and LODs better than 3.7 $\mu g\,L^{-1}$ were attained for seven anions from water samples.

4.3.2 Micro solid-phase extraction

In the miniaturized form of SPE, the amount of the solid sorbent is less than 0.5 g. As a result, the volume of the elution organic solvent can be decreased to a few milliliters. These so-called *micro*-solid phase extraction (μSPE) techniques can be performed in either dispersive or static mode. In dispersive μSPE (batch extraction in micro-scale), the adsorbent is directly mixed with the sample media through a vortex, sonication, or other methods. In static mode, the sorbent is poured into a small cartridge and the sample passes through it. Alternatively, it can be put in a small adsorbent bag or a microcolumn (pipette tip and spin μSPE). A small adsorbent bag (1–4 cm^2) made of a porous membrane, commonly polypropylene, is filled by a small amount (∼0.1 g) of solid adsorbent and directly inserted into the sample (Płotka-Wasylka et al., 2015; Wong et al., 2012; Won et al., 2009). This method can be used for the pre-concentration of analytes in samples containing solid suspensions. A porous membrane prevents adsorbent phase pollution; so, it can reduce the media effect and avoid the blockage usually encountered in the SPE column. Also, it costs less, because less adsorbent is used and a less organic solvent is needed. Each bag can be reused more than 20 times (Płotka-Wasylka et al., 2015; Wong et al., 2012; Won et al., 2009).

μSPE of pollutants of freshwater samples were reported in many research, including using ionic liquid-based membrane-protected μSPE of organochlorine pesticides in agricultural water samples of Saudi Arabia (Abdi Hassan et al., 2020). The extracted compounds were analyzed by GC–MS and LODs were ranged from 0.25 to 3.4 $\mu g\,L^{-1}$. In 2014, graphene oxide-based dispersive μSPE coupled to gas chromatography-flame ionization detection

(GC-FID) was used for separation and preconcentration of nicotine from environmental water samples including Darakeh River, Tehran, Iran (Mahpishanian and Sereshti, 2014). The concentration of nicotine was determined as 11.1 μg L^{-1}. Dispersive μSPE combined with micro-desorption for the simultaneous determination of pesticides in environmental water samples was reported by Nascimento et al. (2021). After performing microextraction, they analyzed Brazilian freshwater and seawater samples using GC–MS and found dimehoate, artazine, L-chyalothrin, molinate, and malathion in them, at the concentration of 20–120 ng L^{-1}, 17.4 ng L^{-1}, 47.2 ng L^{-1}, 1.11 ng.L^{-1} and 13.3–85.7 ng.L^{-1}, respectively. Dispersive μSPE combined with switchable hydrophilicity solvent-based homogeneous liquid–liquid microextraction was used for the enrichment of non-steroidal anti-inflammatory drugs in environmental waters of China (Di et al., 2020). While LODs were in the range of 0.02–0.05 μg L^{-1} (HPLC-UV), no trace of drugs was observed in selected water samples.

Pipette-tip micro-solid phase extraction (PT-μSPE) is another micro-scale model of SPE. To assemble a PT column, two polypropylene pipette tips (i.e., 10 and 100 μL) are used, as shown in Fig. 3A. A mass of 2–5 mg of solid sorbent will be packed into the smaller tip as the extracting phase and then the larger tip will be cut and connected to the packed tip. Degreased cotton will set as a holder at both ends of the pipette tip to avoid the loss of adsorbent, and a micro-pipette or glass syringe will be connected to suck the sample solution into the pipette tip. Sample solution will be aspirated into the conditioned PT column and dispensed back into the same sample tube several times to ensure maximum extraction efficiency. Spin column micro-solid phase extraction (SC-SPE) can be considered as a modification of PT-SPE, in which the passage of the sample solution or solvent is facilitated by centrifugation (Fig. 3B). The SC-SPE requires successive insertion of the column tip in a rotor of a centrifuge, and this is considered a drawback in comparison with PT mode. However, SC-SPE decreases hand manipulation errors and provides a much higher analyte trap capacity than other

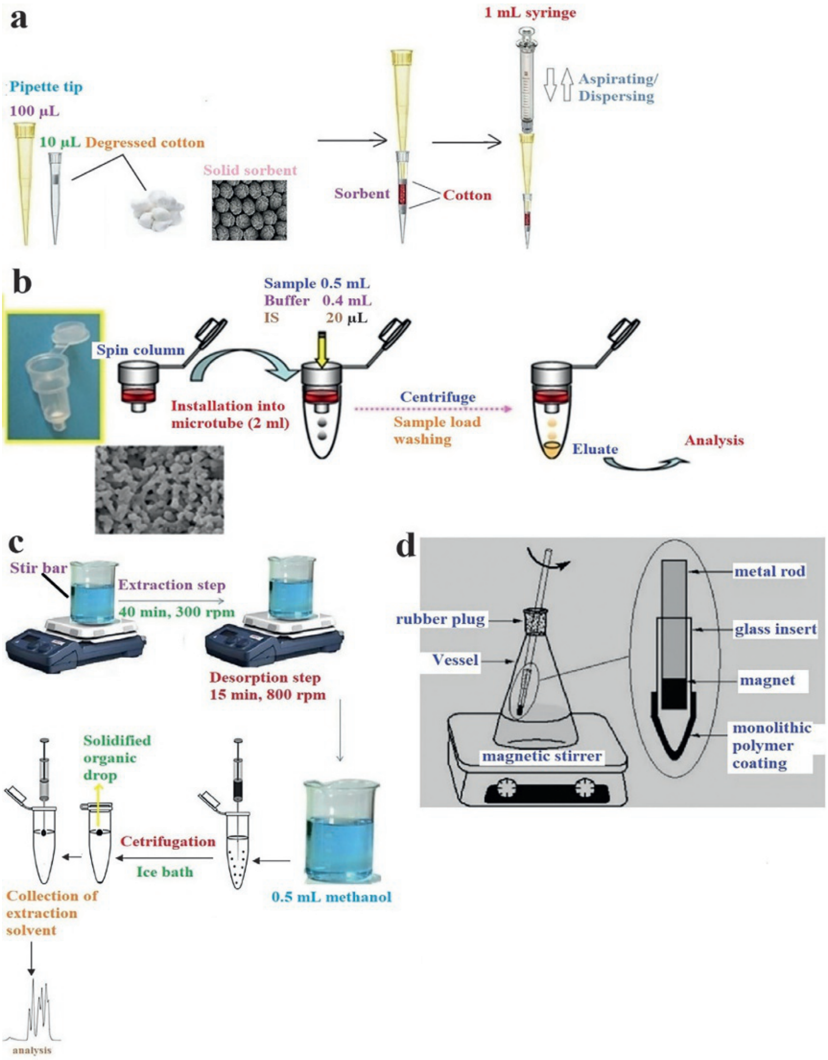

FIG. 3 Schematic illustration of (A) PT-μSPE, (B) SC-μSPE, (C) SBSE, and (D) SRSE (Kaykhaii et al., 2020; Namera et al., 2008; Płotka-Wasylka et al., 2015; Luo et al., 2010; Hashemi and Kaykhaii, 2022).

PT-SPE modes. The existence of porous sorbents such as MIPs and graphene ensures fast mass transfer during extraction which makes the process of extraction more efficient and gets good selectivity and permeability. Moreover, PT-μSPE avoids the problem of irregular packing in the sorbent-packed column and the high back pressure and low flux in the monolithic polymers (Wu et al., 2020a,b).

Some recent applications of PT-μSPE for pre-concentration of different analytes in freshwater samples are included the determination of methyl orange (MO) and acid red (AR) by spectrophotometry in seawater samples of Chabahar Bay (Iran) using graphite based magnetic $NiFe_2O_4$ decorated exfoliated as sorbent. The level of concentration of MO and AR were in the range of 1.1–2.4 $\mu g\,L^{-1}$ and 1.0–2.6 $\mu g\,L^{-1}$, respectively (Hashemi et al., 2019a). Also, graphene oxide/zinc oxide nanocomposite-based PT-μSPE was used by the same group (Hashemi et al., 2018) for the determination of rhodamine B and malachite green by spectrophotometry. They reported rhodamine B concentration in the range of 1.2–2.7 $\mu g\,L^{-1}$ and concentration of 1.6–2.1 $\mu g\,L^{-1}$ for the malachite green in the seawater of Oman Sea. Sun et al. (2014) used graphene PT-μSPE coupled with HPLC/fluorescence detection for the extraction and determination of sulfonamide antibiotics including sulfadimidine, sulfamonomethoxine, and sulfachloropyrazine in environmental water samples of China, with the LOD of the method being 0.5–1.7 $ng\,L^{-1}$. No traces of antibiotics were detected by them. Research was performed by Hashemi and Keykha (2019) on the determination of nicotine in seawater of the Persian Gulf (Iran) (Hashemi and Keykha, 2019). They used MIP PT-μSPE coupled with a spectrophotometer for this analysis and reported 1.7–2.6 $\mu g\,L^{-1}$ concentration of this analyte in different sampling locations. With a similar method and instrument, the same group analyzed samples of Oman Seawater (close to the southeast part of Iran) for nalidixic acid, ciprofloxacin, and acetaminophen content (Hashemi et al., 2020a,b). The concentration of 1.3–2.8 $\mu g\,L^{-1}$, 2.7–4.2 $\mu g\,L^{-1}$, and 1.2–2.4 $\mu g\,L^{-1}$ of ciprofloxacin, acetaminophen, and acetaminophen, respectively, was reported by them. The MIP PT-μSPE coupled with a spectrophotometer was also employed in research performed by Wu and his colleagues (Wu et al., 2020a,b). Using this technique, 2,4-dichlorophenoxyacetic acid was detected in the water of a lake in China at the concentration of 6 $\mu g\,L^{-1}$.

4.3.3 Stir bar sorptive extraction

A sorptive extraction protocol utilizing a stir bar coated by polydimethylsiloxane (PDMS) was first reported in 1999 by Baltussen et al. (1999) and named stir bar sorptive extraction (SBSE). The SPME and SBSE are similar in extraction principle; however, SBSE has higher capacity due to large amount of sorbent phase, so it is more sensitive, more robust, and can be applied to ultra-trace detection of inorganic compounds as well as organics in various real matrices. For liquid samples, it also needs no previous sample preparation neither a solvent with the ability to extract of several analytes simultaneously in a single step. These advantages cause SBSE to have wide applications in many areas such as food, flavor, environmental, life, and biomedical sciences for the analysis of a variety of analytes (Hashemi et al., 2015). The operating principle of SBSE is very similar to SPME and consists of two steps (Fig. 3C). First, extraction of the analytes takes place from the sample into the stir bar coating, either in DI or HS modes. In the second step, SBSE can be introduced directly into the analytical system equipped with a thermal desorption unit or liquid desorption system. SBSE has the same protocol similar to solid-phase microextraction (SPME). However, the volume of PDMS coating the stir bar typically is 25–125 μL which is 50–250 times higher than that of SPME fiber, obtaining better enrichment, extraction efficiency, and sample capacity. For many years PDMS was the only available sorbent on commercial SBSE which cannot efficiently extract nonpolar and weakly polar molecules. As a result, attempts have been made for utilizing other coatings, especially for polar molecules. Coatings such as a molecular imprinted polymer (MIP) and nanoparticles are the most commonly applied so far (Hashemi and Kaykhaii, 2022).

Not very common analytes such as chlorophenols (at the concentration range of 1.24–7.50 $\mu g\,L^{-1}$) (Hashemi and Najari, 2018) and diclofenac (at the concentration range of 1.72–3.29 $\mu g\,L^{-1}$) (Hashemi and Monfaredzadeh, 2019) were extracted from seawater samples by MIP-SBSE, before their HPLC detection. A silver nanoparticle-coated stir bar was employed for SBSE/HPLC of Fe^{3+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} heavy metal cations from drinking water samples (Hashemi et al., 2019c). Concentrations of these cations in local mineral waters were reported in the range of 1.1 to 115.2 $\mu g\,L^{-1}$. Four organophosphate insecticides (i.e., ethion, phosalone, diazinon, chlorpyrifos) and hexyhiazox were determined by HPLC after their extraction by SBSE with a stir bar coated with Fe_3O_4 nanoparticles-multi-walled carbon nanotubes (Gorji et al., 2019). They examined environmental water samples including Babol river water for these analytes, but with a LOD of 0.07–0.89 $\mu g\,L^{-1}$, none of them were detected. Poly (1-vinylimidazole-ethyleneglycol dimethacrylate) monolith was used as a coating for stir bars employed in research by Yao et al. (2018) for simultaneous SBSE of eight perfluoroalkyl acids from East Lake and Yangze river of China. The HPLC-electrospray tandem mass spectrometry was used for their trace detection. Concentrations of $0.47–11.00\,\text{ng}\,\text{L}^{-1}$ of the analytes were measured in the East Lake, while the concentrations of the same analytes were $2.27–38.2\,\text{ng}\,\text{L}^{-1}$ in Yangze River.

Bar adsorptive microextraction (BAμE) was reported as an alternative to the SBSE method. A bar-shaped polypropylene tool (15 × 3 mm) coated using a convenient adsorbent phase is applied, simultaneously by a conventional Teflon magnetic stirring bar at the bottom of the sampling flask. The method operates in the floating sampling technology mode with an analytical tool lighter to water density. The BAμE is very cost-effective and has its main advantage over other sorption-based methodologies is that the analytical tools can be coated by the most selective sorbent phases based on the characteristics of the target compounds (Ide and Nogueira, 2018). The BAμE has been applied for pre-concentration of several emerging pollutants in freshwater samples such as polar solutes including morphine, codeine, formaldehyde–pentafluorohydrazine, acetaldehyde–pentafluorohydrazine, acetone–pentafluorohydrazine, propanal–pentafluorohydrazine, butanone–pentafluorohydrazine, 2-hexenal–pentafluorohydrazine, sulphathiazole, sulphamethoxazole, sulphadimethoxine, trimethoprim and enrofloxacin (Neng et al., 2010). They applied activated carbons and polystyrene divinylbenzene as coating phase and HPLC-diode array detector (HPLC-DAD) as the detection system. Seawater and wastewater samples of Portugal were analyzed using BAμE/HPLC-DAD (Almeida et al., 2013). Modified pyrrolidone and activated carbons were employed as a selective coating for the extraction of benzophenone. They reported the concentration of this analyte in the wastewaters between 2.2 and $2.5\,\mu\text{g}\,\text{L}^{-1}$, but no benzophenone was detected in seawater, considering $0.3\,\mu\text{g}\,\text{L}^{-1}$ LOD. Before GC–MS detection of nitrobenzene, 2-nitrotoluene, 3-nitrotoluene, 4-nitrotoluene, 2,6-dinitrotoluene, 2,4-dinitrotoluene, 1,3,5-trinitrobenzene and 2,4,6-trinitrotoluene explosives in water samples including tap, pond, and river water, Yan et al. (2020) preconcentrate them by BAμE with polyimide microspheres extracting phase. While the LOD of the proposed technique was $0.005\,\mu\text{g}\,\text{L}^{-1}$, no explosives were observed in the samples studied.

Powdered Fe_3O_4 nanoparticles-multi-walled carbon nanotubes coated as an effective phase were used for BAμE coating to monitor trace levels of triazinic herbicides (including atrazine, simazine, and terbutylazine) in environmental water matrices of surface and wastewater in Portugal (Neng et al., 2011). Employing HPLC-DAD, no herbicides were detected in surface water; however, concentrations of the analytes were between 3.6 and $3.7\,\mu\text{g}\,\text{L}^{-1}$ in wastewater.

Stir-cake sorptive extraction (SCSE) using monolithic particle as extraction medium is another version of SBSE which was introduced in 2011 (Huang et al., 2011). Similar to SPME, this technique also combines extraction, pre-concentration, and clean-up into one step. In operation principle, it is similar to SBSE but, the sorbent is a monolithic cake that can be put in a holder with a protected iron wire. This arrangement prevents the direct contact of the extracting phase and the sample vessel. As a result, higher stirring rates can be used during the extraction. In addition, the life span of the monolith is increased allowing its reuse up to 300 times, while the typical reusability of a stir bar is ca. 60. The extraction media monolithic cake can be easily prepared to be flexible for the extraction of compounds of interest (Płotka-Wasylka et al., 2015). The SCSE as extraction media was designed and prepared for extraction of different analytes in water samples. Benzimidazole anthelmintics such as fenbendazole, thiabendazole, mebendazole, albendazole, and oxfendazole were analyzed by HPLC and using this pre-concentration method with a polymeric ionic liquid monolith that was achieved by in situ copolymerization of an 1-allyl-3-methylimidazolium bis [(trifluoro methyl) sulfonyl]imide ionic liquid and divinylbenzene in the presence of *N*,*N*-dimethylformamide (Wang et al., 2014). The LOD of the protocol was $0.020\,\mu\text{g}\,\text{L}^{-1}$ and none of the analytes were detected in the samples analyzed.

Using poly (1-ally-3-vinylimidazoliumchloride-*co*-ethylene dimethacrylate) monolith as SCSE coating phase, estrogens such as bisphenol A,17α-ethinylestradiol, estrone, diethylstilbestrol, dienestrol, and tylphenol were detected in lake, reservoir, and river waters of China at the concentration of $3.38\,\mu\text{g}\,\text{L}^{-1}$ using HPLC (Chen et al., 2016). Zhang et al. (2016) reported that the concentration of antimony was between 0.14 and $0.21\,\mu\text{g}\,\text{L}^{-1}$ in mineral, tap, and well water of China after their analysis by sensitive atomic fluorescence spectrometer instrument. Before analysis, they separated Sb using SCSE with a polymeric ionic liquid-based sorbent prepared by in-situ polymerization of 3-(1-ethyl imidazolium-3-yl) propyl methacrylamido bromide and ethylene dimethacrylate.

Richter et al. (2009) introduced rotating disc sorptive extraction (RDSE) as another suitable analytical device for the separation and enrichment of low polarity micro-pollutants compounds. In this technique, a Teflon® disk which by using the sol–gel method a layer of extraction media is coated on top of it is used for ME. The rotation axis of the disk can be either perpendicular or parallel to its radius, giving rise to two different mass transfer patterns. Like SCSE, RDSE increases the mass exchange efficiency, results in higher compound extraction efficiency with better repeatability and enhanced utilization of the extractive material as compared to SBSE. Also, the disk can be easily fabricated in the laboratory and allows immobilization of a larger exposed surface area of the active phase than what is obtainable by SBSE. After adsorption, disks are dried and adsorbed compounds are eluted by small amounts of a proper solvent. Disks can be used many times. The PDMS is the most common adsorbent; however, a layer of nylon polyamide membrane, octadecyl chemically modified silica, and divinylbenzene/n-vinylpyrrolidone copolymer can be used as disk coating for extraction of different analytes (Vieira et al., 2020; Cañas et al., 2014). Nevertheless, to obtain good analytical performance, the protocol needs a solvent drying apparatus. Because of the large amount of solvent needed to cover the disk height for desorption, high dilution of the extract and consequently an important loss of analytical signal is obtained if no drying step is implemented.

To avoid the friction of monolithic polymer coatings, a stir rod sorptive extraction (SRSE) by monolithic polymer coating was designed (Luo et al., 2010) (Fig. 3D). This device prevents direct contact of the monolithic polymer coating to the wall of the vessel and so efficiently reduces the damage of the coating. The SRSE with a graphene/polymer composite coating was applied for the extraction of 16 PAHs from tap and lake water samples, reported by Luo et al. (2011a). By using HPLC-UV as an instrument, no PAHs in the lake water were detected, whereas the concentration of them was between 0.71 and 1.14 μg L^{-1} in tap water. The LOD of the developed method for PAHs ranged from 0.005 to 0.429 μg L^{-1}. Non-steroidal anti-inflammatory drugs were determined by the same research group (Luo et al., 2011b) with a similar SRSE. They performed the analysis of ketoprofen, fenbufen, and ibuprofen in lake water and sewage outfall of a hospital in China by using poly (4-vinylpyridine-*co*-ethylene glycol dimethacrylate) monolithic polymer as extraction media on a stir rod. Using HPLC for detection, the LOD of the method was calculated as 0.09 μg L^{-1}. No drugs were found in the samples analyzed.

4.3.4 Micro-extraction with packed sorbent

In 2004, Abdel-Rehim (2004), described a new miniaturized version of conventional SPE in a syringe and named it MEPS (micro- extraction by packed sorbent). In MEPS, a small amount of the sorbent, usually 1–4 mg is either inserted into the syringe barrel as a plug or between the needle and the barrel as a cartridge and can extract volumes of a sample between 10 and 250 μL (Fig. 4). While in MEPS the same adsorbent as general SPE columns can be used, unlike SPE, the packing is integrated directly into the syringe and not in a separate column. Hence, there is no need for a separate robot to apply the sample into the solid phase. The cartridge bed can be packed or coated to provide selective and suitable sampling conditions. A significant strength of MEPS is the ability to fully elute the adsorbent by volumes of less than 10 μL via a syringe needle which allows MEPS to be adapted for online application. Compared to SPE, MEPS uses 10–100 times fewer sample volumes and reagents. The small volumes also reduce extraction time to 10%. But MEPS, as any other micro-extraction technique has some drawbacks. Besides the problem associated with reproducible packing, sorbent clogging and consequent cavitation process is a major shortcoming. This is often more serious in complicated matrices with high contents of protein and lipids, resulting in poor recoveries and repeatability. Another drawback for manual MEPS extraction is that the flow rate is not measured and the repetitive handling procedure is user-dependent and leads to experimental errors (Pereira et al., 2019). The MEPS with cobalt/chromium layered double hydroxide nano-sheets as separation media was employed for the extraction of emerging pollutants haloxyfop and hexaflumuron (acidic pesticides) in seawater, river, tap, farmland, and greenhouse waters by Asiabi et al. (2018) and Montagner et al. (2022). The LOD reported was 0.05 μg L^{-1}, using HPLC. While most of the samples were free of the analytes, they were detected in greenhouse and farmland samples with a concentration of 21.0 μg L^{-1} and 15.1 μg L^{-1}, respectively. MIP as sorbent for MEPS was employed for the analysis of dinotefuran in freshwater samples (Brazil) (Silva et al., 2018). HPLC of the samples after microextraction depicted that there is no analyte in the samples taken.

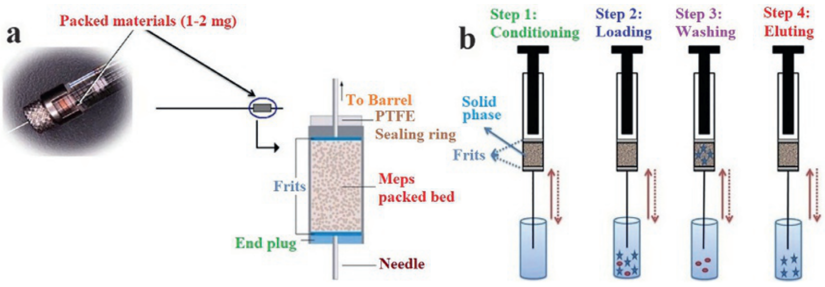

FIG. 4 Syringe for MEPS with packing bed (the dead volume is about 7 μL) (A), MEPS steps (B) (Moein et al., 2015).

4.4 Novel sorptive materials

The conventional, silica-based RP-C_{18}, has been the most popular sorbent in (dispersive) μ-SPE so far. However, functionalized C_{18} was employed in several researches for the analysis of a variety of analytes in aqueous media (Liu et al., 2009; Zhang et al., 2010). Since the efficiency of the miniaturized extraction techniques is dependent totally on the surface area of the solid sorbent, conventional sorbents cannot fulfill this condition, but nanoparticles (NPs) with exceptional properties including tremendous surface area can provide enough adsorbing site for fast and efficient extraction. The first NPs used in this regard were gold and titanium nanotubes NPs. Due to inertness, stability, non-toxicity, low cost, and corrosion resistance, oxides and oxides-hybrid NPs are also among the most common NPs applied for microextraction. The discovery of various forms of carbon allotropes such as fullerenes, carbon nanotubes, and graphene affected many areas of research, including analytical chemistry (Kaykhaii et al., 2017). They have excellent sorbent properties and inertness with very good uniformity which results in excellent reproducibility. Recently, SPE procedures involving NPs with magnetic properties (magnetic solid-phase extraction, MSPE) have increased during the pre-concentration of many analytes. The main advantage of an MSPE is easy separation of the NPs by external magnetic devices. The application of magnetic particles simplifies the sample preparation protocol compared to general SPE methods since MSPE does not need the column to be packed by the adsorbent in batch mode operation. The application of magnetic nanoparticles in SPE highly reduces the analysis time by reducing the number of steps in the extraction protocol. These magnetic NPs have a magnetic core-based on ferrite with a coating of modified silica, alumina carbon nanotubes, or titanium dioxide. Magnetic molecularly imprinted polymers (MMIPs) can be synthesized by copolymerizing a monomer, a cross-linker, and magnetic NPs in the presence of the template molecule (Fig. 5). The MMIPs prepared by this approach are highly selective, stable in both aqueous and organic solvents, and they can be used even for chiral separation such as tryptophan enantiomers (Liu et al., 2020), and (*S*)-citalopram (Gomez-Caballero et al., 2011) in an aqueous medium. The ease of preparation, ability to scale-up, low material costs and pre-determined selectivity of chiral imprinted polymers make them advantageous in comparison with other chiral selector systems (Hashemi et al., 2015).

Metal–organic framework (MOF) are classified as extremely ordered crystalline metal clusters with high porosity (>90%) composed of metal–oxide clusters and organic linkers, and extremely large surface area (up to 7410 m^2/g), which make them suitable for a wide variety of applications, including adsorption. The variation of metal oxides and the proper choice of organic linkers allow the pore size, volume, and functionality to be tailored for designable applications. Also, the characteristics of MOFs mainly depend on the nature of the selected inorganic and organic nodes and ligands and their connectivity (Safaei Moghaddam et al., 2020). The MOFs are also characterized by their ease of synthesis. These features make MOFs an excellent candidate for SPE/μSPE, where a highly selective media with elevated surface area and solvent and thermal stability is required. Recently, different MOFs have been tested as coatings for SBSE and SPME and as packing materials in PT-SPE and other variations of SPE. Organic dyes, mercury, and aspartame are among the analytes whose ultra-trace levels could be extracted by MOFs (Hashemi et al., 2019b; Rezaei Kahkha et al., 2017; Safaei Moghaddam et al., 2020). It was observed that the presence of a MOF in all cases significantly increased the extraction efficiency for the target compounds compared to PDMS or silica, due to the huge surface area available for extraction (Rezaei Kahkha et al., 2017). This feature even leads scientists to perform surface

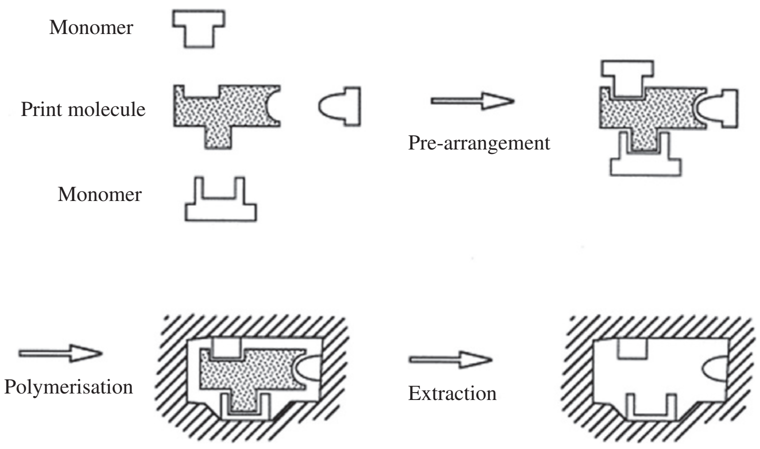

FIG. 5 Schematic diagram of the preparation of a MIP (Andersson, 2000).

modification of a proper MOF by MIP as a capping agent to greatly enhance the surface area and improve its functionality and selectivity as an SPE sorbent.

In industry, sputtering is the most usual thin film deposition method. It works with the ejection of atoms of a compound with energetic ions produced. These ejected atoms are deposited on a sorbent, and usually, strongly adhere to it. For decades, sputtering has been extensively used to improve materials for optical devices, bioarrays, catalysis, and sensors. The fabrication of highly porous, thin, robust SPME fibers was recently reported by Roychowdhury et al. (2020) through sputtering of silicon onto a fused silica fiber. Sputtered fibers were then functionalized using a silanted C_{18} hydrocarbon that resulted in 1 or 2 μm thick sputtered, silanized fibers. This SPME fibered outperformed a commercial fiber such as 7 μm PDMS in the extraction of different analytes.

4.5 Conclusions

From the ‘90s, many efforts have been done to miniaturize the extraction techniques and other analyte preconcentration techniques in chemical analysis. Scaling down the matrix, and hence the invention of microextraction techniques such as SPME and SBSE has been the most important steps toward this aim which also led to more greening the analytical methods. In terms of the sorbent-based techniques, it is obvious that miniaturization of extraction systems accomplished faster sample processing, less sample and solvent requirement, less energy consumption, and better selectivity and sensitivity in measurements. Miniaturization of extraction has advantages such as simplicity of operation, relatively low costs of instrumentation, versatility, easy coupling to chromatographic systems; and short time of extraction. It is observable that shortly, it will be a necessity to conduct chemical analysis onsite and analytical tools should be available to all non-expert people. These devices can be run through commonly available devices such as smartphones (Sargazi and Kaykhaii, 2020). This will not be achievable without scaling down the solid matrix for isolation. Smartphone-based analytical chemistry should be designed in a way that can be operated by non-trained people; therefore, the sample preparations also need to have been designed for such operations; as a result, high specificity in solid sorbents is required to avoid interferences. This, in turn, will reduce the contamination and losses during sample storage and transport. Therefore, the focus of the research on finding new solid extraction phases such as MIPs and MOFs is of high importance (see Tavengwa et al., 2022, Chapter 20). What can be seen for the horizon of the next decade in terms of microextraction based on solid sorbents is probably a shift toward nano-extraction with highly specific materials as sorbents, especially for large bio-molecules. Researchers will also be encouraged to work on multi-analyte simultaneous extraction/preconcentration methodologies for simultaneous one-step sample preparation which reduces the number of steps and time of analysis. This falls under the section on monitoring techniques, current analytical approaches, and instrumental analyses with other chapters, e.g., Mwedzi et al. (2022), Kaserzon et al. (2022), Kebede et al. (2021), Kumar et al. (2022) that aims to understand how emerging freshwater pollutants are analyzed or detected within aquatic ecosystems.

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C H A P T E R

5

The miniaturization of liquid-phase extraction techniques

Temesgen G. Kebede, Sol S. Nety, Simiso Dube, and Mathew M. Nindi

5.1 Introduction

Over the past decade, a growing concern has been expressed regarding the presence and activity of organic pollutants in the environment (Tavengwa and Dalu, 2022, Chapter 1). Cwurrently, the environmental and human health risks associated with the presence of these organic pollutants as contaminants of emerging concern (CECs), or emerging contaminants (ECs) are increasingly being recognized. The release of ECs into the environment in certain cases is not new and coincides with their usage and production, thus has existed for several years, nonetheless, their identification may not have been possible because of the inadequacy of analytical and or instrumental methods (Bataineh et al., 2021). ECs' sources are either point sources or dispersed sources and are partitioned in various media according to their physical and chemical properties. Hydrophilic (polar) compounds are found in water (surface and groundwater), and hydrophobic (less or nonpolar) compounds in the soil and/or sediments, while volatile compounds are found in the air. In biological tissue these chemicals with different functionality are distributed in a more intricate manner (Mohamed and Paleologos, 2018). The ECs can be separated into various groups determined by (1) their mechanisms of operation (2) their function, and (3) their origin and functional assembly. These ECs originate from products such as pharmaceutical and personal care products (PPCPs), steroids, hormones, perfluorinated compounds, artificial sweeteners, gasoline additives, siloxanes, surfactants, phosphoric esters, flame retardants, endocrine-disrupting compounds, final water treatment process disinfection by-products (DBPs), industrial additives, and agents. These products are widely used and may transform when entering organisms, or the environment, resulting in the modification of the original chemical. These are commonly referred to as metabolites in organisms, while there are usually called transformation products (TPs) in the environmental context. The parent compounds, their metabolites, and transformation products continuously enter the environment through various routes and find their way into food and water, and could thus cause adverse ecological and human health effects. In addition, many of these contaminants can be converted in the environment by microbial degradation, photolysis, and hydrolysis, thus resulting in chemicals with totally different physicochemical properties compared to the parent compounds. Consequently, making their identification challenging for the analytical scientists as advanced prediction and data processing techniques are required (Bataineh et al., 2021). Amongst the compounds, the main classes of emerging pollutants (ECs) found in the various surface waters remain PPCPs (Kermia et al., 2016; Mlunguza et al., 2020; Packer et al., 2003). Although most of these compounds are normally detectable at low and substantial concentrations, they are still of great concern because pharmaceutical drugs can induce biological effects at a very low level. To control and monitor the residue level of these ECs, analytical techniques are of paramount importance. Sample preparation has always been considered the bottleneck of the analytical procedure due to its many drawbacks such as tediousness, high degree of manipulation, risk of losses and contamination, the employment of large amounts of sample, solvents, and sorbents, and therefore, generation of large amounts of wastes. For this reason, in recent decades great efforts have been made to minimize this negative aspect of the analytical procedures. Generally, analytes exist in intricate sample matrices. Suitable isolation of

Emerging Freshwater Pollutants
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the target analytes from the sample matrix is required before instrumental analysis since analytical instruments are unable to handle unprocessed matrices. Accurate and reliable results can be guaranteed on some given components of interest in complex samples through a systematic procedure, following a critical stepwise process, which encompasses sampling, sample preparation, separation, quantification, statistical evaluation, and decision-making. Amid the defined steps, sample preparation typically entails some extraction techniques which differ in selectivity, speed, and convenience. These extraction techniques may be either integrated or coupled with clean-up procedures that remove interferences and enrich sample extracts in very complex samples. Several extraction methods, with a diverse degree of advantages and drawbacks, have been conventionally used in an analytical laboratory. Sample preparation methods can be categorized in terms of whether the extraction is exhaustive or nonexhaustive, and extraction techniques may be classified into three groups based on the following fundamental principles:

1. Flow-through equilibrium and preequilibrium
2. Batch equilibrium and preequilibrium
3. Steady-state exhaustive and nonexhaustive

Flow-through equilibrium and preequilibrium extractions can be either exhaustive (e.g., purge and trap, sorbent trap, solid-phase extraction (SPE), supercritical fluid extraction (SFE), and headspace sorptive extraction (HSE), or nonexhaustive (e.g., in-tube solid-phase microextraction (SPME). Similarly, batch equilibrium and preequilibrium extractions can be either exhaustive (e.g., liquid-liquid extraction (LLE), Soxhlet, and sorbents), or nonexhaustive (e.g., headspace, liquid-liquid microextraction (LLME), and solid-phase microextraction (SPME), while steady-state exhaustive and nonexhaustive extractions are membrane techniques. Theoretically, in exhaustive extraction approaches, the bulk of analytes are moved to the extraction medium by employing a large quantity of it, thus these do not require calibration. Yet, the use of surrogate standards to ensure acceptable recoveries in the method is common practice. On the other hand, a small fraction of analytes is distributed between the sample matrix and the extraction phase in nonexhaustive methods due to the limited amount of extraction media used in comparison to the sample volume (Pawliszyn, 2012).

Conventional extraction techniques include and are not limited to liquid-liquid extraction (LLE), solid-phase extraction (SPE), and its enhanced versions such as dispersive SPE (d-SPE) and magnetic SPE (MSPE). The aforementioned techniques have been applied for the extraction of different contaminants from various matrices. Table 5.1 gives a summary of their applications over the past five years. These classical extraction techniques have numerous drawbacks. For example, SPE is a technique requiring a tedious procedure, sorbents are limited, and although the volume of toxic organic solvents is reduced, those employed in the procedure are still essential (Poole, 2012). On the other hand, LLE utilizes large volumes of toxic organic solvents and samples, limited enrichment factors (EFs), and requires tedious procedures. For the reasons mentioned above, miniaturization of the sample preparation process is a promising solution, and these classical techniques have been replaced in the past decades by their miniaturized techniques, thus maintaining their advantages and reducing their drawbacks. The miniaturized SPE technique is solid-phase microextraction (SPME), which was developed by Pawliszyn in 1990 (Arthur and Pawliszyn, 1990). Solvent microextraction (SME) or liquid-phase microextraction (LPME) is the miniaturized form of the LLE technique, which was introduced in the late 1990s (Jeannot and Cantwell, 1997; Liu and Dasgupta, 1995, 1996). The LPME technique is the miniaturized form of the LLE technique and can be defined as the extraction technique where the volume of the extractant phase is equal to or below 100 μL (Kokosa, 2013). The advantages of the LPME technique are its low cost, operational simplicity, rapidity, extremely low or even no solvent consumption, small sample volume, reduced generation of wastes, high EFs, and its affordability to any laboratory. The miniaturized techniques can overcome the shortcomings of classical sample preparation techniques. In addition, these techniques comply with the 12 principles of green analytical chemistry (GAC) (Gałuszka et al., 2013). The focus of the current book chapter is on the miniaturization of LLE techniques.

5.2 Environmental fate of emerging pollutants

The detection of any emerging contaminant (ECs) in the environmental matrix does not inherently mean that it may cause harm. However, the identification of compounds, for which there is evidence that they can adversely affect marine life, poses significant concerns. Some of the key questions about emerging contaminants such as PPCPs in the freshwater aquatic environment are summarized below.

TABLE 5.1 Application of sample extraction method for emerging contaminants and instrumental analysis in water in the recent years.

Sample matrix	Analytes	Extraction methods	Separation and instrumental analysis	Reference
River water, seawater, tap water, rainwater	Total Cr and Cr (VI)	***Liquid-liquid extraction (LLE)*** Methyltrioctylammonium chloride in chloroform (0.1% (*w*/*w*)	Graphite furnace atomic absorption spectrometry (GFAAS)	Béni et al. (2019)
Environmental and drinking waters	Acrylamide	***Solvent exchange*** 2 mL samples aliquot was transferred into a centrifuge tube containing 6 mL of acetonitrile. The sample was then vortexed, placed into a Turbovap LV, and evaporated to a volume of approximately 2 mL under a stream of nitrogen. Then further addition of 6 mL of acetonitrile and sample evaporation cycle was repeated to an approximate volume of 1 mL. The sample was then diluted with an additional 5 mL of acetonitrile, vortexed, and evaporated to an approximate volume of 0.2 mL, after which the sample was reconstituted to 2 mL with dichloromethane. After reconstitution, the sample was centrifuged at 4000 rpm for 15 min	High-performance liquid chromatography-positive electrospray ionization Triple Quad tandem mass spectrometry (HPLC-ESI (+) -QqQ)	Backe et al. (2014)
River water, tap water	Acetaminophen, salicylic acid, caffeine, carbamazepine, ibuprofen, sulfamethoxazole, drospirenone	***Solid-phase extraction (SPE)*** Off-line extraction was carried out to extract seven contaminants of emerging interest (CEI) using three different types of SPE cartridges, SiliaPrepXLRV (Large Reservoir) SAX (10 mL, 60 mg), and Oasis HLB (10 mL, 60 mg) Six CEI were extracted with SiliaPrepXLRV and SAX as follows, cartridge was conditioned using two successive 3-mL doses of methanol and purified water. Approximately 100 mL of sampled water was then loaded through the cartridges in small volumes (~10 mL). Once the water samples passed through the cartridges, the cartridges were washed with 3 mL of C18 nano-pure water. After washing, a vacuum was applied (approximately 5 mmHg) for 5 min to dry the cartridges, after which analytes were eluted with two successive 3 mL doses each of pure methanol and methanol with 2% formic acid. The vacuum was applied (2 mmHg) for approximately 30 s to complete the elution and dry the cartridges. For acetaminophen, the extraction process was comparable to the other CEI. However, 10 mL of sampled water was used for the extraction, and two successive 3-mL doses of methanol were used for elution.	Liquid chromatography tandem mass spectrometry (LC-MS/MS)	Pulicharla et al. (2021)
River water	Bisphenol-A, acetaminophen, salicylic acid, and diclofenac	***Solid-phase extraction (SPE)*** An automated SPE extraction system was designed for the simultaneous preconcentration of two water samples Phenomenex Strata-X reverse phase cartridges were conditioned with 6 mL of methanol, 6 mL of ultrapure water, and 6 mL of ultrapure water acidified with HCl PA to pH values of 2 and 3. The samples (1 L) were loaded, the cartridge was rinsed with 10 mL of ultrapure water and the cartridge was dried under vacuum for 10 min and eluted with 8 mL of methanol.	High-performance liquid chromatography combined with time-of-flight mass spectrometry (HPLC-MS-TOF)	Lopes et al. (2016)

Continued

TABLE 5.1 Application of sample extraction method for emerging contaminants and instrumental analysis in water in the recent years—cont'd

Sample matrix	Analytes	Extraction methods	Separation and instrumental analysis	Reference
Tap water, swimming pool water, water from a spa pool	Methylparaben, ethylparaben, propylparaben, isopropylparaben, butylparaben, isobutylparaben, benzylparaben	***Vortex-assisted dispersive micro-solid phase extraction (VA-D-μ-SPE)*** 20 mL of water sample were mixed with 150 mg of metal-organic frameworks HKUST-1. The mixture was then vortexed for 5 min and equilibrated for 6 min. The supernatant aqueous phase was removed with a Pasteur pipette. Afterward, desorption of the parabens from the HKUST-1 in the tube was carried out through the addition of 2 mL of methanol, while vortexing for an additional 5 min. After 5 min of equilibration, the methanol supernatant solution was filtered and evaporated to dryness	High-performance liquid chromatography with diode-array detection (HPLC DAD)	Rocío-Bautista et al. (2015)
Aquaculture water	Chloramphenicol, thiamphenicol, florfenicol, florfenicol-amine hydrochloride	***Vortex assisted dispersive micro-solid-phase extraction (VA-D-μ-SPE)*** 10 mg sorbent of MIL-101(Cr) was added into a 10 mL water sample (pH 11). The mixture was vortexed for 30 min, then the MIL-101(Cr) was isolated by centrifuging the mixture at 10,000 rpm for 10 min. After discarding the supernatant, 600 μL of methanol was introduced into the precipitate for elution under ultrasonication for 20 min. Subsequently, the mixture was centrifuged at 10,000 rpm for 10 min and the supernatant collected	Ultra-high performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS) detection	Cai et al. (2017)
Environmental waters	Microcystins: MC-LR and MC-RR	***Magnetic solid phase extraction (MSPE)*** To a 100 mL water sample pH adjusted to 4.00 with glacial acetic acid, 10 mg of ionic liquid magnetic graphene (IL@MG) was added. The adsorption was carried out for 18 min by using a variable speed multipurpose oscillator. After the magnetic phase separation, the supernatant was decanted and 1.8 mL of methanol containing 10% ammonia water was added. Followed by a repeated desorption process for 1.5 min	Ultra-high performance liquid chromatography-tandem mass spectrometry (UHPLC-MS/MS)	Liu et al. (2019)
Tap water, lake water, river water	Ethoprophos, parathion methyl, fenthion, parathion, fenamiphos, phosmet, malathion, triazophos	***Magnetic solid-phase extraction (MSPE)*** 20 mg of Fe_3O_4/MoS_2 composites was added to 50 mL of the sample solution in a centrifuge tube. Then the mixture was ultrasonicated for 0.5 min and shaken for 6 min at 150 rpm in an oscillator. A magnet was then mounted on the side of the centrifuge tube to separate the adsorbent from the solvent in the sample. After full removal of the supernatant, the analytes were desorbed with 1 mL of acetone/n-hexane (1:1 *v*/v) per vortex for 1 min, the process was repeated three times	High-performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS)	Zhang et al. (2020)
tap water, river water, domestic wastewater, industrial wastewater	Perfluorobutanoic acid (PFBA) Perfluorooctanoic acid (PFOA) Perfluorooctane sulfonic acid (PFOS) Perfluorodecanoic acid (PFDA)	Fluoro- functionalized paper-based solid-phase extraction (Fp-SPE)	High-performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS) analysis	He et al. (2019)
Spiked lake water Spiked well water Spiked wastewater	Thallium	Chitosan magnetic hydrogel-based ligandless magnetic solid-phase extraction (CMH-LMSPE)	Slotted quartz tube atomic absorption spectrometry	Maltepe et al. (2020)

5.2.1 Persistence of pharmaceutical and personal care products

As observed by their presence in drinking water, the physicochemical properties of PPCPs suggest that many of them are not easily removed by conventional water treatment processes (Snyder, 2008). Failure to eliminate PPCPs from waste treatment facilities completely poses a potential risk to aquatic life and public health. The enormous evidence from monitoring studies is that PPCPs are widespread and have made their way into the aquatic environment (Bu et al., 2013). The prevalent use of PPCPs globally, combined with the growing marketing of new pharmaceuticals, contributes significantly to the presence of these compounds and their active metabolites in the aquatic environment (Daughton and Ternes, 1999). All the PPCPs are not persistent compounds, however, due to their continuous usage and release to the environment, they are considered as "pseudo-persistent." It is proposed that pseudo-persistent PPCPs have a greater capacity for environmental persistence than other organic pollutants such as pesticides, since even when operating on environmental processes such as biodegradation, photodegradation, and particulate sorption, their source continually refills. Therefore, because of their continuous release into the environment, PPCPs that may degrade would inevitably and effectively act as persistent compounds (Houtman et al., 2004). Loffler et al. classified 10 pharmaceuticals and pharmaceutical metabolites according to their dissipation period (DT50) in water/sediment samples into high, moderate, and low persistence compounds. Carbamazepine, clofibric acid and diazepam were rated highly persistent (DT50 ¼ 119–328 days), while oxazepam, iopromide, and ivermectin were deemed moderately persistent (DT50 ¼ 15–54 days), whereas paracetamol, ibuprofen, 2- hyroxyibuprofen, and CBZ-diol were classified as showing low persistent (DT50 ¼ 3.1–7 days) (Löffler et al., 2005). As reported by Klaminder et al. (2015), the anxiolytic drug also (Oxazepam) display extended persistence in freshwater lakes due to past input and growing urban population.

5.2.2 Sources of pharmaceutical and personal care products

Many PPCPs find their way into the environment via various routes after usage. Sewage treatment plants (STPs) (Daughton and Ternes, 1999), WWTPs, and landfill leaching are the main sources of PPCPs for the environment. During traditional wastewater treatment methods, PPCPs are often not completely and reliably eliminated, and are therefore often detectable at concentrations ranging from ng/L to mg/L in reclaimed surface water (Chen et al., 2013). Contamination of the freshwater with PPCPs can occur in different ways including unabsorbed PPCPs by the body after medicinal use, accompanied by excretion and release into the sewage system or septic tank, which is an important pathway. After sewage treatment, wastewater can be used for irrigation with treated sludge that may be used as fertilizer for agricultural purposes. One of the sources which discharge PPCPs waste into the environment is via their manufacture as the wastewater from the manufacturing plant goes directly into STPs (Fick et al., 2009). The sludge is collected as fertilizer on the soil after treatment, with the liquid effluent immediately released into the freshwater setting. In addition, by leaching from the soil, PPCPs can enter the groundwater and this may pose a threat to drinking water. Not only that, by runoff from land treated with digested sludge for agricultural purposes (Nikolaou et al., 2007), pharmaceuticals can also enter freshwater. Veterinary drugs are released into the environment when, as fertilizers, animal waste is sprayed either in solid or liquid states on agricultural fields. Along with their metabolites, these veterinary drugs pollute the soil and can enter the food chain. Agricultural run-off can, therefore, reach freshwater systems and leach to groundwater (la Farré et al., 2008).

5.2.3 Pharmaceutical and personal care products in the freshwater

The presence of pharmaceuticals in the environment was first reported in Kansas City, USA in 1976, where clofibric acid was found in treated wastewater at concentrations ranging from 0.8 to 2 mg/L (Fent et al., 2006). The presence of 25 pharmaceuticals at concentrations of up to 1 mg/L in the River Lee was subsequently investigated in 1981 (Dearden and Nicholson, 1985). Since then, in different aquatic environments, various studies have identified PPCPs around the globe (Hirsch et al., 1999; Kolpin and Meyer, 2002; Ramirez et al., 2009). Although the reported concentrations of these PPCPs are low, many have the potential to last in the natural environment for months to years. The identification of pharmaceuticals in the environment differs not only between countries but also between different areas of the same country (Boxall et al., 2012). Different groups of PPCPs have been detected in freshwater throughout the world including Europe, Asia, Australia, Africa, and America. For example, study in German municipal sewage treatment plants (STPs) and rivers, investigated 32 pharmaceuticals from different classes including lipid regulators, psychiatric drugs, antiepileptic drugs, and beta-blockers in discharged effluents, streams, and river waters. In the sampled river waters, the lipid regulator 'bezafibrate' displayed the highest concentration of 3.5 mg/L (Ternes, 1998). As reported by Hirsch et al., STP effluents and random river water samples were collected in Germany for the presence of antibiotic residues. Results showed repeated detection at concentrations up to 6 mg/L of erythromycin, roxithromycin, and sulfamethoxazole (Hirsch et al., 1999). Contamination of the River Taff and the River Ely with PPCPs, illicit substances, and other endocrine disruptors was recorded in South Wales, UK (Kasprzyk-Hordern et al., 2008) and was mainly due to the substantial discharge of treated wastewater effluent into the rivers. The investigation indicated that the compounds that are heavily dispensed in the Welsh community constitute the most commonly identified PPCPs. These included: anti-inflammatory medicines, antibiotic medicines, and anti-epileptic medicines. Some of these PPCPs have been found in the aqueous system to be widespread and persistent. Illicit substances were also found at low concentrations in both rivers. As reported by Yamagishi et al. 100% and 80% of musk xylene and musk ketone were detected in Tama River and Tokyo Bay in Japan from 74 samples studied (Yamagishi et al., 1983). Elsewhere, in water from the Mekong Delta, Vietnam, the levels and distribution of 12 antimicrobials were investigated and compared with those in the Tamagawa River, Japan. In Vietnam, a few compounds such as sulfamethoxazole, sulfamethazine, trimethoprim, and erythromycin-H_2O were detected at concentrations between 7 and 360 ng/L, while in the Japanese urban river, more antimicrobials were found including sulfamethoxazole, sulfapyridine, trimethoprim, erythromycin-H_2O, azithromycin, clarithromycin, and roxithromycin at concentrations between 4 and 448 ng/L (Managaki et al., 2007). In addition, Fick et al. reported a serious case of pharmaceutical pollution of surface, ground, and drinking water in the Patancheru industrial area of India (Fick et al., 2009). The concentrations of several pharmaceutical residues (cimetidine, caffeine, acetaminophen, and sulfamethoxazole) in surface water in the Han River, Korea, have been investigated by Choi et al. (Choi et al., 2008). In a seminal study, as mentioned above, pharmaceutical concentrations were recorded in treated wastewater in Kansas City, USA in 1976, with Clofibric acid present at concentrations ranging from 0.8 to 2 mg/L (Fent et al., 2006). Stumpf et al. found polar drug metabolites in sewage and natural waters in Rio de Janeiro Province, Brazil, in South America. Clofibric acid, diclofenac, and naproxen were commonly found in surface water at low concentrations in the main river used to generate drinking water (Stumpf et al., 1999). Huang et al. identified estrogenic hormones in effluent from four municipal WWTPs in California, USA, as well as in surface water from the Colorado River and the Sacramento River delta wetlands receiving such effluent (Huang and Sedlak, 2001). Data exists demonstrating the presence of numerous pharmaceuticals in effluents, river systems, marine sediments, and sewage sludge in Australia as well as New Zealand. Pharmaceuticals such as salicylic acid, paracetamol, carbamazepine, and caffeine at maximum concentrations of 1530 ng/L, 7150 ng/L, 682 ng/L, and 3770 ng/L were the most frequently identified contaminants during a national study of trace organic contaminants in Australian rivers (Scott et al., 2014). Research by Watkinson and colleagues confirmed the presence of antibiotics in three hospital effluents, five WWTPs, six rivers, and a catchment of drinking water in the watersheds of Australia's South-East Queensland (Watkinson et al., 2009).

Antimalarial drugs such as artemether and lumefantrine, commonly used in Africa to treat malaria parasites, as well as amoxicillin, have been found in Tanzania at concentrations ranging from 3 to 32 mg/L (Ternes, 1998). The existence of pharmaceuticals such as erythromycin, chloramphenicol, nalidixic acid, tetracycline, sulfamethoxazole, acetaminophen, atenolol, diclofenac, ibuprofen, caffeine, and others in Umgeni surface water and dams along the Umgeni River used for the supply of water in KwaZulu-Natal South Africa was recorded in a study in South Africa. The analytes analyzed in wastewater were 100% present, with caffeine showing the highest average concentration at 61 ± 5 mg/L and nalidixic acid being the most abundant antibiotic at 31 ± 3 mg/L. Except for the removal of atenolol, where the reduction was just 15%, the waste treatment process decreased the influent concentrations by 43%–94% before discharge. In general, analyte concentrations in surface water were much lower (<10 mg/L), except for acetaminophen (16 mg/L) and atenolol (39 mg/L) [1]. In a most recent and comprehensive study by Mhuka et al., the presence of pharmaceutical residues was reported in surface water from the upstream and downstream of Apies River, Pretoria, South Africa (Mhuka et al., 2020). In this study, it has been reported that 60 and 63 compounds were detected in the upstream and downstream of the river samples, respectively. From the findings, it was indicated that the highest average concentrations recorded in the river water samples were ibuprofen (4.14 $\mu g\,L^{-1}$ downstream; 3.19 $\mu g\,L^{-1}$ upstream), estradiol (0.51 $\mu g\,L^{-1}$ downstream), caffeine (2.98 $\mu g\,L^{-1}$ downstream; 1.42 $\mu g\,L^{-1}$ upstream), and paraxanthine (1.22 $\mu g\,L^{-1}$ downstream; 0.798 $\mu g\,L^{-1}$ upstream). In Kenya, 10 groups of pharmaceutically active compounds in the Nairobi River have been investigated (K'oreje et al., 2012). See also Chapter 10 by Madikizela et al. (2022) on PPCPs.

5.3 Sample extraction techniques

The analysis of ECs in environmental water is a challenge due to the huge number of contaminants to be tested, the complexity of the matrices, and the number of invasive compounds. Therefore, new techniques are under continuous progress to allow the isolation, purification, and preconcentration of analytes from the matrix with maximum yield and selectivity. To achieve the maximum yield, an adequate solvent must be used, in such a way that as few potential interfering species as possible are carried into the analytical separation stage. Different classical and miniaturized methods appropriate for environmental water applications have been introduced to extract ECs, this section focuses on improvements in sample preparation.

5.3.1 Classical extraction techniques

Scientists have commonly resorted to the development, optimization, and application of measurement processes to gain knowledge and understanding of natural and/or artificial systems, to build (bio)chemical information that can underpin reliable decision-making in various fields. However, the process as a whole must be achieved such that a substantial amount of quality data is expeditiously gathered using the least amount of resource (sample, reagent, solvent, etc.); and this, with limited human involvement, as well as minimal risk for both operators and environment (Cases et al., 2018). Compelling gathering of specific and useful results is accomplished through a series of analytical steps. Amid the analytical process, sample preparation is thought of as, one of the most time- and labor-intensive steps in the entire analytical method. Samples under study by analytical techniques require to be in a suitable form and this can be achieved through sample preparation. During the sample preparation process, the concentration of the analyte can be brought to a level that is appropriate for detection (Kafle, 2020). As the whole sample preparation involves the extraction of components of interest and may also include cleanup and/or enrichment procedures from the sample matrix. The most used approaches to sample extraction of ECs in environmental water include liquid-liquid extraction (LLE), solid-phase extraction (SPE), dispersive SPE (d-SPE), and magnetic SPE (MSPE). The inherent simplicity and flexibility of traditional off-line solid-phase extraction (SPE) on discs and cartridges allow it to be still the most important and used technique in this research area. Usually, these classical sample preparation methods employ a large volume of solvent (>100 mL) and often necessitate specialize instrumentation. In SPE, although the comprehensive choice of the sorbent makes it possible to obtain high recovery and enrichment factors disadvantages during the loading of dirty samples include reduced sorption power, analyte displacement, and cartridge occlusion (Pérez-Fernández et al., 2017). In addition, they may have high operational cost and limited potential for automation, in many cases to maximize recovery, longer extraction time and effort is required (Jiang and Ouyang, 2015).

5.3.1.1 *Fundamentals and applications of classical extraction techniques*

Liquid-liquid extraction (LLE)

Liquid-liquid extraction (LLE) is a sample preparation method in which unequal partition of solute between two immiscible or slightly miscible liquid phases are in contact with each other and mix thoroughly occurs. The target compounds selective distribution between the two immiscible liquid phases, generally an aqueous phase and an organic phase, is driven by their relative solubility in each phase. The analytes are transferred and will be in higher proportion in the phase in which it has greater solubility when the system reaches equilibrium (Ronco et al., 2019). The mass transfer from the feed to the extract, in LLE, is measure through the distribution ratio K_D which is defined as the ratio of the concentration of solute in each liquid phase at equilibrium.

$$K_D = {}^{Concentration\ in\ extract}\Big/_{Concentration\ in\ raffinate}$$

The value of K_D is typically superior to 1 and a high distribution ratio means more solutes are extracted. Efficient separation can be achieved through a critical choice of solvent and the simultaneous adjustment of parameters such as solvent volumes, pH, ionic strength, method of extraction, etc. (Poole, 2020). LLE can be performed in the batch and the flow modes. Batch extraction is used where the separation can be achieved easily, by limited numbers of extractions and it is commonly employed in small-scale laboratories or low-capacity plants. Batch extraction is typically carried out in single set of devices, such as a separatory funnel or a mixer-settler extractor; a fixed quantity of solvent is added to a fixed volume of feed; the two phases are well mixed by shaking the extraction device or by using mechanical agitation. After the system reaches equilibrium, the extract and the raffinate are allowed to settle and separate. Batch extraction is characterized by its simplicity, flexibility, and low cost while the solute transferred is constrained by equilibrium. The continuous extension of batch operation in tandem is called crosscurrent extraction; in this operation mode the raffinate from the previous stage is the feed for the next extraction and fresh solvent is added to each extraction stage. Mixer-settlers, centrifugal extractors, and column extractors are the three major types of extractors used for large-scale LLE (>2000 mL). Liquid-liquid extraction have proven to be very effective, and is still extensively used for the determination of toxic organic compounds in all types of environmental waters including drinking water, surface waters, groundwater, rainwater, industrial effluents, and even certain hazardous wastes such as dense nonaqueous phase liquids (DNAPLs). Kyra et al. ran a comparative study aimed at determining the extraction efficiency of liquid-liquid extraction (LLE) and stir bar sorptive extraction (SBSE) for the extraction of polycyclic aromatic hydrocarbons, phenols, phthalate esters, anilines, ethers, aromatic nitro compounds, and nitrosamines in aqueous samples (wastewater influent and effluent) (Murrell and Dorman, 2021). With over 70% recovery, LLE permitted a greater number of target analytes to be extracted and more targets were quantified in the influent wastewater. Poor recovery of nonpolar contaminants in the influent water samples due to matrix interference effects was more pronounced with SBSE as compared to LLE. Meanwhile, SBSE displays a better extraction sensitivity for trace contaminants in effluent samples relative to LLE. Consequently, it was found that LLE was more suited for the extraction of a broad range of target analytes in complex matrices such as wastewater influent. While for the nontarget and survey study of trace pollutants in less complicated water samples, SBSE was a more effective tool (Murrell and Dorman, 2021). The LLE is a robust and relatively low-cost separation technique that allows for continuous stepwise extraction performed under diverse conditions and scales. However, it necessitates a large volume of solvent and is labor-intensive (Clement and Hao, 2012).

Solid-phase extraction (SPE)

Solid-phase extraction (SPE) is a method where the analyte of interest present in a fluid, gas, or liquid sample flow through and simultaneously adsorb onto a sorbent material (see Kaykhaii and Hashemi, 2022, Chapter 4; Kumar et al., 2022, Chapter 6). Subsequently, the solid phase is then isolated from the sample, and the analytes are retrieved from the sorbent phase by elution using an appropriately selected fluid or liquid, or by thermal desorption into the gas phase (Poole, 2012). SPE for liquid samples employs disposable cartridges, which typically consist of an open syringe barrel holding a sorbent, with particle size between 20 and 60 mm, sealed between porous plastic or metal frits. A variety of sorbent materials are available commercially to fit the need in the diverse application of SPE. Different disk formats for SPE are also available, providing a higher sample-processing rate for larger sample volumes compare to cartridges. Small sample sizes commonly encountered in bioanalysis laboratory use a multiwall plate and multiple pipettors (Poole, 2012). Depending on the type of analyte of interest, the sorbent(s) used should be carefully selected to achieve significant recoveries. Octadecylsilane bonded stage (C18), graphitized carbon black, N-vinylpyrrolidone-divinylbenzene copolymers (Oasis HLB), and embedded ion-exchange alkyl phases are some sorbent materials available on the market (Pérez-Fernández et al., 2017). The most common sorbent material used in SPE for the extraction and preconcentration of ECs in water remains Waters Oasis HLB, nonetheless, new sorbents continue to be produced to enhance the extraction of specific compounds while eliminating interfering matrix compounds. A mixture of sorbents has also been employed in extensive nontarget screening of a wide range of ECs in water (Bataineh et al., 2021). The cyanotoxins, anatoxin-a, cylindrospermopsin, and homoanatoxin-a, in freshwater samples impacted with cyanobacterial blooms, were extracted using the SPE method (Tran et al., 2020). Four different SPE cartridges with weak anion-exchange properties, Waters OasisWAX 150 mg/6 mL, Pre-sep PFC-II 60 mg/3 mL, Enviro-Clean CUPSA 100 mg/1 mL, Strata-X-AW 200 mg/3 mL were used for the extraction of perfluorooctanoic acid (PFOA) and prefluorooctane sulfonate (PFOS) in surface water and wastewater (Zacs and Bartkevics, 2016). A poly(ethylene glycol dimethacrylate-N-methacryloyl-L-tryptophan methyl ester) [poly(EGDMAMATrp)] microbeads were synthesized and used as sorbent material for the solid-phase extraction of pirimicarb and propoxur in environmental water samples. Various samples of a dam and river waters were spiked with the carbamates then extracted with [poly(EGDMAMATrp)] microbeads packed SPE cartridges and showed high recovery calculated in the range of 95.8%–107.1% (Demir et al., 2020). Although the main advantage of SPE lies in its ease of use and versatility, its drawbacks include the restricted ability for sorption and blocking during loading, as well as sorbent packing problems. Improved models such as dispersive SPE (d-SPE) and magnetic SPE (MSPE) have been developed to resolve the SPE disadvantages. The d-SPE is based on an even dispersion in a sample suspension of the substance chosen. By centrifugation, the sorbent is extracted and eluted with a suitable solvent. This approach has the advantage, in addition to its simplicity, of increasing the active surface of sorbent open to analytes of interest (Bataineh et al., 2021). Multifunctional polymeric microspheres were synthesized and used as a sorbent for dispersive solid-phase extraction (d-SPE) of fluoroquinolones (ofloxacin, ciprofloxacin, enrofloxacin, difloxacin, and sarafloxacin) from spring water, river water, and pharmaceutical plants wastewater samples (Yu et al., 2019). Paramagnetic and high-adsorption properties magnetic materials are employed in MSPE. To facilitate the adsorption of analytes, the paramagnetic sorbent is dispersed into the water sample and incubated. The magnetic material is isolated by a magnet from the aqueous solution and the analyte can then be eluted using an adequate solvent (Yu et al., 2019). For the magnetic solid-phase extraction of diflubenzuron, triflumuron, hexaflumuron, teflubenzuron, flufenoxuron, chlorfluazuron, and lufenuron from river water samples, a magnetic Metal-Organic Frameworks composite material modified with attapulgite (ATP@Fe_3O_4@MIL-100 (Fe)) was employed as an adsorbent. Real water samples spiked with the seven benzoylurea insecticides at the concentrations of 20, 100, and 200 μg/L displayed recoveries ranging from 73.56% to 99.63% (Niu et al., 2020). Compared to conventional SPE, MSPE has many benefits, including better analyte recovery due to the greater contact region between the magnetic material and the analytes in solution, lower solvent consumption, and no cartridge blockage (Pérez-Fernández et al., 2017). Other methods are available in addition to traditional SPE for the isolation and preconcentration of ECs in environmental water. They are known as microextraction and have been proven to be environmentally sustainable as they need a less organic solvent and continue to be used and/or improved further.

5.3.2 Green sample preparation: Miniaturization techniques

Over the past two decades, extensive research has been done on sample preparation to eliminate and/or reduce the consumption of organic solvents to protect the environment. The development of new extraction processes has resulted in miniaturization of conventional techniques, leading to new micro-configurations and solvent-free approaches. The development of these new technologies has brought about advancement in the fundamental understanding of extraction principles. The aforementioned progress has been very important in the introduction of novel approaches and resulted in new trends in sample preparation, such as miniaturization, microextraction, and integration of the sampling and separation and/or quantification steps of the analytical process. Miniaturization of extraction techniques has gained considerable attention for sample preparation as alternatives to classical approaches, since these miniaturized techniques comply with the greener extraction approach. These techniques have been developed in various configurations, reduced the sample volume, solvent use, and size of the extraction device, while they also facilitate rapid and convenient sample preparation. Additionally, the miniaturization of the extraction device enables the automation of the techniques. Moreover, most of the miniaturized microextraction techniques are nonexhaustive approaches, which cause minimal disruption to the sample system. The applications of these microextraction-based techniques provide a better characterization and accurate information of the investigation system or process as compared to exhaustive techniques. The most common microextraction approaches including liquid-phase microextraction (LPME), solid-phase microextraction (SPME), stir-bar sorptive extraction (SBSE), and thin-film microextraction (TFME) have been widely applied to various matrices, including biological, environmental, and food samples (Jiang and Ouyang, 2015).

5.3.2.1 Miniaturization of solid-phase extraction techniques

Solid-phase microextraction (SPME), stir-bar sorptive extraction (SBSE), and microextraction by packed sorbents (MEP) are the main miniaturized version of solid-phase extraction and have been applied in environmental samples. In SPME, a fiber coated with sorbent is dipped into a liquid (mostly aqueous) sample or exposed to the headspace above a liquid sample during the extraction and there is a diffusion of the analytes from the matrix into the polymer sheet until a dynamic equilibrium is reached between the sample matrix and the coating. After the extraction, the analytes adsorbed onto the SPME fiber are eluted by thermal desorption (Bataineh et al., 2021). In SBSE, via a thick film-coated magnetic stir bar immersed in the sample, analytes are removed from the liquid matrix, after extraction analyte is eluted with an effective solvent or thermal desorption. In MEP, the sorbent weighing a few milligrams is packed within a membrane and sealed. Then the small unit is soaked in the sample, stirred, collected and the analyte elutes with an appropriate organic solvent. A spherical conjugated microporous polymer of tetrakis(4-formylphenyl) methane and 1,4-phenylenediacetonitrile were used to fabricate the coating for solid-phase microextraction (SPME). Carbamate pesticides in water samples (drinking water, river water, and underground water) were extracted from water using the newly developed SPME then quantified by ultrahigh performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS). A stir bar sorptive extraction (SBSE) was developed and validated for the determination of selected perfluorinated compounds, preservatives, plasticizers, surfactants, flame retardant, hormones, pharmaceutical compounds, UV-filter and pesticides in environmental waters by liquid chromatography-tandem mass spectrometry (LC-MS/MS) (Aparicio et al., 2017). Maurizio Quinto and colleagues compared two different extraction procedures for the preconcentration of different polycyclic aromatic hydrocarbons (PAHs) in seawater, agricultural irrigation wells, streams, and tap water by micro-extraction by packaged sorbent (MEPS) (Quinto et al., 2014).

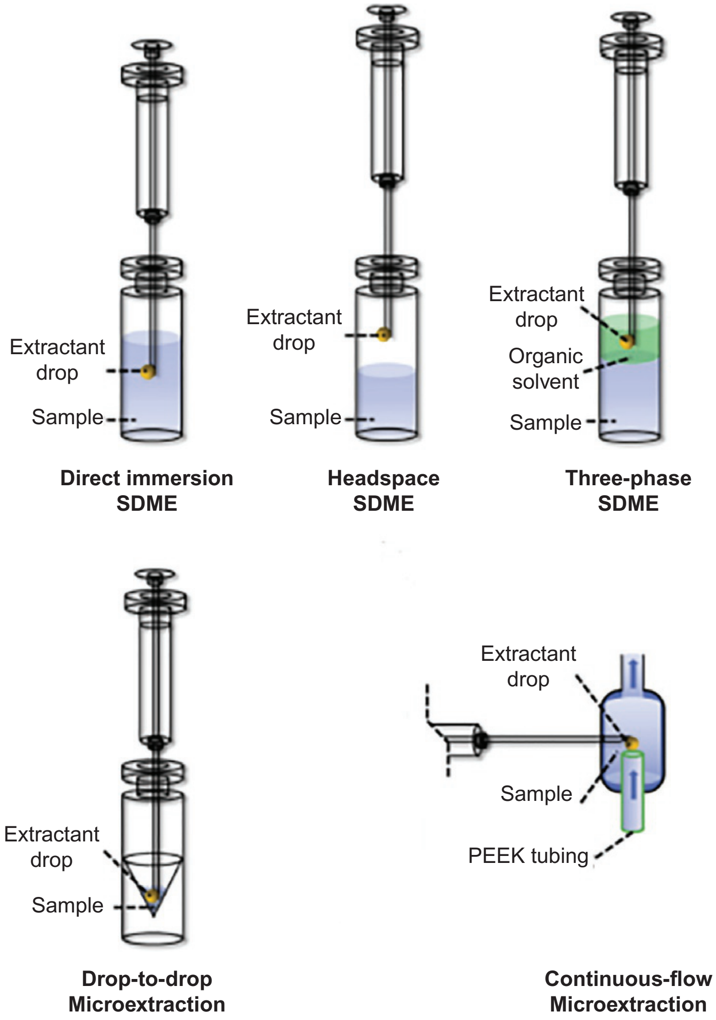

FIG. 5.1 Different modes of SDME. (1) Direct immersion SDME, (2) Headspace SDME, (3) Three-phase SDME, (4) Drop-to-drop microextraction, (5) Continuous-flow microextraction.

5.3.3 Miniaturization of liquid phase extractions

5.3.3.1 Single drop microextractions

The single drop microextraction (SDME) is one of the LPME techniques where a drop of extracting solvent is used for the extraction and it was introduced in 1997 by M.A Jeannot and F·F Cantwell (Jeannot and Cantwell, 1997). In this technique, a drop of immiscible extracting solvent (about 1–10 μL) is suspended from a syringe into the liquid or gaseous sample medium. After extraction, the organic drop is retracted back into the microsyringe and is injected into the required instrument for the quantification of analytes. Passive diffusion mode is used during extraction of the target analytes from an aqueous sample into suspended extracting solvent and extraction recoveries are essentially determined by the organic solvent to water partition coefficients (Pedersen-Bjergaard and Rasmussen, 2008). This method is a simple, cost-effective, fast, virtually solvent-free sample preparation technique based on a great reduction of the extractant phase-to-sample volume ratio and has the possibility of in situ complexation or derivatization. It is not exhaustive and only a small fraction of analyte (s) is/are extracted/ preconcentrated for analysis. However, it has drawbacks including, instability of the drop, limited drop surface, and consequently slow kinetics. From the time it was introduced, a different mode of SDME (Fig. 5.1) such as direct immersion (DI)-SDME, headspace (HS)-SDME, three phases SDME, liquid-liquid-liquid microextraction (LLLME), and continuous-flow microextraction (CFME)have been developed for various analytical applications.

Direct immersion single drop microextraction (DI-SDME)

A micro drop was held at the end of a Teflon rod and suspended in a stirred aqueous sample solution or the drop of a water-immiscible organic solvent was immersed in a large flowing aqueous solution (Liu and Dasgupta, 1996) to complete the extraction process, according to the early study on direct immersion single drop microextraction (DI-SDME). The disadvantage of this approach (also known as static-SDME) was that it was necessary to perform the extraction and injection separately with different appliances. Jeannot and Cantwell (1997) used a microsyringe as the organic solvent holder to overcome this disadvantage. The syringe is filled with a micro-litter of organic solvent before moving the microsyringe through the sample vial septum and submerged in the liquid sample. Then a droplet of organic solvent is suspended at the tip of the syringe needle in a stirred aqueous sample. After extracting for a given period, the organic phase was retracted back into the microsyringe and finally injected into the instrument for the determination of analytes. Since two liquid phases are in direct contact with each other, in the absence of any porous solid support at the interface, then when one of the phases is mechanically stirred, the other will also experience convective mixing. This occurs because the first phase transfers momentum to the second phase as a result of frictional drag at the liquid-liquid interface. During the extraction, the mass transfer of analytes from the aqueous to a droplet of organic solvent continues until thermodynamic equilibrium is attained or extraction is stopped. Jeannot and Cantwell developed a theoretical model based on the film theory of convective-diffusive mass transfer for DI-SDME (Jeannot and Cantwell, 1997). The film theory of convective-diffusive mass transfer is based on the assumption that no movement of the solution at the layer immediately adjacent to the interface and a gradually increasing vigorousness of convection of the solution at a location further away from the interface. Considering the film theory under this condition, instantaneous and complete convective mixing exists in the bulk solution to some distance, the Nernst diffusion film, away from the liquid-liquid interface. The liquid layer of thickness, called the Nernst diffusion film, is postulated to be completely stagnant and none convected so that analytes cross it by pure diffusion only. The extraction with DI-SDME requires the use of an organic solvent (water-immiscible extractant phase) and analytes more soluble in the organic phase than in the sample solution (Psillakis and Kalogerakis, 2002). Although DI-SDME is a quick, fast, and low-cost extraction technique, it has a few weaknesses, such as high stirring velocity or instability, temperature, and complicated matrix samples or samples that are not clean, requiring careful operations. To some extent, this issue is improved by using a smaller microsyringe (1 μL) instead of a larger one (10 μL) and by adjusting the needle tip (Ahmadi et al., 2006), but the organic drop is still unable to withstand the stirring rate above 1700 rpm. To improve the compromised stability of the fall, an additional filtration stage of the sample solution is introduced when dealing with complex matrixes. In addition, because of their high rate of evaporation or dissolution, solvents with relatively low boiling points and high water solubility are not ideal for DI-SDME. Acidic samples, such as digests obtained by acid digestion processes or the presence of large nonpolar species that can saturate the organic phase, may be problematic if applying this microextraction mode. Moreover, the sensitivity and precision of DI-SDME techniques are very low and require further enhancement. This is because extended extraction times and a faster stirring rate are not recommended, which may lead to dissolution and/or dislodgment of the drop.

Headspace single drop microextraction (HS-SDME)

The headspace-solvent microextraction (HSME) or most commonly known as headspace-space single drop microextraction (HS-SDME) was first introduced in 2001, by Theist and co-workers (Theis et al., 2001). It was introduced as a preparation technique that enables volatile or semi-volatile compounds to be extracted and preconcentrated into a micro drop exposed to the headspace above the sample. This extraction mode occurs by suspending a drop of a microliter of a suitable solvent from the tip of a microsyringe located in the headspace of a sample that is thermostated for a preset extraction time at a given temperature. The drop hangs during the whole extraction at the tip of the microsyringe and is then retracted back into the microsyringe. For identification and quantification, the retracted solvent with the analytes of interest is injected into the appropriate instrument. The analytes are distributed in this mode between three stages, the water sample, the headspace, and the organic drop. The rate-determining step of this extraction is aqueous phase mass transfer since the high stirring speed of the sample solution facilitates the mass transfer and the extraction rate (Theis et al., 2001). This mode of extraction is potentially used for the determination of volatile compounds or volatile species provided by acceptable environmental, pharmaceutical, forensic, and food derivatization methods and provides a high degree of extract clean-up as nonvolatile and high molecular weight matrix interferences are reduced, if not eliminated. A solvent with a relatively low vapor pressure is desired in this technique, so the practical difficulties with this technique involve a restricted choice of solvent due to the necessary viscosity and vapor pressure and more work is required to demonstrate the reproducibility of these techniques. However, it could be tolerated with solvents providing a high boiling point in the extraction of organometals, metalloids, and nonmetals.

Three phases single drop microextraction (three-phase-SDME)

In 1999, Ma and Cantwell (1999) reported a solvent microextraction with simultaneous back extraction into a single micro drop for sample clean-up and preconcentration before high-performance liquid chromatography (HPLC-PDA) determination. The organic liquid membrane is confined inside the Teflon ring over the aqueous sample solution in this procedure, which is called the three-phase SDME. A micro drop of the receiving aqueous phase is left suspended within the organic liquid membrane with the aid of a microsyringe. The composition of the aqueous drop / organic membrane is robust and permits the use of very high stirring speeds. Because of the momentum transfer through the liquid-liquid interface, the direct stirring of the aqueous sample results in indirectly induced convection in the other two phases (Pena-pereira et al., 2009). The analytes are converted into neutral, lipophilic forms by modification of pH or the addition of a complexing agent to the aqueous sample phase, which can be extracted into the organic phase. Finally, the analytes are collected back into the receiving phase by changing the state of the aqueous micro drop (receiving phase). It should be noted that this mode of microextraction is ideal for final determination by techniques such as HPLC, capillary electrophoresis (CE), and atomic spectroscopy (AS), as the final extract is in an aqueous phase.

Liquid-liquid-liquid-microextraction (LLLME)

Liquid-liquid-liquid microextraction (LLLME) is a mode of microextraction suitable for ionizable analytes, which was developed by Ma and Cantwell in 1999 (Pedersen-Bjergaard and Rasmussen, 2008) under the name "solvent microextraction with simultaneous back-extraction". The LLLME is based on the extraction of analytes into an organic substrate or membrane with a lower density than water from the aqueous stirred sample and simultaneous back-extraction into an aqueous micro drop. As a result of momentum transfer through both LL interfaces, direct convection (stirring) in one phase (aqueous sample) results in indirectly induced convection in the other two phases (organic layer and aqueous micro drop). It is possible to change the pH of the aqueous solution and the aqueous micro drop to obtain first the analyte's neutral shape, extractable by the organic solvent, and then to ionize it. Finally, within the drop, the ionized analyte is removed. The use of two distinct complexants, one applied to the sample solution and the other dissolved in the aqueous drop, maybe another possibility. The creation of a neutral complex thus makes it possible to extract it into the organic layer and, if the aqueous micro drop contains a complexant that forms a stronger complex with the analyte, to extract it back into the drop.

Continuous-flow microextraction (CFME)

Continuous-flow microextraction (CFME)is another mode of SDME and first reported by Liu and Lee (2000), wherein the extraction is carried out in a glass extraction chamber. Instead of being stirred, the sample is continually pumped at a constant flow rate, and a drop is created at the end of a microsyringe needle when the extraction chamber is full of the sample. A solvent drop allows contact with a new and flowing sample solution, in contrast to the above SDME microextraction modes. The flow induces mass transfer in the drop in CFME by momentum transfer (the extraction process indirectly experiences convection as a result of aqueous sample convection). With the increasing flow rate of the aqueous solution, the rate of extraction increases, consistent with the decrease in thickness of the diffusion films of Nernst. This mode enables mass transfer and can achieve high preconcentration factors. The successful microextraction of analytes without drop dislodgement or bubble formation should be guaranteed by the sample flow rate. Samples should, like Direct-SDME, be perfectly clean to improve the stability of the drop at the tip of the needle. Xia et al. (2004) reported a modification of this microextraction mode, called cycle-flow microextraction, with its introduction into the waste outlet tube from the sample reservoir. Although the conceivable possibilities for Direct-SDME can be extended to CFME, TCFME has been used to remove transition metals by in-drop complexing of metal ions. A study of the various modes of SDME, including CFME, and their combination with various analytical techniques, can be found in a recent review (Xu et al., 2007).

5.3.3.2 *Drop-in-drop and drop-to-drop microextraction*

The drop-in-drop system was the pioneering LPME technique developed by Liu and Dasgupta (1996) where an organic micro drop was suspended inside a flowing aqueous sample drop from which the analyte was extracted. The analytical method was validated by its ion-pair formation with methylene blue for sodium dodecyl sulfate. After the sampling/extraction period, the sample/reagent in the aqueous layer was replaced by a wash solution, resulting in a transparent outer aqueous drop housing a colored organic drop containing the analyte extracted. An automated backwash also resulted in this. A light-emitting diode-based absorbance detector tracked the color intensity of the organic drop, linked to the analyte concentration. This scheme had the benefit of conducting both extraction and analysis processes in the same chamber. Drop-to-drop is an equivalent approach where a static microdroplet of just a few μL in volume is the sample (Wu et al., 2006). The proposed system reduces the size of the sample to typically 7–8 μL, into which was placed less than 1 μL of extraction solvent drop hanging at the needle tip of the microsyringe. The drop is withdrawn back into the syringe until the extraction is done, and injected into the analytical instrument. Because of the limited sample and solvent volume, the equilibrium between the sample and the solvent is easily created. Stirring is not needed, and this also helps to reduce stability and simplify the experimental setup. The higher ratio of organic micro drop volumes and aqueous samples, however, decreases the EF. The low concentrations of extractant solvent are preserved by this procedure, but the extractant solvent is completely dispersed by energy and the spherical drop loses its integrity, becoming more DLLME than drop-to-drop.

5.3.3.3 Solidification of floating organic drop microextraction (SF-ODME)

In methods such as single drop microextraction, the push towards a greener extraction process has led to a remarkable reduction in organic solvent volume so that a single micro drop is appropriate for extraction. Nevertheless, the drawbacks to these forms of extraction are the ability of the droplet to dislodge and the risk of carrying over, as a surface is in contact with the extracting material. These shortcomings were negated by the development of the solidified floating organic drop microextraction (Reza et al., 2007). In this step, to optimize the interaction between the two solutions, a droplet of an immiscible solvent is floating on the surface of the agitated aqueous sample. To solidify the droplet that is readily extracted and is allowed to melt for determination, the sample vial is then put in an ice bath. The SF-ODME is a technique of equilibrium extraction, where the analyte in the concentration of the organic solution rises to a certain degree and subsequently, the system reaches equilibrium and the analyte concentration stays constant vs. time in the acceptor stage. The SF-ODME extraction recovery is calculated by the actual partition coefficient, sample volume, and acceptor phase volume. Thus, when the partition is relatively high and the concentration of analyte in the sample is at trace level, quantitative recovery of analyte in micro-litter of the organic phase is possible. In this method, the solvent should have a melting point in the range of 10–30°C and must be immiscible with water. In the first published application, a group of polycyclic aromatic hydrocarbons (PAHS) were extracted from a water sample and were determined by GC-FID (Reza et al., 2007). The method was then extended for extraction of the metal ion complexes from water samples (Dadfarnia et al., 2011). In 2008, Leong and Huang (2008) reported a novel variation SF-ODME. Instead of retaining one droplet of extractant in the sample, the injection of the mixed solution of the extractant and the dispersive solvent created a dispersion of fine droplets. This creates a large area of interaction between the extractant and the sample, resulting in faster transfer of mass and better extraction times. These two methods demonstrate the speed, simplicity, and high efficiency of green operation while using very small quantities of organic solvent. Both SF-ODME versions are fast, but the dispersive method achieves even lower extraction times than the nondispersive version. While these techniques sound very appealing, it is worth pointing out that, like most other LPME methods, a primary clean-up phase is needed for the extraction of analytes from biological samples or complex matrix samples. Simplicity, low cost, good accuracy and precision, fast extraction time, easy apparatus, and minimal organic solvent consumption are the key advantages of these methods. Nevertheless, the limitation in the selection of appropriate solvent and the need for freezing of the extract can be stated as their disadvantages.

5.3.3.4 Hollow fiber liquid-phase microextraction (HF-LPME)

Pedersen-Bjergaard and Rasmussen introduced an alternative concept for LPME based on the use of single, low-cost, disposable, porous, hollow fibers, typically made of polypropylene (Pedersen-Bjergaard and Rasmussen, 1999). In this method, with the lumen of a porous hollow fiber, the microvolume of the extracting liquid is contained, so that the microextraction solvent is not in direct contact with the sample solution. The main benefit of this technique is that, since it is mechanically covered, the sample can be vigorously stirred or vibrated without any loss of the extracting liquid. The hollow fiber is immersed in the immiscible organic solvent in HF-LPME before extraction, leading to the immobilization of the organic solvent into the hollow fiber pores. Inside the wall of the hollow fiber, the organic solvent, usually 10–20 μL, forms a thin film. The hollow fiber is then put in a sample of interest filled with the aqueous sample. The sample is extensively agitated or stirred to accelerate extraction. In the pores of the hollow fiber, the analytes are collected from the aqueous sample via the organic process, and then into an acceptor solution within its lumen. The hollow fibers disposable design prevents the risk of sample carrying over and ensures high reproducibility, and the pores in the hollow fiber walls allow some selectivity to be seen by preventing high molecular weight materials from being collected. HF-LPME can be done in two-phase and three-phase modes (Pedersen-Bjergaard and Rasmussen, 2008; Rasmussen and Pedersen-Bjergaard, 2004). In two-phase systems, the acceptor solution is the same organic solvent as immobilized in the pores, and the analytes are collected in an organic phase which is compatible with GC (Basheer et al., 2002; Ho et al., 2002; Jiang et al., 2005, 2008; Pedersen-Bjergaard and Rasmussen, 2008). However, in a three-phase mode, the acceptor solution is another aqueous phase and the analytes are extracted from an aqueous sample, through the thin film of organic solvent into an aqueous acceptor solution. So, this mode is compatible with HPLC, CE, and AS (Ho et al., 2002, 2003; Jiang et al., 2005, 2008). Diffusion is the basis of extraction in two-phase and three-phase HF-LPME systems, where high partition coefficients facilitate extraction. The chemical character of hydrophilic analytes such as metal ions, however, results in poor partition coefficients which prevent them from being extracted in diffusion alone-based systems. HF-LPME can be used in these cases in an active mode of transport (Ho et al., 2003; Jiang et al., 2008) in which a carrier is attached to the sample solution. Via complexation or ion-pair formation with the added carrier, the analytes are converted into hydrophobic form and are extracted into an inorganic process in the hollow fiber pores. The analytes may then be released by the proper mechanism into the acceptor solution (i.e., pH modification or sufficient acceptor addition for analytes). HF-LPME can also be carried out in static or dynamic modes. In static mode as described above, the extraction speed is improved by extensive sample agitation or stirring, and the device is carefully designed to reduce the diffusion distance of the analytes. A microsyringe is filled with a few microliters of the same organic solvent in a two-phase dynamic mode (Hou et al., 2003; Zhao and Lee, 2002), immobilized into hollow fiber pores. The hollow fiber fragment is attached to the microsyringe needle and then into the aqueous sample. Using the syringe plunger, small amounts of the aqueous sample are repeatedly pulled in and out of the hollow fiber during extraction. When the aqueous sample is removed, the organic solvent film is built up into the hollow fiber and the analytes are vigorously extracted from the sample segment, and this thin film recombines with the bulk organic phase in the syringe during sample expulsion, and the extracted analytes are stuck in the bulk organic solvent. After the extraction is done for a prescribed repeated cycle, a portion of the bulk organic solvent is used for determination. In three-phase dynamic HF-LPME mode (Hou et al., 2003; Hou and Lee, 2003), the microsyringe is first filled with a few microliters of aqueous acceptor solution and subsequently with a few microliters of organic solvent (Hou and Lee, 2003). The procedure for extraction is similar to what is defined in the dynamic two-phase mode. The dynamic mode extraction speed is greater than the static mode (Hou and Lee, 2003; Zhao and Lee, 2002), but the dynamic mode activity is more complex. The HF-LPME offers excellent sample clean-up from complex biological and environmental samples in both two and three modes and has been fully automated in the CTC robotic system recently (Ouyang and Pawliszyn, 2006). High enrichment factor is also easily achieved. Compared to SDME, this approach has the benefits of improving organic solvent stability and high time and temperature sampling tolerance; it is also inexpensive and has a high potential for automation and miniaturization. Its drawbacks include the need for membrane preconditioning and the risk of memory effects when membranes are reused. In comparison with SDME, a high enrichment factor is also easily achievable, this approach has the advantages of enhancing organic solvent stability and tolerance of higher sampling time and temperature; it is also inexpensive and has a high automation and miniaturization capacity. The drawbacks are the need for membrane preconditioning and the risk of memory effects when membranes are reused.

5.3.3.5 *Dispersive liquid-liquid microextraction (DLLME)*

Dispersive liquid-liquid microextraction (DLLME) was first introduced by Rezaee et al. (2006). It is a simple and quick microextraction technique based on the use of a suitable extractant, i.e., a few microliters of a high-density organic solvent such as tetrachloromethane, chloroform, carbon disulfide, nitrobenzene, bromobenzene, chlorobenzene or 1,2-dichlorobenzene, and a disperser solvent with high miscibility in both extractant and aqueous phases such as methanol, ethanol, acetonitrile, or acetone. When the mixture of disperser and extractant phase is quickly injected into the sample, it produces high turbulence. This turbulent regiment gives rise to the formation of small droplets that are dispersed throughout the aqueous sample. There are large interfacial areas with emulsified droplets. The nature of the emulsifier (disperser solvent) can also have an influence on droplet size distribution, the mean droplet size, and also on emulsion viscosity. Liquid-liquid dispersions play an essential role in separation processes and reaction systems. This is because the large interfacial area due to dispersion facilitates mass transfer and reaction rate. Turbidity is formed in the aqueous phase owing to the fine dispersion of the extractant distributed throughout the aqueous sample, which is facilitated by the disperser solvent. After the formation of the cloudy solution, the surface area between extraction solvent and an aqueous sample is very large, so the equilibrium state is achieved quickly and therefore the extraction time is very short. In fact, this is the principal advantage of DLLME. The sedimented phase at the bottom of a conical tube is retrieved after centrifuging the cloudy solution and used with the most suitable analytical technique. The syringe is not used as a drop holder during the extraction process in DLLME, unlike SDME, but in the extract collection and injection, thereby preventing issues such as drop dislodgement. Nevertheless, this approach is limited to a small number of extractants that should extract the analytes of interest effectively, since the required conditions, i.e., to have higher density rather than water, form a stable cloudy solution and be easily removed from the bottom of the conical vial after centrifugation, are met by a few organic solvents. In addition, this microextraction technique appears to be difficult to automate. Very recently, Shemirani et al. developed a modification of the DLLME approach called "cold-induced aggregation microextraction" (CIAME) (Baghdadi and Shemirani, 2008). The procedure involves the addition of an ionic liquid (IL), a nonionic surfactant, and a derivatizing reagent, if necessary, to an aqueous sample placed into a conical-bottom centrifuge tube. The dissolution of the IL in the sample is achieved by heating the centrifuge tube in a thermostated bath. After that, the centrifuge tube is placed in an ice bath, and like DLLME, a cloudy solution is obtained. The process after that is similar to that for DLLME. As the solubility of the IL increases with increasing salt content in the sample, the common ion effect can be employed by adding another IL to decrease the solubility of the extractant phase. Therefore, the extraction of analytes into samples with a high salt content involves two distinct ILs. CIAME uses ILs rather than organic solvents as extractant phases compared to DLLME, thereby eliminating the use of a disperser solvent. However, this technique introduces several steps before centrifugation, so it takes time and, due to the high viscosity of ILs, it is important to apply a nonionic surfactant as an anti-sticking agent to the sample as ILs bind to the tube wall after centrifugation.

5.4 The phase of extractions: Low-toxicity (green) solvents for LPME

Liquid phase microextraction (LPME) has become an essential tool employed in analytical laboratories, it uses a low volume of solvents for the extraction, purification, and enrichment of trace levels of organic and inorganic species present in various samples matrices (aqueous, solid, gaseous, and oil). It has found applications in the research and development units in many fields including biotechnology, food, forensic, pharmaceutical, clinical, and industrial laboratories amongst others. LPME also referred to as solvent microextraction (SME) involves three core micro solvent extraction approaches; namely single drop microextraction (SDME), hollow fiber-liquid phase microextraction (HF-LPME), and dispersive liquid-liquid microextraction (DLLME). Each of these essential microextraction methods has specific requirements for extracting solvent as compared to conventional extraction and purification techniques (Kokosa, 2019). The need for cost-efficient, reliable, and sensitive sample preparation methods underpin LPME development for trace chemicals occurring in samples from various origins (clinical, environmental, foodstuff, pharmaceutical, etc.), as well as the necessity to alleviate the environmental concerns associated with the traditional techniques. Liquid phase microextraction according to the principles of green analytical chemistry thus can be classified as such, green analytical chemistry is born from the need for creating a more sustainable future through the development of environmentally friendly procedures. Individuals, scientists, and institutions in all branches of chemistry and industry have devised the concept of "green chemistry" which consist of 12 principles, of which seven apply to green analytical chemistry (Yilmaz and Soylak, 2020a):

1. Prevention or reduction of wastes generating process.
2. Use of solvents more environmentally friendly.
3. Design and use of more energy-efficient analytical systems and procedures.
4. Preventing or minimizing the usage of auxiliaries, chemical catalysts, and derivatizing agents.
5. Prioritize the use of catalysts over stoichiometric reactions.
6. Whenever possible, performed an analysis in situ instead of offline.
7. Promote the use of safer chemistry protocols.

There is a possibility of coupling LPME with other analytical sample preparation methods while it is also well-suited with standard analytical instrumentation. In addition, liquid-phase microextraction procedures use small amounts of solvents (usually a few microliters) and small volumes of samples solution. LPME modes require substantially lower energy consumption for solvent concentration and extraction conditions, as well as lower energy requirements for analytical waste because small volumes of samples are needed. Since much smaller volumes of solvents and samples are required, potential toxicity and safety risks for the analyst and those at work are minimized. The precedent is the main reason why the approach fits the classification as green analytical chemistry. The question then remains to choose a suitable solvent for an LPME mode extraction (Kokosa, 2019; Poole, 2020). It is not always as easy to pick an extraction solvent as it would seem. Several physicochemical and economic variables should be considered when selecting a solvent for the LPME process. The nature of the extraction solvents employed have a substantial impact on extraction efficiency; traditional solvents such as 1-octanol, n-hexane, toluene, dodecane, and hexadecane have high volatility which, in turn, affect negatively the selectivity of the extraction resulting in lower precision and efficiency (Azqhandi et al., 2020). Typical physicochemical properties include boiling and melting points, density, viscosity, and surface tension, etc. The forces of attraction which exist between the solvent and the analytes in the matrix (ionic, hydrogen bonding, London forces) must be known and taken into consideration as the performance of solvent extraction depends on it. Furthermore, economic considerations include the cost link to the solvents production, purchase,

FIG. 5.2 New generation green solvents used in the sample preparation process.

recycling, and pollution control. Lastly, it is also vital to consider solvent compatibility with the final analytical instrumentation (Kokosa, 2019). Recently, chemists have extensively used newly available solvents such as ionic liquid (IL), supramolecular solvent (SUPRAS), and deep eutectic solvents (DES) for LPME. The substitution of conventional macro extraction solvents by these novel solvents stems from the inherent advantages that the latter offer, including wide liquid range, low vapor pressure, hypo-toxicity, safety, convenient phase separation amongst others (Azqhandi et al., 2020). The new generation green solvents that are mostly used in sample preparation are shown in Fig. 5.2. This section addresses the green analytical chemistry alternative LPME solvents and the approach on which to select them.

5.4.1 Magnetic extraction solvents

Magnetic ionic liquids (MILs) and magnetic DESs (MDESs) are a new type of ionic liquids (ILs) or deep eutectic solvents formed through the combination of ILs or DESs with magnetic materials that have recently been developed and used in many analytical processes. The incorporation of lanthanide metals (such as iron, cobalt, manganese, lanthanum, cerium, and lanthanum) as cations or anions results in MILs which exhibit extreme sensitivity to external magnetic fields. The physicochemical properties of MILs can be regulated, like traditional IL, by modifying the cation/anion configuration. In sample solutions, MILs are easy to disperse, and they can be isolated magnetically from the other phases thus dispensing the use of centrifugation step widely applied in LLME procedures (Khezeli et al., 2020a; Sajid, 2019). Most of the MIL-based extractions approaches are performed using DLLME. The magnetic ionic liquids (MILs) based on trihexyl (tetradecyl) phosphonium cation and different magnetic anions, $[P^{+}_{6,6,6,14}][FeCl_4^{-}]$, $[P_{6,6,6,14}{}^{+}]_2[MnCl_4^{2-}]$, $[P_{6,6,6,14}{}^{+}]_2[CoCl_4^{2-}]$ and $[P_{6,6,6,14}{}^{+}]_2[NiCl_4^{2-}]$ were synthesized and used for the dispersive liquid-liquid microextraction (DLLME) of estrone, estradiol, 17-α- hydroxyprogesterone, chloromadinone 17-acetate, megestrol 17-acetate and medroxyprogesterone 17-acetate in milk and cosmetics. The $[CoCl_4^{2-}]$-based MIL were better suited as an extraction solvent for the isolation and concentration of estrogens for several reasons including the absence of hydrolysis, high extraction capacity, separation visual recognition, and ease of solution acquisition. In addition, direct analysis of the extraction solvent by HPLC-UV is possible because $[CoCl_4^{2-}]$-based MIL have low UV absorbance. The extraction parameters were optimized and under the optimum condition, the recoveries of estrogens ranged from 98.5% to 109.3% in milk and from 96.3% to 111.4% in lotion (Feng et al., 2020). Tian Yao and Kaifeng Du described in 2020 the synthesis and characterization of four novel organic magnetic ionic liquids

[C_nMIM-TEMPO]Cl ($n=2,3,4,5$). Then the four MILs were evaluated for the extraction and determination of sulfamethazine (STZ), sulfamonomethoxine (SMM), sulfadiazine (SDZ), sulfamerazine (SMZ), and sulfamethizole (SMT) in milk samples using DLLME. This method involved several steps. Briefly, 4 mL sulfonamides working solution or sample solution was transferred into a 5 mL sample vial. Then a given amount of powdered MIL was weighed and dissolved in the mixture along with a specific volume of an aqueous solution of KPF_6 or $LiNTf_2$. Immediate generation of hydrophobic MIL occurs along with the formation of a light red turbid solution. The tiny drops of hydrophobic MIL contained already the extracted analytes. The dispersed hydrophobic MIL droplet swiftly congregated at the top of the magnetic bar following its immersion into the solution. Finally, the magnetic bar with MIL attached was withdrawn and diluted in methanol before analysis by HPLC (Yao and Du, 2020). Four MILs [$P_{6,6,6,14}$]$FeCl_4$, 1-octyl-3-methylimidazolium, tetrachloroferrate(III) ([C_8mim]$FeCl_4$), trihexyl(tetradecyl) phosphonium hexacyanoferrate(III) ([$P_{6,6,6,14}$]$_3$Fe(CN)$_6$) and 1-octyl-3-methylimidazolium hexaciancianoferrate(III) ([C_8mim]$_3$Fe (CN)$_6$) were evaluated for the extraction of Cr (III) in honey samples and determination by electrothermal atomic absorption spectroscopy (ETAAS). The imidazolium MILs showed high solubility in the aqueous phase thus could not be used as an extractant phase. While phosphonium MILs were immiscible with water, therefore, could potentially be used as extractant. Trihexyl(tetradecyl)phosphonium hexacyanoferrate(III) ([P6,6,6,14]3Fe(CN)6) failed to be withdrawn fully with the magnetic rod, while [$P_{6,6,6,14}$] $FeCl_4$ owing to its strong paramagnetism was fully collected. Consequently [$P_{6,6,6,14}$] $FeCl_4$ was selected applied for Cr extraction. Extraction efficiency of 98% and an enrichment factor of 105 were achieved under optimized experimental conditions (Fiorentini et al., 2020). Magnetic ILs (MILs) and magnetic DESs (MDESs) have been used in SDME and DLLME modes successfully. They are particularly useful, either with or without the use of solvent-assisted dispersion, for collecting the solvent after DLLME extraction. The solvents may not be chromatographed by GC, but are compliant with HPLC since they are ionic in nature (Kokosa, 2019).

5.4.2 Deep eutectic solvents

In the past decade, to address the expense and toxicity of traditional solvents, a new form of ionic solvent called deep eutectic solvents (DES) has arisen. Deep eutectic solvents have been used for a range of applications, such as the extraction of bioactive compounds from different materials and as solvents for chemical or enzymatic reactions (Gonzalez et al., 2020). Deep eutectic solvents are combinations of two or more compounds with a melting point far below the melting point for any of the initial individual components. The intramolecular hydrogen bonds between the constituent components are the key driving force for the formation of these solvents (Yilmaz and Soylak, 2020a). The DESs have high thermal stability, low volatility, low vapor pressure, and a relatively wide liquid range. DESs are prepared through the complexation of a hydrogen bond acceptor (HBA) with a hydrogen bond donor (HBD). The HBAs usually consist of quaternary ammonium salts, while the HBD's are often alcohols, amines, carbohydrates, carboxylic acids, and polyols. These materials are readily available and low cost. The synthesis of DESs can be carried out with ease and high efficiency, no solvent is required and because no side products are produced final product purification is not needed. Furthermore, DESs purity is only influenced by the purity of the starting raw materials. Many DESs, relative to their molecular precursors, have specific properties such as low-toxicity, biodegradability and are easily recyclable while being liquids at room temperature. These characteristics make DESs superior to traditional solvents thus are ideally suited as solvents for LPME extraction (Khezeli et al., 2020b). In 2019 Tülay Borahan et al. used vortex-assisted deep eutectic solvent to remove lead from milk samples and provided a liquid phase microextraction (DESLPME) extraction method for this process. For this purpose, the DES solvent was prepared by mixing phenol as a hydrogen bond donor with choline chloride (ChCl), a quaternary ammonium salt at a ratio of 1:2. The optimum volume of DES resulting in high extraction efficiency of lead was chosen as 0.50 mL (Borahan et al., 2019). Heng Qian and colleagues extracted deltamethrin, etofenprox, fenpropathrin, and bifenthrin from three water samples (Yongdinghe River, Bahe River, and Wenyuhe River) and three different kinds of tea beverages, including jasmine tea, iced tea, and black tea, using hydrophobic deep eutectic solvents-based membrane emulsification-assisted liquid-phase microextraction. The ternary DESs used as extractant were synthesized by mixing at different molar ratios of the HBD and HBA. With N_{8888}Br as the hydrogen bond acceptor, and three different hydrophobic acids (1-dodecanoic acid, 1-octanoic acid, and 1-decanoic acid) and 1-dodecanol were tested as the hydrogen bond donor. The potential three components HBDs of the DES were chosen based on the relative recovery of pyrethroids using each HBD; N_{8888}Br, 1-dodecanol, and 1-decanoic acid at a molar ratio of 1:2:2 was confirmed as the optimum molar ratio for this application. The relative recovery of deltamethrin, etofenprox, fenpropathrin, and bifenthrin was from 89.3% to 97.7%, with relative standard deviation (RSD) values ranging from 1.75% to 2.73% (Qian et al., 2020). Mohammad Reza Afshar Mogaddam et al. in a 2020 study, described a sensitive, efficient, and easy approach for the isolation and enrichment of phenol, chlorophenol, 2,4-dichlorophenol, 2-nitrophenol, α-naphthol, and Bisphenol A in various beverage samples packed in plastic bottles. The samples consisted of three fruit juices (orange, mango, and sour cherry) from different brands, three mineral waters, and five soda samples purchased from local stores in Tabriz, Iran. The extraction method developed was a hollow fiber-liquid-phase microextraction technique based on a new deep eutectic solvent. Three individual DESs were prepared by mixing 8-hydroxyquinoline (as an HBA) with different HBDs including phenylacetic acid, pivalic acid, and pyruvic acid at a ratio of 1:2 for HBA:HBD in a flat-bottom flask. The low viscosity of 8-hydroxyquinoline: pivalic acid DES lead to it being selected as the ideal extractant for the subsequent experiments (Afshar Mogaddam et al., 2020).

5.4.2.1 *Supramolecular solvents*

Supramolecular restricted access solvents (SUPRASs) are colloidal solutions of amphiphilic compounds formed in water through spontaneous and sequential coacervation phenomena occurring on the nano and molecular scales. While in water, at a concentration exceeding the critical aggregation concentration, the amphiphiles primarily form a three-dimensional aqueous aggregate referred to as reverse micelles or vesicles. Then through self-organization, these nanostructures develop into larger clusters. Thereafter, a polymer-rich dense phase, the supramolecular solvent, and a transparent solution of lower density are obtained through liquid-liquid phase separation of the homogeneous solution of charged macromolecules (Yilmaz and Soylak, 2020a). The substantially weaker non covalent interactions such as cation-π, dispersion, hydrogen bonding, ion-ion, ion, dipole-dipole, etc.; combined to hold together and stabilize the supramolecular structures. Supramolecular solvents have polar and apolar regions which allow for interaction with analytes in different ways. Furthermore, it is possible to alter the hydrophobicity and polarity of the amphiphilic groups, in doing so the interactions with analytes can be altered (Caballo et al., 2017). The SUPRAS's nanostructures feature regions of different acidity, polarities, and viscosity, hence offering attractive sites for substrate solubilization. Consequently, solutes can be extracted simultaneously and effectively in a wide polarity range. Another important aspect of SUPRASs is that by choosing suitable amphiphilic molecules and the right environment for their self-assembly, the properties of the solvents can be controlled, and the resulting nanostructures can be customized to carry out a specific function. These properties make SUPRASs very useful for applications in extraction procedures. SUPRAS's are a modern generation of environmentally friendly solvent solutions used by analytical chemists in separation and preconcentration techniques as an alternative to conventional organic solvents. The synthesis method of SUPRASs meant for analytical extractions processes is usually carried out in-situ or ex-situ. Several articles have been published in the scientific literature on both approaches (Arain and Soylak, 2020). In 2019 Jia Chen et al. developed a hexafluoroisopropanol (HFIP)/ Polyoxyethylene lauryl ether (Brij-35) supramolecular solvent (SUPRAS) for the liquid-phase microextraction (LPME) of methyl-paraben, ethyl-paraben, propyl-paraben, butyl-paraben, heptyl-paraben, and octyl-paraben in water samples. An aqueous sample solution was placed in a centrifuge tube, followed by the respective addition of a certain amount of Brij-35 and HFIP solution. There was an immediate formation of a cloudy solution which was subsequently vortex then centrifugated. Liquid-liquid phase separation occurred, the denser SUPRAS phase at the bottom of the tube was withdrawn with a syringe and brought for analysis using an HPLC-DAD. The HFIP/ Brij-35 SUPRAS-based LPME method for the extraction of six parabens was fast (3.3 min), consumed little amount of solvent (0.3 mL), and showed a large enrichment factor (26–193). The recoveries ranged from 90.2% to 112.4% and relative standard deviation was below 8.9% for spiked real samples (Chen et al., 2019). Six phenoxy acid herbicides including 2,4-dichlorophenoxyacetic acid, 2-methyl-4-chlorophenoxyacetic acid, 2-(2,4-dichlorophenoxy)propanoic acid, 2-(4-Chloro-2-methylphenoxy) propanoic acid, 4-(2,4-dichlorophenoxy)butanoic acid, and 4-(4-Chloro-2-methylphenoxy) butanoic acid were simultaneously extracted from water and rice samples using supramolecular solvent-based liquid-phase microextraction and analyzed using high-performance liquid chromatography. A stable SUPRAS was synthesized ex-situ at ambient temperature and in the presence of $AlCl_3$, from the self-assembly of sodium dodecyl sulfate and tetrabutylammonium bromide at the molar ratio of 1:4. Rice samples were homogenized before extraction using a modified QuEChERS method, the ensuing QuEChERS extract was dried and subsequently re-dissolved in water before extraction by SUPRAS-LPME. While water samples were filtered through filter paper before preconcentration by SUPRAS-LPME. The SUPRAS based liquid phase microextraction procedure was as follows, to a centrifuge tube containing a solution of sample or standard, an aliquot of the previously synthesized SUPRAS and an amount of $AlCl_3$ were added. A cloudy solution was obtained after vortexing the mixture, then the emulsion was centrifugated for complete phase separation. The top aqueous phase was drawn out with a long needle syringe and the sedimented phase was diluted with acetonitrile before HPLC analysis. Under the optimum conditions, the percentage recovery of the herbicides in this study ranged from 81% to 110% in water samples and 81%–108% in rice samples, with an enhancement factor of 37–149 (Seebunrueng et al., 2020). Polina Bogdanova et al. described the formation of supramolecular solvents in aqueous solutions containing primary amine (1-hexylamine, 1-heptylamine, 1-octylamine, 1-nonylamine, and 1-decylamine) and monoterpenoid compound (thymol and menthol), followed by liquid-phase microextraction of sulfonamides (sulfamethoxazole, sulfamethazine, and sulfapyridine) and determination using HPLC-UV. A sample solution was spiked with each primary amine and the blend was mixed to obtain an isotropic solution of 1-hexylamine, 1-heptylamine, 1-octylamine, 1-nonylamine, and 1-decylamine. Then to the mixture, an amount of thymol (or menthol) was added with subsequent mixing, which generated in situ micro drops of SUPRAS. Finally, the resulting system was centrifugated and the upper SUPRAS phase was separated and analyzed by HPLC-UV. System with 1-decylamine provided a higher extraction efficiency relative to the other primary amine, while thymol offer a better residual standard deviation, therefore was selected in the subsequent investigations. The enrichment factor values for all analytes ranged from 6.1 to 6.7, and recoveries ranged from 70% to 77%. The relative standard deviation values for all analytes at two concentration levels were 8% and 10% at 0.06 mg/L, 3% and 5% at 50 mg/L for inter-day and intra-day repeatability, respectively (Bogdanova et al., 2020). A vesicular supramolecular solvent-based liquid phase microextraction was developed for the preconcentration of antibiotics tetracycline hydrochloride, oxytetracycline hydrochloride, chlortetracycline hydrochloride, methacycline hydrochloride, and doxycycline hydrochloride, in whole fresh milk, UHT milk, egg white, egg yolk, and two samples of honey before their analysis by reversed-phase high-performance liquid chromatography. The cationic surfactants, didodecyl dimethylammonium bromide (DDAB) and dodecyl trimethylammonium bromide (DTAB) were mixed under NaCl salt addition for the preparation of SUPRAS. An aliquot of the resulting SUPRAS solvent was added in a centrifuge tube containing the sample solution previously conditioned with NaOH solution. Following the addition of an amount NaCl, the mixture was vortexed then centrifugated. Finally, the extraction phase (upper phase) was collected by a syringe and taken for analysis by an HPLC system (Gissawong et al., 2019).

5.4.3 Ionic liquid

Ionic liquids (ILs) are thought of as environmentally friendly replacement extraction solvents for traditional volatile organic solvents. They are organic salts with low melting points which form liquids usually composed of a variety of large asymmetric organic cations such as imidazolium, pyrrolidinium, pyridinium, tetraalkylammonium, or tetraalkylphosphonium and diverse small organic or inorganic anions such as tetrafluoroborate, hexafluorophosphate, bromide. ILs for all LPME modes were used with great enthusiasm because the preferred physical and chemical properties of the ILs such as miscibility with water and other solvents, density, viscosity, etc. could be planned out through a proper modification of their chemical composition. This particularity made it possible to selectively extract polar compounds from oils and nonpolar compounds from water (Khezeli et al., 2020c; Kokosa, 2019). A subset of ionic liquids referred to as room-temperature ionic liquids with melting points below room temperature has been commonly used extraction solvents. In recent years, different IL-assisted extraction methods have been explored in-depth, and wide application of ILs in LPME has been reported. In situ DLLME for the extraction of microcystin-RR and microcystin-LR from aqueous sample employed three structurally different ionic liquids (ILs), 1-butyl-3- methylimidazolium chloride ([BMIm][Cl]), 1-(6- hydroxyethyl)23-methylimidazolium chloride ([HeOHMIm][Cl]), and 1-benzyl-3-(2-hydroxyethyl) imidazolium bromide ([BeEOHIm][Br]) as extraction solvents (Yu et al., 2015). In 2018 Shalene Xue Lin Goh and colleagues developed a fully automated membrane bag-assisted liquid-phase microextraction (LPME) procedure for the extraction of cortisol, cortisone, dexamethasone, prednisone, and prednisolone in water. A mixture of 10% *v*/v of ionic liquid, 1-butyl-3- methylimidazolium methylsulfatein n-octanol was used as solvent. The favorable ionic and hydrogen-bonding interactions with the targeted compounds, provided by 1-butyl-3- methylimidazolium methylsulfate, used as an additive, resulted in an enhanced extraction efficiency (Goh et al., 2018). A dynamic single-interface hollow fiber membrane liquid-phase microextraction (HF-LPME) procedure was developed. A supported liquid membrane containing an ionic liquid, methyltrialkylammonium chloride (Aliquat 336), was used for the extraction of Cr(VI) in drinking, surface, and tap water samples. Kerosene, 1-octanol, and 1-heptanol were explored as organic co-solvents and the analyte of interest was extracted online and eluted inside the lumen of the HF membrane (Pimparu et al., 2016). Although ionic liquid has been used in various extraction techniques, its characteristically high viscosity is accompanied by a moderate mass transfer of analyte thus in some cases negatively affecting the extraction efficiency. Though much work remains in the application of ILs in LPME, caution needs to be taken about their usage. It is recognized that they can have significant environmental impacts, such as environmental persistence and bioaccumulation, because of their unique properties (Kokosa, 2019).

5.4.4 Amphiphilic solvents

Amphiphilic molecules are any compound containing in the same molecule two distinct covalently bonded components with different solvent affinities; one part has a high polar solvent affinity (such as water) and another part has a strong nonpolar solvent affinity, such as hydrocarbons. Amongst the amphiphilic solvents, surfactants are the most important and are used particularly in sample preparation as substitutes for toxic organic solvents. Surfactants have either a charged or uncharged hydrophilic head and a hydrophobic tail consisting of one or more hydrocarbon, fluorocarbon, or dimethylsiloxane chains (Carabias-Martínez et al., 2000; Wu et al., 2010). In the aqueous sample phaseat a concentration above the critical micelle concentrations, surfactants self-assembled to form regular micelle aggregates which have good dissolution, allowing them to associate with compounds with different polarity properties. This makes it particularly useful in extraction-based separation and preconcentration methods as an alternative to conventional extraction solvents. Various micelle-assisted extraction (MAE) techniques have been applied over the years in the isolation and preconcentration of different contaminants, including azo dyes, heavy metals, persistent organic pollutants amongst others, from diverse matrix media (Yilmaz and Soylak, 2020b). A dispersive liquid-liquid micellar microextraction (DLLME) method was studied for preconcentration and ultra-high-performance liquid chromatography (UHPLC) using Diode Array Detector (DAD) for the determination of caffeine, ornidazole, carbamazepine, ketoprofen and naproxen in wastewaters samples. In this procedure, a micellar solution of polidocanol surfactant and chloroform was used for the dispersive liquid-liquid micellar microextraction of five pharmaceutical compounds. The sample solution was heated to a temperature above its critical temperature, and the cloudy solution formed was centrifuged. After phase separation, the denser chloroform and the surfactant layer settle at the bottom of the tube and were withdrawn with a microsyringe. The extract was evaporated to near dryness by heating to its boiling point, then reconstituted in methanol prior to injection into the UHPLC-DAD system. The proposed method provided enrichment factors of up to 47-fold under the optimum conditions, and a relative standard deviation lower than 26% for all five pharmaceutical compounds (Montesdeoca-Esponda et al., 2015). In 2019 Çiğdem Arpa and Itır Arıdaşır studied an ultrasound-assisted ion pair based surfactant-enhanced dispersive liquid-liquid microextraction (UA-IPSE-DLLME) with solidification of floating organic drop for the separation and preconcentration of nickel (Ni(II)) and cobalt (Co(II)) ions from vegetable and herb samples before flame atomic absorption spectrometry (FAAS) determination. In this procedure, the solution of a complexing agent (Congo Red) and ion-pairing agent (didecyldimethyl ammonium chloride) was used to form a complex and give a more hydrophobic character. The process resulted in a more efficient ultrasound-assisted ion pair-based surfactant-enhanced dispersive liquid-liquid microextraction of the target analytes into 1-dodecanol. The sample contained in a conical tube was sonicated, and the formation of a cloudy solution was observed. The cloudy solution was centrifuged, and after phase separation, the test tube was placed in an ice bath. The congealed 1-dodecanol phase was transferred into another conical tube and allow to reach room temperature. Ultimately, methanol was added into the 1-dodecanol phase before analysis with FAAS. Under the optimum conditions, the suggested procedure provided enrichment factors of 65 and 48 for nickel and cobalt, respectively, and relative standard deviation was lower than 4% for all analytes (Arpa and Arıdaşır, 2019). Quercetin is the most abundant compound in the family of flavonoids present in vegetables and shows antioxidant activity. It mostly exists in plant as glycosides, such as quercetin-4- glucoside, quercetin-3-rutinoside (rutin) and quercetin-3-galactoside. To investigate the pharmacokinetics and bioavailability of quercetin glycosides, Samereh Ranjbar Banforuzi and coworker, in 2017, developed a two-phase hollow fiber-liquid microextraction based on reverse micelle (HF-LLME-RM) method for the extraction of quercetin in human plasma, onion and tomato samples. The procedure involved the hydrolysis of the sample, containing flavone glycosides, with hydrochloric acid to obtain free quercetin before HF-LLME-RM. During the separation, the analyte solubilizes in the aqueous core of the reverse micelle of the cationic surfactant cethyltrimethyl ammonium bromide (CTAB), present in the organic phase and used as acceptor phase in hollow fiber-liquid phase microextraction. Extraction parameters were optimized, and the optimum condition were as follow, pH = 7.5, organic solvent = 1-octanol, CTAB concentration = 7 mmol L^{-1}, stirring rate = 900 rpm at room temperature and extraction time = 30 min. Under those conditions, the extraction recovery and relative standard deviation were 97.4%, and 3.5% respectively, for tree replicated measurements on a 15 ng/L quercetin standard solution. Finally, the method was applied for the preconcentration of quercetin in plasma, onion, and tomato samples followed by determination using high-performance liquid chromatography (HPLC) with ultraviolet (UV) detection (Banforuzi and Hadjmohammadi, 2017).

5.5 Solvents' selection

Liquid phase microextraction (LPME) is known as a 'green' technique and is characterized by the low sample and solvent volume consumption for chemical analysis. One of the major steps in developing an LPME mode is the selection of an appropriate extraction solvent, which seems a tedious process due to the numerous LPME modes existing in the literatures. However, the process gets less cumbersome by identifying that these solvent microextractions stem from the three basic modes, namely hollow fiber liquid-phase microextraction (HF-LPME), dispersive liquid-liquid microextraction (DLLME), and single drop microextraction (SDME) (Kokosa, 2019).

Solvent selection for green analytical chemistry LPME method is a stepwise procedure that requires a wholesome/ thorough view/ understanding of the extraction procedure and must incorporate (as well as) the diverse factors that may affect its successful completion. For instance, DLLME is only applicable to fairly clean aqueous solutions, hence it is perfectly suited for tap water, while it would not perform so well with untreated biological samples. Volatile analytes in solid, liquid, and oily samples are preferably extracted using headspace SDME or headspace HF-LPME (Kokosa, 2017). The factors involved in the solvent selection include but are not limited to the scale of the extraction process, the chemistry, properties, and health concerns of the extraction solvent, properties of the sample, its analytes, their concentrations, instrumentation accessibility, operator expertise. Regrettably, this cannot be accomplished by choosing solvents from a menu. Some basic green analytical chemistry guidelines in selecting solvent can be followed nonetheless and are described below along with some commonly used solvents (Kokosa, 2019).

- Except for pure water, it is safe to believe that there is certainly no green solvent.
- For all LPME modes, reduce or avoid the use of most conventional chlorinated solvents (such as CH_2Cl_2, $CHCl_3$, CCl_4, and tetrachloroethene), benzene, and other potentially highly toxic or carcinogenic solvents.
- Use aqueous solutions for HS-SDME and HF(3)LPME extractions of polar, acidic, or basic analytes and DI-SDME and DLLME extractions of oils. Polar ILs and DEss may also be used.
- To reduce water sample contamination, especially for DLLME modes, apply solvents with limited solubility in water, such as cyclohexane, the xylenes, and decane. Highly volatile solvents, such as pentane should also be avoided in all LPME modes.
- For DISDME and HS-SDME the use of solvents with moderate viscosities, surface tensions, and boiling points such as 1-octanol, m-xylene, or decane are recommended. ILs and DESs may be suitable as well though longer extraction times will be involved.
- Use near room temperature melting solvents, such as 1- undecanol, 1-dodecanol, and hydrophobic DESs, for DLLME SFO modes.
- DESs and ILs, have very high viscosities, resulting in lengthier extraction times in SDME and HF-LPME modes, and could probably necessitate both solvents aided dispersion and ultrasound energy for DLLME modes.
- Limit operator exposure to ILs containing the imidazole and hexafluorophosphate (PF6) groups and lower the volumes of ILs used, particularly for DLLME modes.

The overarching considerations in LPME process development for research publication or large-scale analytical use involve the selection of solvents, mode of extraction, and an environmentally friendly method of waste recycling. The aforementioned should lead to global minimization of the effect on the environment and human health. This entails the use of a minimal amount of solvent and sample to reach the analytical sensitivities requirement for the process (Kokosa, 2019).

5.6 Automation of liquid-phase microextraction (LPME)

The automation of analytical procedures arises from increasing demand for methods providing time- and cost-effective analyses, increased sample throughput, enhanced selectivity and sensitivity, greater reproducibility with lesser human error, simplicity, as well as environmentally friendly practices. This process is one of the key challenges for analytical researchers as it is very difficult to create a fully automated system. However, through the advances in science and technology, partially or fully automated methods have been developed with a certain level of success (Azqhandi et al., 2020). A high-throughput parallel-single-drop microextraction (Pa-SDME) was developed for extraction and determination of methylparaben, ethylparaben, propylparaben, bisphenol A, butylparaben, benzophenone, and triclocarban from environmental aqueous samples using the $[P^{+}_{6,6,6,14}]_2[MnCl_4^{2-}]$ MIL as the extraction phase. This experimental setup consisted of a 96-well plate system containing a collection of magnetic pins that helped to stabilize the MIL drops and allowed up to 96 samples to be collected simultaneously. The sample throughput per sample was lower than 1 min per sample using this low-cost experimental device. Even with high stirring rates in direct immersion mode, the system configuration allowed a relatively large volume of extraction solvent to perform a series of extraction and desorption/dilution steps while retaining micro drop stability (Mafra et al., 2019). A fully automated HF-assisted LPME method using mesofluidic platforms for the extraction of ketoprofen, ibuprofen, diclofenac, and naproxen in urine was demonstrated. In the pores of a single-stranded polypropylene hollow fiber (CNF@HF) membrane, dispersed carbon nanofibers (CNF) were immobilized. Then the membrane was housed in a stereolithographic 3D-printed extraction chamber without glued components for ease of assembly. The analytical method involves continuous flow extraction from a flowing stream donor (pH 1.7) of acidic drugs into an alkaline stagnant acceptor (20 mmol L^{-1} NaOH) containing 10% MeOH (*v*/v) across a CNF@HF membrane impregnated with dihexyl ether. The flow setup features complete automation of the microextraction process, including organic film regeneration and online injection of the analyte-laden acceptor phase into a liquid chromatography (LC) after downstream neutralization for reverse-phase core-shell column-based separation (Worawit et al., 2018). In 2018 Shalene Xue Lin Goh and Hian Kee Lee developed an automated bundled hollow fiber array (BHF)-liquid-phase microextraction (LPME) for the preconcentration of eight perfluorinated compounds including perfluoroheptanoic acid, perfluorooctanoic acid, perfluorononanoic acid, perfluorodecanoic acid, perfluoroundecanoic acid, perfluorododecanoic acid, perfluorotridecanoic acid, perfluorotetradecanoic acid in water samples followed by analysis using liquid chromatography-tandem mass spectrometric. The BHF extraction system consisted of 4 HFs 2 cm long, held compactly in a bundle and heat-sealed at one end and mounted, with the heat-sealed ends at the bottom, into the middle section of the 200 mL pipette tip, before being connected to a steel metal ring to form the final extraction assembly. The extraction was carried out using CTC Analytics CombiPAL autosampler with a 32-vial tray plate, and the BHF extraction assembly was controlled by a macro-editor supplied with the autosampler (Goh et al., 2018). Partially or fully automate DLLME methods fall roughly into two groups, those that employ syringe pump or valve systems and those that involve the use of commercial autosampler robotic systems. Although these techniques have yielded fully automated procedures, the requisite instrumentation is often complicated. Therefore, these methods have not created commercial interest (Kokosa, 2020). All extraction steps were performed by a fully automated headspace bubble-in-drop microextraction method, namely the creation of a solvent drop at the tip of the microsyringe needle, the insertion of an air bubble, the recovery of the drop by the syringe, and the injection into the GC-MS (Jain and Verma, 2020).

5.7 Evaluation of liquid phase miniaturized techniques

Almost 20 years ago, microextraction was suggested with assisted liquid membranes. Scientists around the world have been designing various technological configurations and applications for two decades, and this has been a very active area of study. Despite this, microextraction based on SLM has mainly been performed in academia and has yet to be applied routinely in laboratories. There are likely to be many explanations for this, but the shortage of commercial equipment and consumables is one. The hollow fibers in use are commercially available for two- and three-phase HF-LPME and SBME. However, they have not been adapted for microextraction purposes, as such the hollow fibers, before use, must be cut in appropriate length, sealed, and attached to some sort of guiding tube. This research sector has generated a lot of interest lately and presents a lot of advantages including limited organic solvent consumption per sample, high enrichment factor, and no evaporation and reconstitution of the extraction solvent is required. Therefore, it is more likely that properly tailored commercial products appear in the future (Pedersen-Bjergaard, 2020). The SDME has been used for the extraction of a broad range of compounds in a variety of matrices. It is a well establish and accepted microextraction technique that usually employs common laboratory equipment and limited amounts of organic solvents. Drop dislodgement is the main drawback of this technique, which may be overcome through the fitting of the microsyringe needle with PTFE sleeves, application of a magnetic field to immobilize magnetic ionic liquids or the use of an optical probe with an extraction solvent hole. The application of solvents, such as ionic liquids and deep eutectic solvents, for extraction at higher temperatures and longer extraction periods, has advanced the potential of SDME. The ease of automation and application of microfluidic instruments for online analysis with really small sample sizes, low reagent, and solvent usage, and rapid analysis is a major reason for the strong interest in SDME (Jain and Verma, 2020).

The DLLME's compatibility with various analytical techniques such as GC, LC, AAS, ICP, UV-VIS spectrophotometry, CE, etc. has led to a wide variety of applications. Hydrophobic compounds from water or hydrophilic compounds from oils may be separated, preconcentrated, and purified using DLLME. Green analytical chemistry (GAC) principles should be followed when designing a new DLLME method. In solvent-assisted DLLME, a nondispersion solvent

TABLE 5.2 Application of miniaturized liquid phase micro extractions.

Miniaturized extraction techniques	Matrices	Analytes	LOD	LOQ	Analytical instruments	Ref.
DLLME	drinking water	Disinfection by-product (DBPs)	0.22–1.19 μg/L	0.75–3.98 μg/L	GC-MS	On et al. (2018)
DLLME-SFOD	River water, tap water	Steroids	1.0–9.7 ng mL^{-1}		HPLC-DAD	El-Deen and Shimizu (2019)
DLLME	Water and Sugarcane Juice	Pesticide	0.005 to 0.02 μg/L	–	GC-MS	Tolcha and Megersa (2018)
DLLME	Water	Pesticides	0.1–1.8 μg/L	0.4–5.9 μg/L	HPLC-DAD	Tadesse et al. (2015)
DLLME	Wastewater	Insecticides	0.5–1.0 ng/L	1.5–3.5 ng L – 1	LC-QqLIT-MS/MS	Vázquez et al. (2014)
DLLME	Water	NSAIDs	7–95 ng mL^{-1}	–	HPLC-DAD/FLD	Toledo-Neira and Álvarez-Lueje (2015)
DLLME	Water	Pharmaceuticals	0.006–0.091 ng mL^{-1}	0.018–0.281 ng mL^{-1}	UPLC-MS/MS	Guan et al. (2016)
SDME	Seawater	Hydroxylated polycyclic aromatic hydrocarbons	0.0387–1.0741 mg/L	1.11–25.00 L^{-1}	GC/MS	Wang et al. (2017)
DI-SDME	Water	Decabromodiphenyl ether	0.7 ng mL^{-1}	–	RP-HPLC	Wang (2007)
DI-SDME	Water (tap and river)	Phenols	0.05 μgmL^{-1}	0.017–0.167 μgm L^{-1}	HP^{3D}CE	Wang et al. (2010)
DI-SDME	Water	Pesticides	0.02–0.50 ng mL^{-1}	–	GC/MS	Chen et al. (2009)
DI-SDME	Wastewater	Organochlorine pesticides	0.022–0.101 μg L^{-1}	0.074–0.337 μg L^{-1}	GC/MS	Cortada et al. (2009)
HS-SDME	Water and urine	Volatile aromatic hydrocarbons	0.05–0.90 ng mL^{-1}	0.17–3.00 ng mL^{-1}	GC/FLD	Yousefi et al. (2018)
HS-SDME	Lake water and leaf	PHAs	0.004–0.247 ng mL^{-1}	–	HPLC-FLD	Wu et al. (2008)
HS-SDME	Water	Chlorobenzene	0.1–3.0 μg/L	–	GC/ECD	Khajeh et al. (2006)
HS-SDME	Water	Chlorobenzene	0.003–0.031 μg/L	–	GC/MS	Vidal et al. (2005)
Three phase-SDME	Water	Alkylphenols	0.01–0.07 μg L^{-1}	–	HPLC	Yiantzi et al. (2010)
Three phase-SDME	Water	1,8-Dioxyanthraquinone	0.1–20 mg/L	–	HPLC	Yangcheng et al. (2006)
LLLME	Water	Alkaloids	–	–	HPLC	Ma and Cantwell (1999)
LLLME	Biological and Water samples	Fentanyl	0.1 ngL^{-1}	0.3 ngL^{-1}	HPLC	Ebrahimzadeh et al. (2008)
CFME	Water	PAH	1–7 ng/L	–	GC/MS	Liu et al. (2007)
CFME	Wastewater	Phenolic Compounds	2.32–2.95 mgL^{-1}	–	GC-FID	Chen et al. (2006)
CFME	Water samples	PAHs	0.0012–0.0101 μg L^{-1}	0.0041–0.0336 μg L^{-1}	GC/MS	Li et al. (2018)

Continued

TABLE 5.2 Application of miniaturized liquid phase micro extractions—cont'd

Miniaturized extraction techniques	Matrices	Analytes	LOD	LOQ	Analytical instruments	Ref.
Drop-to-drop microextraction	Water	Methoxyacetophenone Isomers	1.0 ng mL^{-1}	–	GC/MS	Wu et al. (2006)
Drop-to-drop microextraction	Water, urine, and blood of rats	Trimeprazine in	0.05, 0.06 and 0.1 mg mL^{-1}	–	GC/MS	Agrawal and Wu (2007)
SF-ODME	Water	PHA	0.07–1.67 μgL^{-1}	–	GC/FID	Reza et al. (2007)
SF-ODME	Water samples	Organochlorine pesticides	7–19 ngL^{-1}	–	GC/ECD	Farahani et al. (2008b)
SF-ODME	Water	Phthalate esters	0.02–0.05 μgL^{-1}	–	GC/MS	Farahani et al. (2008a)
SF-ODME	Water	Benzene,toluene, ethylbenzene and xylenes	0.08–0.18 μgL^{-1}	0.22–0.49 μgL^{-1}	GC/FLD	Faraji et al. (2012)
SF-ODME	Water	Phthalate esters	0.27–2.36 μgL^{-1}	–	HPLC	Online et al. (2016)
SF-ODME	Cosmetic and environmental water samples	Phthalate esters	0.005–0.01 μgL^{-1}	–	HPLC-DAD	Kamarei et al. (2011)
HF-LPME	Aqueous and plant samples	Nonsteroidal anti-inflammatory drugs	0.05–0.41 μg kg^{-1}	0.09–0.59 μg kg^{-1}	QTOF-MS	Mlunguza and Ncube (2020)
HF-LPME	Water	Endocrine disrupting compounds	0.52 and 0.54 ng mL^{-1}	1.76 and 1.83 ng mL^{-1}	HPLC	Villar-navarro et al. (2013)

approach is also a safer option since the latter increases the solubility in water of both the analyte and the extraction solvent. As a result, lower extraction solvent and analyte recoveries are observed. The newly developed nonpolar ILs and DESs are useful alternatives to conventional extraction solvents and can be used in the DLLME procedure with or without a dispersion solvent (Kokosa, 2020).

5.8 Application of miniaturized liquid phase techniques

Liquid phase micro extractions are selective, fast, virtually solvent-free and relatively inexpensive sample-preparation techniques. In the last decade, quite a number of research have been done on the determination of emerging pollutants using LPME techniques. These extraction techniques are also been utilized for preconcentration of organometal and metal ions in different matrices. The application of the LPME techniques is summarized in Table 5.2 for the analysis of emerging pollutants. For the determination of nonylphenol and 4-t-octylphenol alkylphenols, the two most ubiquitous EU-regulated alkylphenols, in complex water samples, hollow fiber liquid-phase microextraction (HF-LPME) in a two-phase configuration was applied (Fabregat-Cabello et al., 2014). A good enrichment factor (~800) was obtained using 1-Octanol as the acceptor phase. In another study made by On et al. (2018), eleven disinfection by-products (DBPs) were extracted using a simple, rapid, and environmentally friendly DLLME from drinking water.

5.9 Conclusions

The LPME approaches can integrate many pretreatment stages needed before measurement (e.g., preconcentration, matrix separation, filtration, and clean up) with outstanding performance. Additionally, LPME meets the requirements to be considered a green sample preparation technique, as a result of the negligible use of extractant phases and the minimal waste generation involved. For the extraction of target analytes from different sample solutions, all LPME techniques can be used effectively. Fast analysis with high performance, environmentally sustainable operation due to limited solvent consumption, and highly selective analysis by systems designed for unique applications are the key advantages of miniaturized systems. In the future, the combination of microscale sample preparation and microscale liquid-phase separation promises good applications in different areas of research, especially for trace amounts of analytes in complex sample matrices (see Tavengwa et al., 2022; Chapter 20). However, to find complete solutions to many separation issues, continuous developments in extraction materials and integrated analytical systems are also needed. This falls under the section on monitoring techniques, current analytical approaches, and instrumental analyses with other chapters e.g. Kaserzon et al. (2022), Kaykhaii and Hashemi (2022), Kumar et al. (2022), and Mwedzi et al. (2022) that aims to understand how emerging freshwater pollutants are analyzed or detected within aquatic ecosystems.

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C H A P T E R

6

Head-space miniaturization techniques

Ramesh B. Kumar, Rahul K. Varma, Saikat Sen, and Srinivas Oruganti

6.1 Introduction

The global population is expected to exceed 9.8 billion by 2050. The rapid rise in population will put an increased demand for clean and safe water. The quality of water is essential to maintain the proper health of living organisms. Approximately 70% of the world's freshwater sources are used in the agriculture sector. But there has been a consistent decrease in the availability and quality of drinking water (Vashisht et al., 2020). So, the demand for safe and pure water can be met by protecting freshwater sources from detrimental land-based pollution sources and by introducing effective wastewater treatment methods (Gani et al., 2016; Patel et al., 2020).

During the past two decades, several drinking waters, groundwater, and surface water sources have been found to be contaminated with broad-spectrum micro-pollutants known as emerging contaminants (ECs) (Gani et al., 2016; Tavengwa and Dalu, 2022, Chapter 1). These ECs encompass a wide range of products including pharmaceuticals, personal care products (PCPs) (see Madikizela et al., 2022, Chapter 10), and various endocrine-disrupting compounds (EDCs). These chemicals are collectively known as emerging organic contaminants (EOCs) (Pal et al., 2010). These pollutants are highly pervasive, bioactive, and bioaccumulative. The major sources of these EOCs are wastewater released from hospital effluents and chemical industries, agriculture and livestock, and wastewater treatment plants (WWTPs) treating domestic sewages (Pal et al., 2010; Patel et al., 2020; Mashile et al., 2022, Chapter 8). The other source of entry for these pollutants includes wastes from animal disposal, overflow of sewer, run-off from farmland and septic tank effluents, cleaning agents, household wastes, and disposal of unused or expired drugs in sewage systems or septic tanks (Patel et al., 2020). ECs arise from a wide range of product types including:

(a) Bioterrorism/sabotage agents
(b) Personal care products such as antibacterial, essential oils, and herbal medicines (see Madikizela et al., 2022, Chapter 10).
(c) Persistent organic pollutants such as flame retardants and dioxin-like compounds.
(d) Antibiotic and antiparasitic agents (Ntshani and Tavengwa, 2022, Chapter 11)
(e) Nanomaterials and human medicines (Ajayi et al., 2022, Chapter 18).
(f) Synthetic hormones, androgens, and estrogens (see Sanganyando and Kajau, 2022, Chapter 7).
(g) Metabolites obtained from the biological, chemical, and physical breakdown of man-made chemicals (Stefanakis and Becker, 2016).

The occurrence, distribution, and fate of the ECs in the aquatic ecosystems are influenced by various factors. Physico chemical parameters such as water solubility, polarity, volatility, and environmental parameters including pH, precipitation, organic matter content, and temperature play a vital role in the transport of ECs. These properties define the time of existence of the ECs in the aquatic environment (Stefanakis and Becker, 2016). A methodological approach for the sources and release of EOCs and their determination and identification from aquatic sources is represented in Fig. 6.1.

Emerging Freshwater Pollutants
https://doi.org/10.1016/B978-0-12-822850-0.00018-1

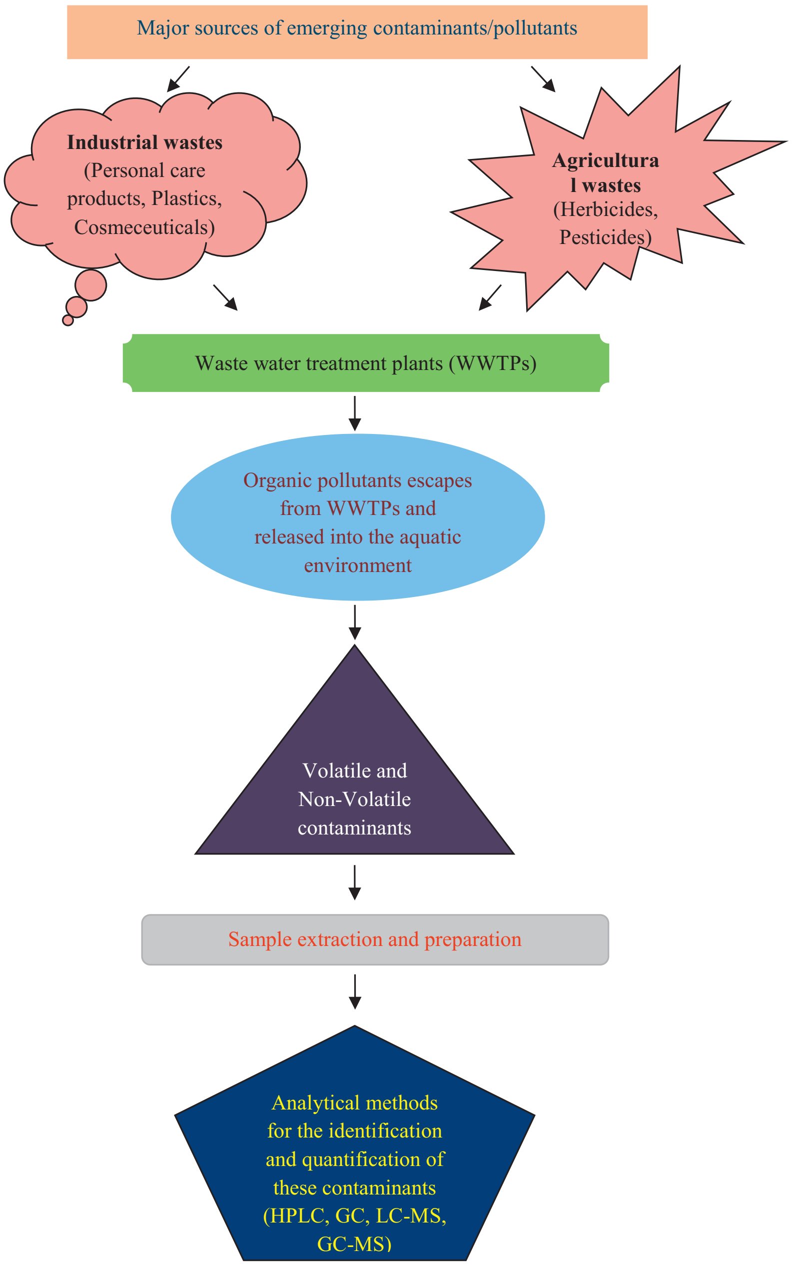

FIG. 6.1 Systematic way of organic contaminants/pollutants released into the aquatic environment and their analysis by analytical methods.

There is a growing concern over the accumulation and release of hazardous chemicals in different environmental sources which needs immediate attention. For example, persistent organic pollutants (POPs) are rated as dangerous toxic chemicals and have been under scrutiny for years. Many international societies have been continuously working on and took several measures to stop the production of these pollutants but have failed to a greater extent. Representatives of 127 countries signed the "Stockholm Convention on POPs" in Stockholm whose major agenda was to reduce the emission of POPs and to protect the environment and human health from their adverse effects. Similarly, polycyclic aromatic hydrocarbons (PAHs), a class of POPs have been regulated under the UNECE Convention on Long-Range Transboundary Air Pollution (LRTAP) and OSPAR Convention (Zhao et al., 2019). Therefore, it is evident that the production and release of these chemical compounds have triggered an alarming situation and threw a serious challenge to the scientific community and policymakers.

6.2 Headspace sampling

Determination of volatile organic compounds (VOCs) in water samples requires direct injection of sample, static HS techniques, dynamic HS techniques, LLE, SPE, SPME, and distillation techniques as sample preparation methods. Due to the low concentration of the analytes in natural waters (ng L^{-1} to μg L^{-1}), the preconcentration step is pivotal before instrumental analysis and detection (Safarova et al., 2004). To isolate the targeted analytes, they need to be separated from the sample matrix containing various other components. This approach will give results but is time-consuming and involves several steps. But, if the targeted compounds are volatile, it is preferred to use gas as a solvent medium to simplify the sample preparation method. As the samples are placed in a closed vial, the volatile compounds will be present in the atmosphere of the vial above the bulk sample. So, the distribution of the volatile compounds in the vial represents two phases—a sample phase (solid or liquid) and the gaseous phase above the sample. The above gaseous phase is called Headspace (HS) which is governed by basic physicochemical laws (Ettre, 2001). Fig. 6.2 represents a headspace vial. HS analysis involves the separation and collection of volatile compounds (gaseous phase) from various environmental matrices such as foods, solids, and water (Fatemi et al., 2013).

An HS vial generally consists of two phases: sample (condensed) phase represented by subscript S and gaseous (headspace) phase represented by subscript G. Usually, the volatile analytes soluble in the condensed phase of the system gets distributed between these two phases to attain controlled equilibrium. The below equation represents the system in the headspace vial

V_V = total volume of the vial
V_S = volume of the sample phase
V_G = volume of the gas phase
$V_V = V_S + V_G$

The thermodynamically controlled *equilibrium constant* represents the distribution of the analytes between these two phases. The *Partition coefficient* is a primary factor that represents the mass distribution in two-phase system. The partition coefficient depends on the solubility of the analytes in the condensed phase. Highly soluble compounds will have high concentrations in the condensed phase relative to the gaseous phase thus indicating higher partition coefficient values. The analytes with a lower solubility in the condensed phase will have low partition coefficient values (Kolb and Ettre, 2006).

Since its inception, HS sampling is considered as a sample preparation and clean-up method analogous to the GC technique utilized for the analysis of volatile contaminants from different compartments of the environment (Liberto et al., 2019). HS sampling is generally a gas extraction technique that allows the direct analysis of volatile compounds from the matrix containing a nonvolatile matrix (Ettre, 2001). HS analysis of the samples can be performed by hyphenation with other spectroscopic techniques such as Fourier-transform infrared spectroscopy (FT-IR) and mass spectrometry (MS). However, gas chromatography (GC) is the most suitable method for such measurements, as GC favors the separation and detection of compounds in the gas (vapor) phase (Kolb and Ettre, 2006). In headspace-gas chromatography (HS-GC), the separation of compounds is based on the interaction between the gas phase and the condensed liquid or solid phase.

HS-GC consists of two steps-

(1) Initially, the sample (liquid or solid) is positioned in a vessel (generally a vial) containing gas volume above it and the vial is closed. Then, the vial is thermostatted at a constant temperature to attain between two phases.
(2) Finally, the routine analysis is carried out by the introduction of an aliquot of the vial's gas phase into the carrier gas stream which is being further carried out onto the column (Kolb and Ettre, 2006).

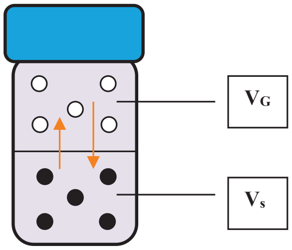

FIG. 6.2 A headspace vial containing a liquid sample.

Most of the automated instruments in recent times have thermostats containing a number of vials and these thermostats sequentially process them. Further, it is important to have précised temperature-controlled thermostats. Temperature plays a crucial role as it influences the volatility and the headspace sensitivity of different compounds in different ways (Kolb and Ettre, 2006).

The transfer of samples can be done in numerous ways such as by gas-tight syringe (manually), by automatic processes such as pressurization of the sample vial, or by the time or volume-controlled transfer of an aliquot of headspace into the column (Kolb and Ettre, 2006). There are two main types of headspace sampling- static (equilibrium) HS sampling and dynamic HS sampling (also known as purge and trap method). Static HS sampling involves the gas extraction in a single or limited number of steps whereas dynamic HS sampling consists of two to three steps of which the initial step is continuous gas extraction (Ettre, 2001). Both the modes of HS sampling are successful owing to their flexibility, simplicity, reproducibility, and the probability of automation and online connection with GC methods. Another useful advantage with HS is its ability to meet the criteria of green chemistry (Liberto et al., 2019).

(a) Static headspace sampling

Static headspace (S-HS) sampling is also called as a one-step gas extraction technique (Liberto et al., 2019). The sample is thermostatted for a certain time at the selected temperature where the equilibrium is reached between the sample and gas phase (HS) of the sample vial. Afterward, a single aliquot is introduced into the carrier gas flow, which then carries it to the column. Finally, the volatile components are separated onto the column (Ettre, 2001). Static HS shows good reproducibility, higher resolution, simpler instrumentation, and wide linearity range with detection limits up to 100 mg L^{-1} (Fatemi et al., 2013). The transferring of an aliquot of the headspace gas directly into the GC column is called Static Headspace-Gas Chromatography (SHS-GC) (Ettre, 2001).

(b) Dynamic headspace sampling

Novel techniques with additional traps have been introduced which can separate the volatile analytes from the excess of the diluted HS gas (Kolb and Ettre, 2006). Dynamic headspace (D-HS) sampling is a dynamic process that involves three main steps—(a) the volatile fraction released from the matrix is continuously renewed, (b) To capture and concentrate the compounds through cryo-trapping or other materials having the ability to detain volatile analytes via different approaches (adsorption, sorption, etc.), and (c) the recovery of the targeted analytes from the trap by thermal desorption or solvent elution or via connecting to GC or GC-MS in offline mode. The D-HS sampling is a nonequilibrium continuous gas extraction method usually called as purge and trap (P & T) method. Major factors for a successful D-HS sampling include the temperature of HS generation and sampling, trapping process, materials used, and the purge volume (Liberto et al., 2019).

Apart from its higher sensitivity capabilities, the P & T method is also known for its ability to reduce the matrix effect. But this is only possible in the cases where all the analytes in the sample are completely purged. However, this extensive procedure is practically not feasible due to the broad range of polarities and volatilities being observed in a multicomponent mixture. The volatility of each dissolved component is highly influenced by the matrix effect which ultimately varies the purge time for each compound (Kolb and Ettre, 2006).

6.3 Applications of static and dynamic headspace sampling methods

Static HS coupled with GC-MS was developed for the extraction and identification of VOCs in Babolroud river water samples. A central composite design was used for optimizing various experimental factors such as extraction temperature and time, salt concentration, and stirring speed. It was observed that the use of sodium chloride and extraction temperature proved to be the predominant factors responsible for enhanced extraction efficiency. Furthermore, the proposed method reduced the risk of sample contamination. The compounds identified were benzene, ethylbenzene, *m*/*p*-xylene, naphthalene, and toluene. The observed LOD values for the identified compounds were in the range of 0.1–4.9 μg L^{-1} (Fatemi et al., 2013). Conventional methods require large amounts of highly expensive organic solvents which are hazardous in nature. Further, these methods are time consuming and suitable to fine emulsions. To overcome these drawbacks, several environment-friendly techniques have been developed such as static headspace knotted hollow fiber microextraction (HS-K-HPME), headspace single-drop microextraction (HS-SDME), and headspace liquid-phase microextraction (HS-LPME), etc. (Li et al., 2016). Static HS knotted hollow fiber microextraction technique (HS-K-HFME) along with GC-MS has been developed for the determination of VOCs in Da-Han River and wastewater (National Taiwan University Hospital and Tucheng Industrial Park) samples. The use of knot-shaped fiber was found to be effective in overcoming the issues related to HS liquid phase microextraction due to its larger extraction contact interface thus improving the extraction efficiency. The GC-MS analysis confirmed the presence of diethyl ether, dichloromethane, ethyl acetate, toluene, and xylene. The LOD values ranged from 0.2 to 10 μg L^{-1} for the analyzed compounds (Chen et al., 2015). A static HS analysis combined with GC-MS was used for the determination of VOCs in river waters, wastewaters, and treated water samples. The variables optimized including autosampler parameters, sample thermostat time and temperature, and the ionic strength. The optimized conditions favored the extraction conditions and enhanced the extraction efficiency of the VOCs from water samples. The identified compounds were from different groups belonging to alkenes and chlorinated alkanes, chlorinated monocyclic aromatic hydrocarbons, mono and polycyclic aromatic hydrocarbons (Safarova et al., 2004). Five volatile chlorinated hydrocarbons in water samples have been determined by using static headspace sampling in combination with GC with electron capture detection (ECD). The identified compounds were dichloromethane, perchloromethane, perchloroethylene, trichloromethane, and trichloroethylene. Furthermore, during the analysis of real water samples, no adverse effect was observed for the proposed static HS method. The LODs of these compounds was found to be very low (0.001–0.3 μg L^{-1}) (Li et al., 2016). Both static HS-GC and P & T methods have been employed for the detection of methyl-tert-butyl ether (MTBE) in water samples (Nouri et al., 1996). Due to a high degree of automation, the static HS-GC method was used to obtain routine screening. The P & T method was used due to its higher sensitivity and provides a chance of additional confirmation in case of a negative result. It was observed that the detection limit of MTBE was found to be 50 μg L^{-1} and 2 μg L^{-1} for static and P & T methods, respectively (Kolb and Ettre, 2006). Detection limits of the static HS method are 10 times higher than that of the dynamic HS method. The major drawback of the P & T method is that it requires complex instrumentation and also the water vapor being generated at the purge stage (Safarova et al., 2004).

Other than sensitivity, the degree of automation is equally important in the selection of analytical methods. During the routine analysis, automation provides a high sample throughput and is a prerequisite for method development. Huge amounts of quantitative data are required for validating an analytical method, which further depends on automated instrumentation. Due to its simplicity and automation, static HS-GC is a supreme method in comparison to other HS techniques (Kolb and Ettre, 2006). One of the main advantages of HS-GC is that a small number of targeted analytes inside a large amount of other sample matrices can be analyzed without having to inject the matrix inside the chromatographic column. This will result in clean analysis with easy sample preparation and also a minimum burden on the column and the GC instrument (Fatemi et al., 2013). In recent times, static HS-GC has been widely used to determine toxic impurities in the environment. Most modern HS-GC instruments use static sampling with a heated transfer line. This causes to pressurize the sample vial over the capillary column head pressure. This results in quick sample transfer and ready equilibration which aid in interfacing the sampling device to GC. However, one major limitation with classical static HS-GC is its limited sensitivity than P & T and other techniques using online concentration such as SPME (Jerkovic and Marijanovic, 2009). A headspace analysis combined with gas chromatography-mass spectrometry (HS-GC-MS) has been used for the identification of VOCs from water samples. The present study uses an experimental design with the help of response surface methodology (RSM) for effective and quick separation of these compounds. The experimental design used was based on three factors- temperature, thermostat time, and sodium chloride quantity. The results showed that mathematical models developed for relating peak surface to temperature, thermostat time, and ionic strength proved to be a competent strategy for optimizing the (HS-GC-MS) parameters. The optimized experimental conditions used were successful in the determination of six VOCs (benzene, chlorobenzene, dibromomethane, tetrachloroethane, toluene, and *p*-xylene). The observed LOD and LOQ values using (HS-GC-MS) were in the range of 0.08–0.27 μg L^{-1} and 0.25–0.83 μg L^{-1} (Missaoui et al., 2009). The advantage with HS-GC-MS methods includes the appropriate selection of the equilibrium conditions (specifically temperature) which permits the measurement of the volatile concentrations in the headspace and simpler determination of the trace analytes in the sample. Another benefit is the use of MS in selected ion monitoring (SIM) mode, which enhances the sensitivity and specificity (unwanted masses are ignored) (Cao et al., 2013).

The Environmental Protection Agency/US Environmental Protection Agency (EPA) has several publications on both static HS-GC and dynamic HS-GC methods. Vinyl chloride monomer (VCM) traces have been determined by the static HS-GC method in wastewater. Work related to headspace methods dealing with the identification and quantification of volatile organic contaminants (VOCs) has been published in EPA (Kolb and Ettre, 2006). The DIN

(Deutsche Industrienormen), EN (European Norm), and VDI (Verein Deutscher Ingenieure) standards in Germany have used static HS-GC for the analysis of waters, wastewaters to determine benzene and its derivatives, volatile halogenated hydrocarbons, and vinyl chloride monomers. Further, the applications of this method have been explored in the measurement of atmospheric pollutants such as vinyl chloride and 1,3-butadiene as well as in the determination of halogenated hydrocarbons in soil samples (Kolb and Ettre, 2006). An HS method coupled with GC was developed for the identification of volatile organic sulfur compounds (VOSCs) in surface and tap water samples. Different variables such as sample volume, ionic strength, headspace duration, and temperature were optimized to obtain higher sensitivity of the developed method. Four compounds including dimethyl sulfide, dimethyl disulfide, diethyl sulfide, and dimethyl trisulfide were detected in the water samples. The observed method detection and quantification limits were in the range of 0.02–0.2 $\mu g\ L^{-1}$ and 0.06–0.5 $\mu g\ L^{-1}$, respectively. Dimethyl sulfide was the only compound detected in partial surface water samples between 1 and 7 $\mu g\ L^{-1}$ whereas the remaining compounds detected were below method detection limits (Feng et al., 2018). The US Food and Drug Administration (USFDA) also has accepted static HS-GC methods for the determination of vinyl chloride monomer in corn oil, solvents used as food stimulants, oils and vinegar, and polyvinyl chloride food packaging. During the year 1992–94, three standards were issued in Japan to control the permissible concentrations of fewer amounts VOCs in drinking and wastewater. These documents also suggest static and dynamic HS-GC as an appropriate analytical method (Kolb and Ettre, 2006).

6.4 Headspace sample concentration methods

Sample preparation is an important step in the analysis of EOCs from various environmental compartments. Before the instrumental analysis, the samples have to undergo various processes of extraction. Several steps have been categorized:

- The first and foremost step is to separate the desired compound or compounds from the complex aqueous samples (marine waters, sewage waters). This helps to remove the interference.
- Due to their low concentrations, the target analytes should be enriched for better resolution and improved detectivity and sensitivity by employing various sample extraction and concentration procedures.
- Finally, compatibility should exist between the sample matrix and the instrumental analysis. For example, during GC analysis, aqueous samples are not being analyzed immediately where a normal solvent extraction procedure is used (Wu et al., 2010).

The HS sampling for the analysis of volatile components came into light during the 1990s where the focus was on the development of high-concentration capacity HS techniques. These sample techniques are solvent-free in which the targeted analytes are concentrated on S-HS polymers using adsorption, sorptive, and solvent partition (Liberto et al., 2019). Various high concentration-based sampling techniques have been developed as an alternative to S-HS and D-HS sampling methods. Frequently applied sampling methods include HS-liquid-phase micro-extraction (HS-LPME), HS-solid-phase microextraction (HS-SPME), HS-single drop micro-extraction (HS-SDME) and HS-stir-bar sorptive extraction (HS-SBSE) (Wu et al., 2010).

(a) Headspace-solid-phase microextraction

In solid-phase microextraction (SPME), the extraction of analytes is carried out by stationary phase coated fused silica fibers. This approach combines the concentration, extraction, sampling in a single step effortlessly. Commonly used SPME fibers are of two types—adsorbent and absorbent. The extraction of compounds by physical interaction is observed in adsorbent type fiber whereas, absorbent type fiber extracts the analytes based on partitioning mechanisms. The SPME method favors the extraction of nonpolar organic compounds such as polyaromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in water samples. However, recent developments in in situ derivatization techniques may be useful in the extraction of many aliphatic amines, organic acids, pesticides, and phenols. The derivatization step is not required during the SPME analysis of organic acids and bases. The SPME fibers are costly and fragile and they can be used for up to 100 extractions. A thermal conditioning step is a prerequisite during the initial use of fiber but may lead to a partial loss of coating which can result in additional peaks during chromatographic analysis (Merkle et al., 2015).

The HS-SPME method is an extension of the SPME method, first developed by Arthur and Pawliszyn in 1990. It is the most widely used method due to its flexibility and consistency (Liberto et al., 2019). The sampling process in SPME is classified into immersion sampling and headspace sampling. In immersion sampling, the fiber is immersed in an aqueous sample which leads to an enhanced extraction procedure. In headspace sampling, the fiber is exposed to the headspace above the solid or liquid sample which is helpful to detect low molecular weight analytes followed by the transfer of these components directly into the GC or GC-MS system. One of the major obstacles of the HS-SPME method is its ability to achieve limited concentration factors due to the usage of low volume and the conventional fiber coating materials which are being overcome by the latest advancement of the HS-SPME method (Liberto et al., 2019). The SPME method was optimized for the determination of volatile halogenated compounds (VHCs) and semivolatile halogenated compounds (SVHCs) in surface waters and sewage samples. Three different types of SPME fibers poly-(dimethylsiloxane(PDMS)/divinylbenzene(DVB)/carboxen(CAR)) (PDMS, CAR/PDMS, and PDMS/DVB) were used to evaluate their extraction effectiveness of these compounds. The HS-SPME-GC/ECD method was used to analyze these compounds in low levels. The results revealed that CAR/PDMS fiber was found to be most effective in the extraction of these volatile compounds. The analytical instrumentation used showed good linearity and precision and the detection limits of the identified compounds were in the range of 0.005–0.8 μg L^{-1} (Grażyna and Gaca, 2008). A rapid and reliable method comprising headspace-solid-phase microextraction (SPME) followed by gas chromatography coupled to tandem mass spectrometry (GC-MS/MS) was developed for the determination of VOCs in surface waters and wastewater samples. The extractions conditions were optimized using a factorial design. The SPME extraction was carried out using carboxen/polydimethylsiloxane fiber. The results revealed that optimized SPME conditions were able to overcome the matrix interferences and made the extraction procedure simpler and easier to extract the volatile compounds with lower detection limits. The GC-MS/MS methods used were able to quantify the identified compounds with precision and accuracy. Various compounds such as benzene, bromoform, chloroform, dibromochloromethane, tetrachloroethylene, trichloroethylene, toluene, and xylenes were detected in all the water samples analyzed (Cervera et al., 2010). SPME method combined with Gas chromatography flame ionization detector (GC-FID) was used for the analysis of BTEX and other substituted benzenes in ground and surface water samples. PDMS/DVB/CAR fiber was used in this study. The identified compounds were benzene, toluene, chlorobenzene, ethylbenzene, xylenes, styrene, dichlorobenzenes, chlorooctane and trichlorobenzene. The proposed optimized method showed good reproducibilities. The minimum detection level (MDL) and minimum quantification level (MQL) were ranged between 0.015–0.26 μg L^{-1} and 0.050–0.87 μg L^{-1}, respectively (Almeida and Boas, 2003). A solvent-assisted headspace sampling using SPME was developed for the analysis of phenols (4-chlorophenol, 2,6-dichlorophenol, 5-chloro-2-methylphenol, and trichlorophenol) in water samples. The SPME polydimethylsiloxane (PDMS) microfiber was used for headspace sampling. The proposed method improves the volatilization of the analyzed phenols. Further significant preconcentration and analysis benefits have been achieved with this method (George et al., 2015). Direct immersion (DI)-SPME methods using PDMS-DVP, PA, Sol gel-based amino fiber was utilized for the extraction of pyrethroids, pesticides, OPPs, EDCs, and steroid hormones from different water (groundwater, surface, and river) sources (Vázquez et al., 2008; Bagheri et al., 2010; Filho et al., 2010; Yang et al., 2006; Wang et al., 2006). Similarly, Headspace (HS)-SPME application has been observed in the analysis of OCPs, OPPs, triazines, pesticides, BTEX, polychlorinated bisphenyls, and PAHs from lake, river, ground, and surface waters (Dong et al., 2005; GonÇalves et al., 2007; Lee et al., 2007; Derouiche et al., 2007; Coelho et al., 2008). Table 6.1 represents examples of both the SPME methods.

(b) Head space-single drop microextraction

A lot of research efforts have been going on to develop combined sample preparation techniques in which the preconcentration of the analytes can be done additionally. Single drop microextraction (SDME) is such a technique that can provide such a facility (Zichova et al., 2018). The SDME is the first of its kind miniaturized solvent extraction method used for the extraction of analytes from water and gaseous samples (Tang et al., 2018). Due to its simplicity, effectiveness, low cost, and rapidity, it has been frequently used in the determination of pesticides and other organic pollutants in various matrices of the environment. The principal mechanism of the SDME method includes the distribution of analytes between the micro drop of an organic solvent and an aqueous phase or headspace phase above the solid/liquid sample. The SDME method uses a conventional microsyringe and simplifies the extraction procedure by combining manipulation and injection of the sample into a single step. However, certain drawbacks of this method can be observed such as instability of the micro drop, partial loss of solvent due to higher temperatures, and excess

TABLE 6.1 SPME methods used for the determination of contaminant from different water sources.

S. no.	Sample source	Identified compounds	Extraction method	Fiber	Recovery %	Reference
1	Groundwater	Pyrethroids and pesticides	DI-SPME	PDMS/DVP	92–109	Vázquez et al. (2008)
2	Lake water	Organochlorine pesticides (OCPs)	HS-SPME	PMPVS	72–116	Dong et al. (2005)
3	Surface and Ground water	Pesticides	DI-SPME	PA	78–109	Filho et al. (2010)
4	River water	Organophosphorous pesticides (OPPs)	DI-SPME	Sol gel-based amino fiber	80–115	Bagheri et al. (2010)
5	Groundwater	OCPs, OPPs, triazines, pyrethroids, and other pesticides	HS-SPME	PDMS-DVB	–	GonÇalves et al. (2007)
6	Groundwater	BTEX	HS-SPME	PDMS-CAR	–	Lee et al. (2007)
7	River water	OCPs and Polychlorinated biphenyls	HS-SPME	PDMS	75–105	Derouiche et al. (2007)
8	Surface water and Underground water	PAHs	HS-SPME	PDMS	71–109	Coelho et al. (2008)
9	River water	Endocrine-disrupting chemicals and Steroid hormones	DI-SPME	PA	–	Yang et al. (2006)
10	River water	Polybrominated diphenyl ethers (PBDEs)	DI-SPME	MWCNT	90–119	Wang et al. (2006)

solubility of the drop in the sample affecting repeatability. The SDME modes can be divided into two subcategories—two phase and three-phase techniques found in equilibrium. All these modes follow the same principle—direct passing of the analytes from the sample or via headspace to the final extraction solvent (Zichova et al., 2018). The application of SDME has been extended to Headspace (HS) mode. The main advantage of HS mode lies within its capability to analyze a wide range of more volatile compounds and removes the interferences from the sample matrix. It is highly preferred over DI mode. The mode of operation of SDME is very easy and it doesn't require the help of sophisticated instruments. A common microsyringe is used in most cases and provides advantages over other miniaturized extraction methods in terms of complex tools, devices, and operational setup (Tang et al., 2018). Volatile organic solvents such as hexane or toluene make this method compatible with GC. The use of SDME in the extraction of organic pollutants from water and soil samples is highly appreciated.

Accumulated evidence suggests that SDME methods have been successful in the extraction of various organic pollutants from water samples including aliphatic amines, fungicides, organochlorine pesticides (OCPs), organophosphorous pesticides (OPPs), PAHs, nitro-PAHs, and quinones. A study was carried out to extract phenols from river water using the direct immersion (DI-SDME) method followed by derivatization. A range of polar organic solvents was used for extraction. However, hexyl acetate was found to be suitable. Further, the manipulation of hexyl acetate with micro drop was done and no stability problems were observed during the entire extraction process (Saraji and Bakhshi, 2005). Headspace SDME (HS-SDME) was used for the extraction of organic compounds (benzene, ethylbenzene, toluene, and xylenes) from water samples. The GC combined with a flame ionization detector was used for their detection. Among all the solvents used, higher extraction efficiency was observed for 1-Octanol and *n*-hexadecane (Przyjazny and Kokosa, 2002). Further, using HS mode, aliphatic amines were extracted using benzyl alcohol and butanone (Kaykhaii et al., 2005). The organic free solvent method was applied for the extraction of PAHs from the lake waters. β-Cyclodextrin was used as an extraction solvent (Wu et al., 2007). For the enhanced performance of the SDME method, the choice of extraction solvent is a critical step. A study has reported the use of a stable drop procedure for the determination of OPPs from the tap and surface waters. The organic solvents compatible with GC and those that differ in K_{ow} values were chosen for the study. Among them, toluene provided the stable drop and the bubble formation was avoided during the extraction (Lamboropoulou and Albanis, 2007). Toluene was also used for the extraction of Diemethoate methyl parathion ethion, permethrin, PAHs, nitro-PAHs, and quinones from the river, surface, and groundwater (De Souza Pinheiro et al., 2011; Santos et al., 2017). Similar results were observed for using *n*-hexane as an extraction solvent for the analysis of pesticides from river water. Due to its low solubility in water, it increases the stability of micro drop, higher than that of toluene (Soares et al., 2014). But, during the extraction of pesticides (fenpro-pathrin, bifenthrin, chloropyrifos, and parathion-methyl) from lake water, bubble formation in the drop was required by exposing the compound pendant drop (CPD) to the sample. The formation of organic droplets (toluene, chlorobenzene) was observed which confirms the stability of the CPD. Compared to the DI-SDME method; the limitation of droplet instability was overcome (Xie et al., 2014). A study by Carlos et al. (2013) has reported *n*-hexane as an appropriate solvent for the extraction of OCPs and pyrethroids from drinking water. GC combined with ECD was used for the identification of these volatile components. The observed LOD values were less than 1 μg L^{-1}. The DI-SDME method was used for the extraction of atrazine, desethyl-atrazine, desisopropyl-atrazine from river, tap, lake, and surface waters (Yohannes et al., 2016). Among the solvents used for extraction, 1-octanol proved to be an efficient extraction solvent. The higher efficiency was achieved by the formation of stable drop under vigorous stirring. Micro solid phase extraction and headspace single-drop microextraction techniques were combined to determine VOCs in water samples. GC-MS was used for the identification of these compounds. Optimized parameters (time and temperature) were used for SDME extraction and 1-Octanol was used as an extraction solvent. The hyphenation of these methods resulted in the enrichment of the extracted compound (BTEX) values from 118 to 504 and also the LOD value obtained was below 0.2 μg L^{-1} (Bagheri et al., 2010). Though introduced 20 years ago, SDME has become a primary method widely used in various disciplines including food, pharmaceuticals, biologics, and chemicals. Due to its unfriendly operation and almost solvent-free approach, it can enrich the targeted analyte in a quick time and is compatible with analytical techniques such as GC-MS and HPLC-UV for analysis (Tang et al., 2018). Table 6.2 represents examples of the SDME methods.

(c) Head space-Stir bar sorptive extraction

Stir bar sorptive extraction (SBSE) has been developed to provide more sorptive phase mass and surface area (Telgheder et al., 2018). It was introduced in 1999 by the group of Sandra and Cramers to improve the recovery of

TABLE 6.2 SDME methods used for the determination of contaminant from different water sources.

S. no.	Sample source	Identified compounds	Method	Extraction solvent	Solvent volume (μL)	Analytical technique	Reference
1	River water	Pesticides	DI-SDME	*n*-Hexanes	1.6	GC-ECD	Soares et al. (2014)
2	Lake water	Fenpro-pathrin, bifentrin, chloropyrifos, parathion-methyl	CPD-DI-SDME	Chlorobenzene	1.0	GC-MS	Xie et al. (2014)
3	Drinking water	OCPs, Pyrethroids	DI-SDME	*n*-Hexane	1.6	GC-ECD	Carlos et al. (2013)
4	Lake, Tap water, and Groundwater	Atrazine desethyl-atrazine (DEA), desisopropyl-atrazine (DIA)	DI-SDME	1-Octanol	3.0	HPLC-DAD	Yohannes et al. (2016)
5	River water	Diemethoate methyl parathion ethion, permethrin	DI-SDME	Toluene	1.0	GC-MS	De Souza Pinheiro et al. (2011)
6	Tap water	Aliphatic amines	HS-SDME	Benzyl alcohol + 2-butanone	1.0	GC-FID	Kaykhaii et al. (2005)
7	Surface and Ground water	PAHs, nitro-PAHs quinones	DI-SDME	Toluene	1.0	GC-MS	Santos et al. (2017)
8	Tap and surface water	OPPs	DI-SDME	Toluene	1.5	GC-MS	Lamboropoulou and Albanis (2007)
9	Lake water	PAHs	HS-SDME	β-Cyclodextrin	10	HPLC-FLD	Wu et al. (2007)

low concentrated analytes from aqueous samples. The extended use of SBSE to gas phase sampling was introduced by Bicchi et al. and Tienpont et al. in the year 2000 known as headspace sorptive extraction (Liberto et al., 2019). The phase used in this method is coated and bonded onto a magnetic stir bar which is immersed into a liquid sample for extraction. A large amount of PDMS fiber used on the surface of the stir bar helps to achieve good recovery of the analytes and enhances the sensitivity which is a major drawback in SPME method. The stir bar has three major components—a magnetic stirring rod, a thin glass jacket, and a layer of PDMS sorbent. The magnetic stirring rod which is covered by a thin glass jacket transfers the rotational movement of the stirring plate to the liquid sample. Finally, the targeted compounds are extracted using PDMS sorbent (Telgheder et al., 2018). Finally, the PDMS stir bar is placed in a thermal desorption system where, the sampled compounds are transferred online to a GC or GC-MS system (Liberto et al., 2019). The use of thermal desorption can be seen during the analysis of thermally stable volatile and semivolatile compounds in GC analysis. Compared to SPME fibers, stir bars have shown good robustness and also uses larger sample sizes than other headspace methods (Telgheder et al., 2018).

The extraction phase is a vital parameter in sorptive extraction which determines the selectivity and extraction efficiency of the method. Generally, the materials used for coating stir bars improve the concentration factors of the targeted compounds and also removes the interfering substances. Majority of the application uses PDMS as an extraction phase due to its high availability. Recently various SBSE stir bars with polar coating materials available in the market such as ethylene glycol-PDMS copolymer (EG-Silicone) and polyacrylate (PA).

The application of SBSE has been explored in terms of extraction of volatile and semivolatile compounds such as PAHs, PCBs, pesticides, and volatile aromatics (Telgheder et al., 2018). A study was done using the SBSE method followed by HPLC combined with a fluorescence detector for the extraction and identification of PAHs in water. The conditions used for SBSE were optimized. The results showed that the proposed method provided good linearity, precision, and sensitivity. The LOD values ranged between 0.5 and 7.3 ng L^{-1} (Garcia-Falcon et al., 2004). Another study has used β-cyclodextrin bonded-silica (CDS) as a novel sorbent to improve the extraction efficiency and surface area of the SBSE method for the analysis of phenolic compounds in water samples. Thermal desorption and GC-MS were used for detection. The results revealed that the porous structure of CDS coating enriched the extraction efficiency of the SBSE method. The LOQ and LOD values obtained ranged between 0.08–3.3 μg L^{-1} and 0.02–1.0 μg L^{-1}. The recovery rate for all the tested water samples was above 81% (Faraji et al., 2011). Silva et al. have investigated the presence of six acidic pharmaceuticals acetyl salicylic acid (ASA), ibuprofen (IBU), diclofenac sodium (DIC), naproxen (NAP), mefenamic acid (MEF), and gemfibrozil (GEM) in environmental water matrices. SBSE method consisting of polyurethane (PU) and PDMS phases was used as sorbent material. The SBSE method enhanced the recovery rate and reduced the extraction time of the targeted analytes (Silva et al., 2008).

6.5 Enrichment techniques in headspace-gas chromatography

For the detection of analytes with lower detection limits in the headspace gas sample, enrichment techniques are mandatory. Increasing the amount of analyte by increasing the headspace volume is a limitation as band broadening and poor resolution restricts permissible volume. To overcome this situation, the separation of majority of the air in the headspace sample from the volatile analytes needs to be performed. This is a natural process in the HS-SPME method which doesn't allow further enrichment. In other headspace methods, adsorption or cold trap can be used to separate the volatile analytes from the headspace gas. In both cases, the analytes are retained while the air passes through the trap. The P & T method uses an adsorption trap to handle larger gas volumes. However, it may also be used in combination with static HS-GC with smaller gas volumes. A larger aliquot volume of a sample from the headspace vial is withdrawn by one of the headspace sampling techniques. The above volume is first passed through the adsorption tube (tenax, carbon black, and molecular sieve) and allows the analytes to remain adsorbed. Thus, the analytes are separated from the headspace gas (air and carrier gas). Finally, the adsorbed compounds are thermally desorbed and transferred onto the column as a concentrated bulk sample. This method can avoid using a liquid cryogen and may be appropriate for routine analysis. But in the case of slow desorption of the analytes, additional cryogenic trapping can be used to suppress band broadening. It should be observed that factors such as strong adsorption energy and high temperatures don't alter the compounds during the adsorption trap procedure.

Cold traps are used mainly for two reasons; enrichment and the concentration of solute bands. The use of a cold trap depends on the specific application of a technique and based on various factors-

(a) Only a single analysis for a unique sample should be performed and
(b) The entire headspace method including cryogenic trapping should be done usually in an automated system.

There are various fundamental principles and different versions of cold traps such as cryogenic condensation and cryogenic focusing. *Cryogenic trapping* represents both of them. In cryogenic condensation, the volatile compounds are condensed in such traps which either have no stationary phase or liquid phase solidified at low temperatures thereby losing its chromatographic phase properties. Cryogenic focusing is based on the trapping of volatile compounds in the liquid phase of a column at low temperatures but above the glass transition temperature. This method is similar to thermal focusing; the only difference is the temperature ranges (cryogenic focusing—below ambient and thermal focusing—above ambient temperatures). In addition to thermal focusing, effective focusing can be created if a temperature gradient is established during the trapping and/or desorption of the analytes (Kolb and Ettre, 2006).

6.6 Gas chromatography-mass spectrometry (GC-MS)

The introduction of gas chromatography (GC) and liquid chromatography (LC) with specific and universal detectors has enabled to overcome difficulties in the identification and quantification of organic contaminants from complex environmental matrices (Finnigan, 1990). The GC is appropriate for the detection of volatile and semivolatile nonpolar compounds. In addition, the hyphenation of GC with MS has further enhanced the separation and detection capabilities. Most of these compounds are structurally similar and their positive identification has been tricky. A high number of organic contaminants with low concentrations in the environmental samples makes their analysis difficult (Sebok et al., 2009). The identification and sensitivity problems of the target analytes from different complex environmental matrices have been solved by the introduction of gas chromatography coupled to mass spectrometer (GC-MS) (Finnigan, 1990). The interface of GC with MS is a well-established and powerful approach for the detection and quantification of volatile and thermally stable organic pollutants in water samples. This combined method includes the efficient separation by GC and reasonable sensitivity offered by MS. Compared to liquid chromatography-mass spectrometry (LC-MS), this method offers several advantages such as improved chromatographic resolution and peak capacity, a single source of mobile phase (helium or hydrogen), low solubility issues, and an optimized temperature-controlled program (Li et al., 2015).

(a) GC-MS instrumentation

The heart of the GC is a capillary column. The separation of analytes is based on three specific criteria—stationary phase, column dimensions, and the velocity of carrier gas. The selection of stationary phase ranges from polar to nonpolar (van Leeuwen and de Boer, 2008). Some of the important and commonly used ones are DB-624, DB-Wax, BPX-5, DB-1, DB-5, DB-5MS, and HT-8. The column diameter typically used is in the range of 0.25–0.32 mm, but narrow bore columns (0.10–0.15 mm) provide considerable theoretical plates at the same column length (van Leeuwen and de Boer, 2008).

Carrier gas usually provides a gas flow that facilitates the transport of compounds through the column and ultimately reaches the detector. Efficient separations and reproducible chromatogram depend on the flow and purity of the carrier gas. The inert nature of the carrier gas avoids reaction with the target compounds in the GC and can safeguard the detector. Nitrogen is the preferred choice for most compound analysis, due to its less cost and safe use. Hydrogen should be used during the use of a hydrogen detector (de Jonge, 2013). The optimum resolution can be obtained with hydrogen gas at higher velocities. The use of nitrogen is limited due to the longer analysis period (van Leeuwen and de Boer, 2008).

The injection port is an important component of GC. The sample is injected via syringe, autosampler, and other sampling devices into the injection port. Higher temperatures up to 300°C are used for the injection port to vaporize the introduced sample. Generally, for the detection of low concentrated analytes with trace amounts, programmable temperature vaporization (PTV) injector is used. The maximum amount of sample that can be injected is up to 1 mL. Lower detection limits can be achieved without preconcentration of the targeted analytes by using PTV injectors. The ballistic heating capacity to the Split/Splitless injector allows injecting larger volumes of the sample. For certain targeted compounds with higher boiling points, the PTV injector can separate those compounds and the solvents with lower boiling points to avoid any interruption (de Jonge, 2013).

An appropriate autosampler is required for an efficient GC-MS operation. For routine environmental sample analysis, three types of autosampler can be preferred

1. for liquid samples (semi and less volatile compounds)
2. for head-space samples (volatile compounds)
3. A Combipal hybrid autosampler, with different liquid (headspace [HS] and solid-phase extraction [SPE] modules).

The first two types of autosamplers are commonly preferred due to their low cost and suitability for routine environmental samples analysis. Combipal autosampler is also used for routine analysis but is more expensive. The main advantage of this autosampler is that it can automate the pretreatment procedure of the analytes. A Combipal can add the injection standard solution to the sample extract before their injection or derivatization (de Jonge, 2013).

Detectors play a crucial role to determine the number of targeted compounds in a complex mixture. Various types of detectors are available for GC. The ideal properties of a detector include higher sensitivity, good linearity, ease of use, stability and accuracy, quick and nondestructive. The detector must be capable of acquiring data with a high sampling rate. Many commercial detectors are available for GC including flame ionization detector (FID), electron capture detection (ECD), sulfur chemiluminescence detector (SCD), nitrogen chemiluminescence detector (NCD), and nitrogen phosphorous detector (NPD) (Alam and Harrison, 2016).

Derivatization is an important chemical process done in most of the GC-MS analyses to modify the functionality of the analyte for enhanced chromatographic separation. For GC-MS analysis, the sample should be volatile in nature. Derivatization in GC-MS avoids the thermal decomposition of an analyte and allows their separation at reasonable temperatures. Derivatization can either increase or decrease the volatility of the desired compounds. Further, this process improves the detector response in GC by reducing the analyte adsorption onto the column (Bajpai et al., 2016). Derivatization reactions can be classified into alkylation or arylation, acylation, silylation, formation of cyclic compounds, etc. In the case of the use of nonselective detectors such as thermal conductivity detectors (TCD) and FID detectors, derivatization reactions are not preferred for enhancing sensitivity whereas, the use of NPD, improves the sensitivity by derivatization with nitrogenous compounds (Bajpai et al., 2016).

Endocrine-disrupting compounds (EDCs) commonly found in different water sources are polar in nature. Therefore, these group of compound requires derivatization which prevents them from thermal degradation at the injector port. Most of the studies have omitted the derivatization process during GC-MS analysis of flame retardants involving PBDEs. However, most of the organic compounds belonging to phenolics, pharmaceuticals, and natural and synthetic hormones have been reported to be analyzed by silylation with *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA), or *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide (MSTFA) to form methoximated trimethylsilyl (TMS) derivatives (Pozo et al., 2019).

Ionization techniques are commonly coupled to chromatography techniques for better separation and identification of analytes. The commonly used ionization techniques for GC are chemical ionization (CI) and electron ionization (EI). The CI mode is referred to as soft ionization and detects molecular ion during the GC-MS analysis. CI has comparatively less fragmentation than EI but has reduced sensitivity (Li et al., 2015). The CI source can be operated under positive and negative ionization modes giving $[M+H]^+$ and $[M-H]^-$ ions. But its use in the analysis of multiresidue components is limited. Often, it requires multiple injections of samples for covering a range of compounds. Moreover, the CI source has certain limitations for analyzing a particular group of highly electronegative compounds such as organochlorine pesticides (OCPs), organophosphorous pesticides (OPPs), and polybrominated diphenyl ethers (PBDEs) (Fang et al., 2020). EI mode involves the formation of ions via the collision of electrons with gaseous molecules. EI has the potential to ionize a spectrum of organic contaminants. During the ionization process, the molecule undergoes extensive fragmentation. For most of the compounds, characteristic mass spectra are obtained (Li et al., 2015). Atmospheric pressure ionization (API) methods are gaining popularity and can be an alternative to GC-EI-MS. The API has less fragmentation and is more sensitive than EI and CI ionization. The process of ionization for atmospheric pressure chemical ionization (APCI) and CI occurs at atmospheric pressure and vacuum respectively. The ionization pressure used for APCI is 760 Torr whereas, for CI, 10^{-2}–1 Torr is used (Fang et al., 2020).

The hyphenation of GC to MS with the aid of quadrupole or ion trap analyzers has been established as an efficient analytical method for the qualitative and quantitative analysis of organic contaminants from water samples owing to their less cost and user-friendly nature. For targeted analysis, Ion trap mass spectrometers and Quadrupole mass spectrometers are frequently used. However, the use of MS/MS can limit the number of analyzed compounds (Gomez et al., 2011).

6.7 Application of GC-MS in the determination of EOCs

A vast range of studies has been carried out to highlight the significance of GC-MS in the analysis of ECs from various sources of water. The presence of 31 pesticide residues (19 agricultural and 12 nonagricultural) in the waters of the Hooghly River in West Bengal, India using GC-MS/MS coupled with multiple reaction monitoring (MRM) mode was examined. Sixty-four samples from different water sources including river, river sediment, pond, and tube-well water were used for the study. Water samples were extracted with conventional liquid-liquid extraction using organic solvents and a modified QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) for residual analysis. The identification of individual pesticides by GC-MS/MS combined with MRM mode was based on retention time and transition ions. It was observed that approximately 42% of the samples analyzed were found to contain 19 pesticides. The highest concentration of pesticides were observed in river water (3.008 ng mL^{-1}) with the least one in tube-well water (0.019 ng mL^{-1}) (Mondal et al., 2018). The combined method of Headspace solid phase microextraction (HS-SPME) and gas chromatography-mass spectrometry (GC-MS) was used to determine the presence of pharmaceuticals and personal care products (PCPs) in water samples. The identified compounds include antioxidants, antiseptics, antiinflammatories, fragrances, pesticides, UV-blockers, polycyclic aromatic hydrocarbons (PAHs), and plastic components. The highest sensitivity of the analytes was obtained from water samples by SPME extraction procedure after optimizing certain parameters including derivatization, extraction temperature and time and desorption temperature, and time. These analytes were quantified by the GC-MS method. The LOD values obtained for the analyzed samples were between 0.7 and 9.0 ng L^{-1}. For derivatized analytes, the LOD values obtained were 2.5–9.0 ng L^{-1} (Basaglia and Pietrogrande, 2012). The GC-TOF-MS was used for the screening and qualitative analysis of 150 organic contaminants from natural and wastewaters. The investigated organic contaminants were from different chemical families such as fungicides, herbicides (chloroacetanilides and triazines), insecticides (carbamates, organochlorines, organophosphorous, and pyrethroids), and other metabolites. It was observed that GC-TOF-MS allowed the identification of other contaminants from water samples in a nontarget way. Most of the analytes were satisfactorily detected (0.1 μg L^{-1}) (Portoles et al., 2011). A stir bar sorptive extraction (SBSE) followed by GC × GC-TOF MS was developed for the identification and quantification of emerging organic pollutants in wastewater effluent and river waters in Spain. The study revealed the identification of target compounds including (13) PCPs, (15) PAHs, and (27) pesticides. For most of the identified compounds, an exceptional detection limit (1 ng L^{-1} or below) was observed with improved separation efficiency. In wastewater effluents, the values obtained ranged between 0.02 and 2.5 ng L^{-1}, whereas the river water showed levels between 0.01 and 2.15 ng L^{-1}. It was concluded that most of the analytes were explicitly determined with high reliability even at low concentrations in complex environmental matrices by GC × GC-TOF MS (Gomez et al., 2011). A comprehensive two-dimensional gas chromatography coupled with TOF-MS (GC × GC-TOF-MS) involving HS-SPME was employed for the determination of short-chain chlorinated paraffins (SCCPs) in groundwaters, lake, and river waters. The detection (0.06–0.13 μg L^{-1}) and quantification (0.18–0.40 μg L^{-1}) limits of the examined compounds in all the water samples were achieved by this hyphenated method (Zhan et al., 2018). A GC-MS method coupled with NCI was established for the determination of EDCs from the water samples. Derivatization with pentafluorobenzoyl chloride (PFBOCl) was done before GC-MS analysis. The results revealed the presence of trace amounts of bisphenol—A (1,040 ng L^{-1}), estradiol (7.7 ng L^{-1}), estrone (79 ng L^{-1}), triclosan (355 ng L^{-1}), 4-nonylphenol (11,300 ng L^{-1}), and 4-Tert-octylphenol (11,300 ng L^{-1}) (Zhao et al., 2009). Commercial UV filters Eusolex namely (benzophenone-3, butylmethoxydibenzoylmethane, ethylhexyl methoxycinnamate, homosalate, 4-methylbenzylidenecamphor) and common antimicrobial agents (clorophene and triclosan) were detected and quantified using the SPE method followed by GC-MS analysis. It was observed that LOD for UV filters was 13–266 ng L^{-1}. benzophenone-3 (11–400 ng L^{-1}) was the most abundant UV filter detected (Cuderman and Heath, 2006). A novel approach of GC coupled to quadrupole high-resolution time-of-flight mass spectrometer with APCI (GC-APCI-QTOF-MS) was used for the screening of organic contaminants in groundwater samples. Target and nontarget screening approach were adapted. The results showed that at cone voltage 20 V, the highest abundance of the molecular ion and/or protonated molecule was observed. The higher sensitivity of GC-APCI-QTOF-MS was observed for all the water samples analyzed as five additional targeted compounds belonging to pesticides families including atrazine, atrazine desisopropyl, terbumeton desethyl, and terbutryn were detected along with PAHs (naphthalene), insect repellents (*N*,*N*-diethyl-meta-toluamide [DEET]), musks (Tonalide), and UV filters (2-ethylhexyl 4-methoxycinnamate [EHMC], Benzophenone, and Octocrylene) (Portolés et al., 2014). The river waters of Portugal were explored for the identification and quantification of organic pollutants and pesticides using the GC-MS method in full scan and SIM mode. It was observed that the recovery rate for most of the identified compounds was more than 70%. The GC-MS analysis revealed significant LOD values for most of the identified compounds in the range of 0.002–0.08 μg L^{-1}. The presence of Atrazine and Simazine was observed in most of the water samples analyzed (de Almeida et al., 2000). A GC × GC-HRMS was developed for the nontarget screening and identification of organic contaminants in sediments from an urban channel and a lake in Copenhagen, Denmark. GC × GC-HRMS was used for the identification of samples from nonpolar fractions. Quadrupole time-of-flight (QTOF) mass analyzer was operated in TOF mode with a resolving power of 13,500 and m/z range between 200 and 1000. It was observed that the two-dimensional GC × GC-HRMS method was able to identify 67 compounds out of 109 compounds. These identified compounds were found to be a group of isomers with similar monoisotopic mass and the molecular formula (Lubeck et al., 2020). The chromatographic conditions used for the above studies are represented in Table 6.3.

TABLE 6.3 GC and MS used for the identification and quantification of EOCs from different sources of water.

S. no.	Instrumentation	Source of water samples	Method of extraction	Gas chromatography (GC) conditions	Mass spectrometer (MS) conditions	Targeted/identified contaminants	Limits of detection/limits of quantification (LOD/LOQ) values	Reference
1.	GC-MS/MS	River water, Sediment water, Pond water, Tube-well water	Liquid-liquid extraction (LLE), Quick Easy Cheap, Effective, Rugged and Safe (QuEChERS)	*Column*-HP-5MS 5% phenyl-methyl polysiloxane column Phenyl-methyl polysiloxane column (30 m × 0.25 mm × 0.25 μm) *Oven temperature*-70–290°C *Heater temperature*-280°C *Carrier gas*-Helium (20 mL min^{-1}) *Injection volume and mode*-1 μL/Splitless *Solvent delay*-6 min	*Scan mode*-Multiple reaction monitoring (MRM) *Ionization*-Electron ionization (70 eV) *Ion source temperature*-150°C and 230°C. *Collision gas*-N_2 at 1.50 mL min^{-1}	Pesticides	River water (3.01 ng mL^{-1}), Sediment water (1.25 ng g^{-1}), Pond water (0.40 ng mL^{-1}), Tube-well water (0.02 ng mL^{-1})	Mondal et al. (2018)
2.	GC-MS	Effluent water of an urban waste water treatment plant (WWTP)	Head space solid phase micro-extraction (HS-SPME)	*Column*-Fused silica RTX-5MS column (30 m × 0.25 mm × 0.25 μm) *Oven temperature*-50–300°C *Injection mode*-Splitless *Injector temperature*-260°C *Carrier gas*-Helium (1 mL min^{-1})	*Scan mode*-Single ion monitoring (SIM) *Ionization*-Electron ionization (70 eV) *Ion source temperature*-250°C. *Mass scan range*-40–650 m/z	Pharmaceuticals and Personal Care products (Fragrances, UV-filters, antiseptics, estrogens, antiinflammatory) and pesticides	0.7–9.0 ng L^{-1}	Basaglia and Pietrogrande (2012)
3.	GC-TOF-MS	Surface water, Ground water, Effluent & Influent water from WWTP	Solid-phase extraction (SPE)	*Column*-Fused silica HP-5MS capillary column (30 m × 0.25 mm × 0.25 μm) *Oven temperature*-90–300°C *Injection volume and mode*-1 μL/Splitless *Interface and source temperature*-250°C *Carrier gas*-Helium (1 mL min^{-1}) *Solvent delay*-3 min	*Mass scan range*-50–650 m/z TOF-MS at 1 spectra s^{-1} *Resolution of TOF-MS*-8500 (FWHM) at m/z 614	Insecticides (Organochlorines, Organophosphorous, Carbamates, and Pyrethroids), Herbicides (Triazines, Chloroacetanilides), Fungicides, and other metabolites	0.02–1.0 μg L^{-1}	Portoles et al. (2011)

4.	GC × GC-HRMS	Lake water, Urban channel	Pressurized liquid extraction (PLE)	*Column*- ZB 5 column (60 m × 0.25 mm × 0.25 μm) and ZB 50 column (1.5 m × 0.18 mm × 0.18 μm) *Injection volume and mode*- 1 μL/Splitless *Oven temperature*- 60–310°C *Injector temperature*-300°C *Carrier gas*- Helium (1.5 mL min^{-1})	*Ionization source*- Electron ionization *Quadrupole temperature*- 150°C *Resolving power*- 13,500 *Mass scan range*- 200–1000 m/z *Transfer line temperature*- 310°C *Data acquisition*- 20–700 Da with 25 spectra s^{-1}	Alkanes, Benzenes, Alkylphenyl ketones, Anthracenes, Biphenyls, Chloronapthalenes, Cyclic Organosulphur, etc.	–	Lubeck et al. (2020)
5.	GC × GC-TOF MS	River water and wastewater	Stir-bar sorptive extraction (SBSE)	*Column*- Rtx-5 coated with 5% diphenyl 95% dimethyl polysiloxane (10 m × 0.18 mm × 0.20 μm) Rxi-17 coated with 50% diphenyl 50% dimethyl polysiloxane (1 m × 0.1 mm × 0.10 μm) Liquid crystalline phase Rt-LC50 (1 m × 0.1 mm × 0.10 μm) *Oven temperature*- 15–315°C *Maximum program temperature*- 270–350°C *Programmed temperature vaporization (PTV) temperature*- 30–315°C *Solvent delay*-5 min	*Ionization*- Electron ionization (70 eV) *Transfer line temperature*- 280°C *Ion source temperature*- 250°C *Mass scan range*- 50–450 m/z *Data acquisition*- 100 spectra s^{-1}	Personal care products, Polycyclic aromatic hydrocarbons, and pesticides	<1 ng L^{-1}	Gomez et al. (2011)

Continued

TABLE 6.3 GC and MS used for the identification and quantification of EOCs from different sources of water—cont'd

S. no.	Instrumentation	Source of water samples	Method of extraction	Gas chromatography (GC) conditions	Mass spectrometer (MS) conditions	Targeted/identified contaminants	Limits of detection/limits of quantification (LOD/LOQ) values	Reference
6.	GC-MS	River water	Solid phase extraction	*Column-* Fused silica HP-5MS column (30 m × 0.25 mm × 0.25 μm) *Oven temperature-* 60–300°C *Injection mode-* Splitless *Interface temperature-*270°C *Ion source temperature-*200°C *Injector temperature-*250°C *Carrier gas-*Helium	*Scan mode-* Multiple reaction monitoring (MRM) *Ionization-* Electron ionization (70 eV) *Mass scan range-* 70–450 amu	Atrazine, Simazine, Terbuthylazine, Alachlor, Metolachlor, Irgarol, Propanil, Tributhylphosphate, 2,4,6-trichlorophenol	0.005–0.03 μg L^{-1}	de Almeida et al. (2000)
7.	GC-TOF-MS	Ground water	Solid phase extraction (SPE)	**For, GC-EI-TOF-MS** *Column-* Fused silica HP-5MS column (30 m × 0.25 mm × 0.25 μm) *Oven temperature-* 90–300°C *Injection volume and mode-* 1 μL, Splitless *Interface and source temperature-* 250°C *Injector temperature-* 280°C *Carrier gas-* Helium (1 mL min^{-1}) *Solvent delay-* 3 min **For GC-APCI-QTOF-MS** *Column-* Fused silica DB-5MS capillary column (30 m × 0.25 mm × 0.25 μm) *Oven temperature-* 90–300°C *Injection volume and mode-* 1 μL Splitless *Interface temperature* 310°C *Carrier gas-* Helium (2 mL min^{-1})	**For, GC-EI-TOF-MS** *Mass scan range-* 50–650 *m/z* TOF-MS at 1 spectra s^{-1} *Resolution of TOF-MS* 8500 (FWHM) at *m/z* 614. **For GC-APCI-QTOF-MS** *Mass scan range-* 50–650 *m/z* *Resolution of TOF-MS-* 18,000 (FWHM) at *m/z* 614. *Collision energy-* 10–40 eV	PAHs, PCBs, PBDEs, Pesticides, PCPs (UV filters, musks), Polychloronapthalenes (PCNs), Antimicrobials, Insect repellents	–	Portolés et al. (2014)

8.	GC × GC-TOF MS	Fresh water, Ground water, Lake water, and River water	Headspace solid-phase microextraction (HS-SPME)	*Column-* Rxi-5Sil MS column (5% phenyl + 95% methyl polysiloxane) (30 m × 0.25 mm × 0.25 μm) and Rxi-17Sil MS column (50% diphenyl di methyl polysiloxane) (1.0 m × 0.15 mm × 0.15 μm) *Oven temperature-* 100–290°C *Injector temperature-* 260°C *Injection mode-* Splitless *Carrier gas-* Helium (1.0–1.6 mL min^{-1})	*Ionization-* Electron ionization *Scan mode-* Full scan *Transfer line temperature-* 280°C *Ion source temperature-* 240°C *Mass scan range-* 50–500 m/z	Short-chain chlorinated paraffins (SCCPs)	0.06–0.40 μg L^{-1}	Zhan et al. (2018)
9.	GC-MS/MS	River water, Influent and Effluent waste water	Solid-phase extraction (SPE)	*SGE forte capillary column-* (30 m × 0.25 mm × 0.25 μm) *Injector temperature-* 100–270°C *Column temperature-* 100–300°C	*Transfer line temperature-* 280°C *Ion source temperature-* 210°C *Collision energy-* 70 eV	Pharmaceuticals, Benzoic acids and its derivatives, aromatic carboxylic acids, cholic acids, aliphatic dicarboxylic acids, aromatic carboxylic acids, 2,4-di-*tert*-butylphenol, and different phthalates	0.92–600 ng L^{-1}	Sebok et al. (2009)
10.	GC-MS	River water, Lake water, and wastewater	Solid-phase extraction (SPE)	*Column-* Fused silica HP-5MS capillary column (30 m × 0.25 mm × 0.20 μm) *Oven temperature-* 100–280°C *Injector temperature-* 240°C *Injection volume and mode-* 1 μL, Splitless *Carrier gas-* Helium	*Transfer line temperature-* 280°C *Collision energy-* 70 eV *Scan mode-* Total ion current (TIC) and SIM	UV filters (homosalate, 4-methylbenzylidenecamphor, benzophenone-3, octocrylene, butyl methoxy dibenzoyl methane, and ethyl hexyl methoxycinnamate) and antimicrobial agents (triclosan and clorophene)	Surface waters (10–266 ng L^{-1}) and wastewater (90–250 ng L^{-1})	Cuderman and Heath (2006)

Continued

TABLE 6.3 GC and MS used for the identification and quantification of EOCs from different sources of water—cont'd

S. no.	Instrumentation	Source of water samples	Method of extraction	Gas chromatography (GC) conditions	Mass spectrometer (MS) conditions	Targeted/identified contaminants	Limits of detection/limits of quantification (LOD/LOQ) values	Reference
11.	GC-NCI-MS	River water	Solid-phase extraction (SPE)	*Column-* DB35-MS capillary column (30 m × 0.25 mm, 0.25 μm) *Carrier gas-* Helium (1.0 mL min^{-1}) *For phenolic compounds-* *Injection volume and mode-* 2 μL, Splitless *Column temperature-* 80–310°C *For acidic pharmaceuticals and herbicides-* *Injection volume and mode-* 2 μL Splitless *Column temperature-* 100–310°C	*Scan mode-* Negative chemical ionization (NCI) and SIM	Phenolic compounds and Acidic pharmaceuticals	**Phenolic compounds** LOD values—0.2–2.0 ng L^{-1} LOQ values—0.5–7.0 ng L^{-1} **Acidic pharmaceuticals** LOD values—0.2–2.2 ng L^{-1} LOQ values—0.7–7.5 ng L^{-1}	Zhao et al. (2009)

6.8 Conclusion and way forward

The growing use of chemical-based products has posed a severe threat to the environment owing to their release into the aquatic system. The continuous release of these organic contaminants into the aquatic system has detrimental effects on aquatic organisms as well as human beings. The main routes of emission of these contaminants are the wastewaters. These contaminants escape from the conventional WWTPs due to their low concentrations. These organic contaminants are present in low concentrations ranging from ng L^{-1} to μg L^{-1}. Surface waters accumulate these contaminants as a result of wastewater discharge. However, the main problem arises when these surface waters are used for drinking purposes. These contaminants are detected in many natural water systems including reservoirs and lakes. There is a growing increase in the number of ECs in the aquatic system and their transformation products are even more toxic (see Sanganyado, 2022, Chapter 19; Tavengwa et al., 2022, Chapter 20). These ECs have different physicochemical characteristics which makes them more difficult to extract and identify.

Efficient sample preparation and clean-up procedures before separation and detection by chromatographic techniques are mandatory for the successful determination of these organic contaminants from different water sources. The clean extraction procedure with enriched targeted analytes and identification of these ECs should be done in the early stages to avoid further damage. This alarming situation has goaded the development of improved extraction methods and specific and sensitive analytical methods for the detection of these EOCs.

However, the recent advancements in the sample extraction techniques have facilitated the easy determination of these emerging pollutants. Due to its high selectivity, robustness, and higher retention capacity for polar compounds, SPE is the preferred extraction method for majority of the organic contaminants. But, the evolution of SPE techniques has given rise to other methods such as SPME, SDME, SBDE, and LPME. The hyphenation of HS-SPME, HS-SBDE, and HS-SDME with GC-MS offered a great opportunity for the isolation and detection of a wide spectrum of organic contaminants starting from moderate volatile to extremely volatile. Miniaturized extraction methods are receiving a great deal of interest among the scientific community as efficient sample preparation methods for analytical detection. Much attention is focused on the solvent-free methods such as SPME and SBSE. Recent development in SPME methods such as thin-film microextraction (TFME), solid-phase dynamic extraction (SPDE), fiber-packed needle microextraction (FNME), and microextraction by packed syringe (MEPS) has widened the scope for the analysis of environmental samples. Moreover, the availability of commercial fiber coating is on the rise and opens a new gateway for future applications. Apart from these available sorbents, coating procedures are under development which promises improved efficiency and wider applications. These recent trends in sample preparation methods consist of automation, miniaturization, high-performance, online coupling with analytical instruments, and most importantly their less expensive operation mode with minimal or no solvent use. More selective and sensitive phases can be developed soon for their further miniaturization as it reduces sample preparation steps. Also, the main advantage is the trace and ultra-trace trace analysis of these contaminants in complex sample matrices. Automation can lead to faster procedures and result in increased precision and cost-effectiveness. The last few years have witnessed the automation of sample preparation devices and their coupling to analytical methods.

The role of analytical techniques in the analysis of organic contaminants from water samples has been phenomenal over the years. Multiresidue analytical methods are required for the comprehensive characterization of a wide range of emerging pollutants from different water sources. The identification of these contaminants along with their transformation products has been challenging. These issues have been addressed by the introduction of hyphenated techniques such as GC-MS or LC-MS. These techniques are capable of target and nontarget analysis. The coupling of GC to MS has proven to be a viable option to obtain realistic information about these volatile and semivolatile organic contaminants from complex water samples. The GC-MS has been excellent in solving various industrial problems related to novel compound identification and the development of an optimized method for complex sample matrices. The capabilities of this hyphenated method have increased over the years in the determination of organic contaminants due to the improvements in GC-MS and 2D GC instrumentation. These methods provide unique separation power, high speed, increased resolution, and sensitivity.

Therefore, it is evident that efficient sample preparation methods combined with a high-throughput and sensitive analytical instrument can be a productive approach for the isolation, identification, and detection of these volatile and semivolatile pollutants. The potential risk caused by their adverse effects can be minimized to safeguard the human race and other living organisms for a healthy and safe environment.

This falls under the section on monitoring techniques, current analytical approaches, and instrumental analyses with other chapters, e.g., Mwedzi et al. (2022), Kaserzon et al. (2022), Kaykhaii and Hashemi (2022), and Kebede et al. (2021) that aims to understand how emerging freshwater pollutants are analyzed or detected within aquatic ecosystems.

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PART 2

Fate and occurrence of emerging pollutants in aquatic systems

CHAPTER

7

The fate of emerging pollutants in aquatic systems: An overview

Edmond Sanganyado and Tatenda A. Kajau

7.1 Introduction

The presence of emerging pollutants in aquatic systems is an issue of global concern. Emerging pollutants are a diverse group of unregulated or newly regulated synthetic or natural chemicals (and their transformation products and metabolites) that may pose adverse human or environmental health risks (Tavengwa and Dalu, 2022, Chapter 1). Examples of emerging pollutants include pharmaceuticals and personal care products (see Madikizela et al., 2022, Chapter 10), illicit drugs (see Ntshani and Tavengwa, 2022, Chapter 11), flame retardants (see Cristale, 2022, Chapter 16), pesticides (see Montagner et al., 2022, Chapter 12), disinfectant byproducts (see Vizioli et al., 2022, Chapter 14), surfactants, biocides, plasticizers, potentially toxic elements (see Moodley et al., 2022, Chapter 13; Hashemi and Kaykhaii, 2022, Chapter 15; Galhardi et al., 2022, Chapter 17), and nanomaterials (see Yardy et al., 2022, Chapter 9). It is estimated that there are more than 350,000 chemicals in current use (Wang et al., 2020). Global production of synthetic chemicals increased from 1 million tons in 1930 to 400 million tons in 2000 (United Nations Environment Programme, 2019). In addition, the production capacity of chemical industries worldwide increased from 1.2 billion tons to 2.3 billion tons between the year 2000 and 2017 (United Nations Environment Programme, 2019). However, of the 345 million tons of synthetic chemicals consumed in the European Union in 2016, 62% and 22% were known to be hazardous to human and environmental health (Fig. 7.1) (Eurostat, 2020). The World Health Organization estimated that in 2018 chemical pollution contributed to more than 1.6 million deaths globally (Das and Horton, 2018; Landrigan et al., 2018). The chemical industry is expected to double by 2030 from the US$5 trillion reported in 2017 (United Nations Environment Programme, 2019). Hence, increased awareness of the detrimental health and ecological effects of synthetic chemicals has not slowed their global production.

More than two million tons of municipal, domestic, and agricultural waste are discharged into aquatic systems globally each day. It is estimated that the volume of global wastewater produced annually is at least six times the volume of freshwater bodies worldwide. Exposure to emerging pollutants often causes toxicological effects in biota even though they often occur at ng L^{-1} to μg L^{-1} concentrations (or ng kg^{-1} to μg kg^{-1} in solid matrices). A comprehensive understanding of the fate and transport of emerging pollutants in aquatic environments is essential for developing effective monitoring and mitigation strategies.

7.2 Sources and occurrence of emerging pollutants in aquatic systems

Rapid urbanization, industrialization, and an increase in the standard of living have resulted in a surge in the discharge of emerging pollutants into the environment. Emerging pollutants enter aquatic systems through municipal, domestic, industrial, and hospital wastewater as well as landfill leachate, urban stormwater, and agricultural runoff (Mandaric et al., 2016; Rainieri et al., 2017). Pharmaceuticals such as antidepressants, anti-cancer drugs, non-steroidal anti-inflammatory drugs, anti-retroviral drugs, and antimicrobial agents are frequently detected in hospitals, the pharmaceutical industry, and municipal wastewater effluent (Sanganyado et al., 2017). In contrast, pesticides and veterinary drugs are frequently and abundantly detected in agriculture runoff and sometimes in urban stormwater (Pereira

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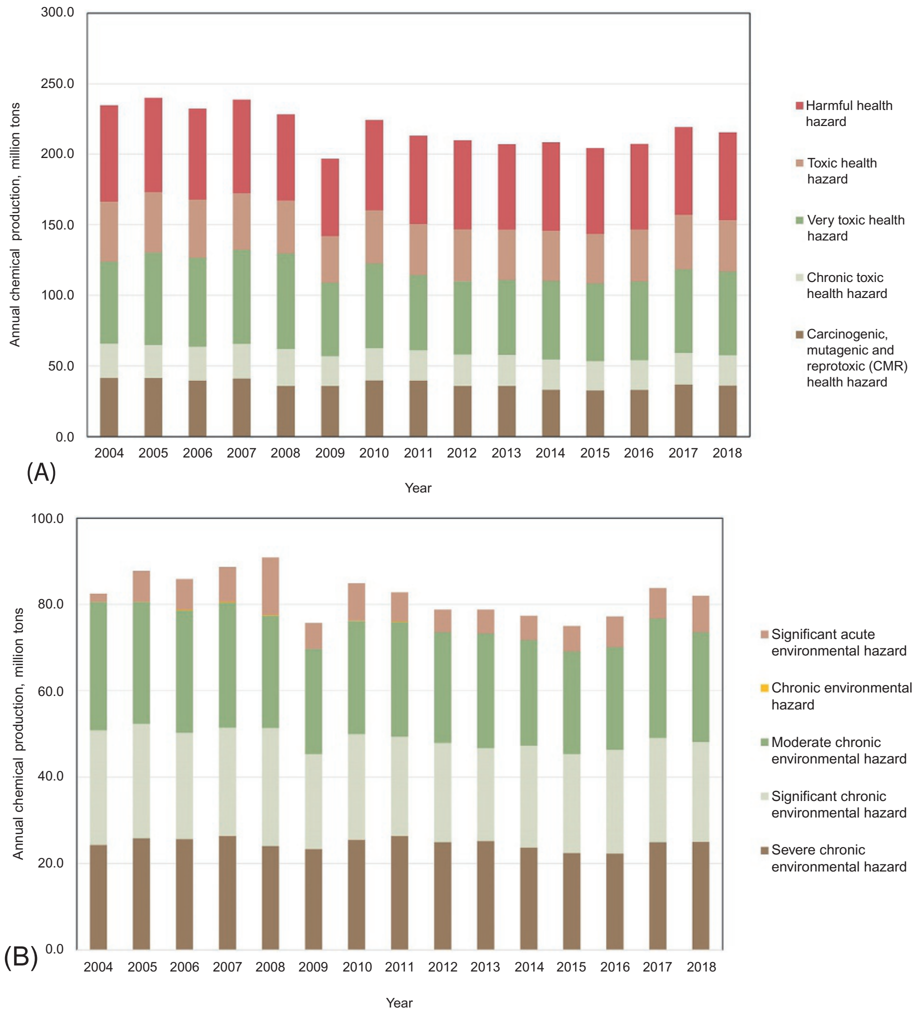

FIG. 7.1 Production of chemicals hazardous to (A) human health and (B) the environment in the European Union between 2004 and 2018 (Eurostat, 2020).

et al., 2016). Landfill leachate is often associated with the discharge of industrial chemicals such as flame retardants, plasticizers, and rare earth elements (Gwenzi et al., 2018). Hence, the contaminant profile in the effluent and runoff is often influenced by the source.

Emerging pollutants are ubiquitous in aquatic systems due to their diverse use in various anthropogenic activities (Table 7.1). There are more than 5000 pharmaceuticals in current use, of which 631 have been detected in freshwater systems across the globe (aus der Beek et al., 2016). The highest concentrations of pharmaceuticals reported in aquatic systems range from 30 to 6500 $\mu g\,L^{-1}$ (Hughes et al., 2013). In Europe, the Network of reference laboratories, research centers, and related organizations for monitoring of emerging environmental substances (NORMAN) detected more than 700 emerging pollutants in European aquatic systems (Dulio et al., 2018). Recently, the European Commission Joint Research Center identified more than 2700 emerging pollutants as priority contaminants in marine ecosystems. Previous studies detected antimicrobial and antiviral drugs in the Nairobi River Basin, Kenya (Ngumba et al., 2016) and surface water from a peri-urban area in Lusaka, Zambia (Ngumba et al., 2020). A study in western Kenya found 68 previously undetected emerging pollutants in freshwater systems with biocides and pesticides being the most frequently detected compounds (Kandie et al., 2020). In the Ikpa River Basin, Nigeria, bisphenol A, erythromycin, chloramphenicol, triclosan, and triclocarban were detected frequently and posed the highest risk to aquatic biota (Inam et al., 2015). However, there are fewer emerging pollutants detected in African and Latin American aquatic systems possibly due to the lack of advanced chromatographic and mass spectrometry equipment required for analyzing trace contaminants in complex environmental matrices rather than the lower discharge of emerging pollutants in aquatic systems (Madikizela et al., 2020).

TABLE 7.1 Examples of emerging pollutants frequently detected in aquatic systems.

Contaminant	Description	Environmental concern[a]	Main sources
Pharmaceuticals	• Continuous entry into the aquatic environment, low concentrations, impacting water supply in ecosystems and human health. Studies on its effects were recently initiated • Extensive use in human and veterinary medicine. Includes compounds such as antibiotics, analgesics, antidepressants, anti-diabetics, among others • The vast majority is excreted without metabolizing after its application, reaching the sewage. There is no complete elimination with water treatment	• Pose chronic and possible acute toxicity to aquatic organisms • Antibiotics promote the emergence and transmission of antibiotic-resistant bacteria and genes	Domestic wastewater; hospital effluent; livestock breeding; aquaculture
Personal care products	• Substances of common use for health, beauty, and cleaning purposes, such as cosmetics, soaps, perfume, tubes of toothpaste, shampoos, etc. Being used in day-to-day life, they have been detected in groundwater and wastewaters from both domestic and industrial sources • Do not undergo metabolic changes, so they are released more easily into water resources, causing an impact on groundwaters and urban runoff • The main entrance of this type of pollutants to water is in the effluents of the sewage treatment plants because many of these compounds cannot be completely degraded and are ultimately discharged into receiving water sources	• Pose chronic toxicity to aquatic organisms • Although PCPs can elicit a decline in aquatic wildlife populations, acute toxicity is highly unlikely	Domestic wastewater; landfills
Hydrocarbons	• Fires release polycyclic aromatic hydrocarbons, which enter the atmosphere and surface waters and sediments. They also reach water resources for untreated industrial wastewater, cooking, and combustion reactions of fossil fuels	• High toxicity, mutagenicity, and carcinogenicity	Industrial, biomass, and petrogenic combustion
Disinfection products	• Transformation products formed during tertiary wastewater treatment using chlorination, ozonation, or chloramination among other disinfection treatments	• Many disinfection byproducts are • mutagenic, cytotoxic, genotoxic, carcinogenic, or teratogenic	Domestic wastewater
Food additives	• Synthetic organic pollutants, including sweeteners, antioxidants, etc. Sweeteners are quite soluble in water and are found mostly in the water column. Antioxidants, on the other hand, are not water-soluble and are found in groundwater	• Ecotoxicological studies found sweeteners have low toxicity at environmentally relevant concentrations	Domestic wastewater
Fire retardants	• Chemicals are added to consumer products to meet the needs of fire retardation. These are water-soluble compounds found in some aquifers	• Accumulate primarily in the serum, kidneys, and liver, potential adverse effect on developmental, reproductive, and other systemic outcomes	Industrial and domestic effluent, firefighting discharges
Pesticides	• Compounds that control the spread of pests and diseases in crops; used in agriculture, forestry, horticulture, etc. At the time of application, these compounds reach the soil from rainwater or irrigation water washing. Once there, they can infiltrate into ground and surface waters	• Toxic to wildlife, marrow cells, carcinogenic, an association between childhood leukemia and for Parkinson's disease with pesticide exposure, toxic to earthworms	Agricultural and urban runoff

[a] *Environmental concerns were obtained from Besha et al. (2020).*

Data on description was obtained from Peña-Guzmán, C., Ulloa-Sánchez, S., Mora, K., Helena-Bustos, R., Lopez-Barrera, E., Alvarez, J., Rodriguez-Pinzón, M., 2019. Emerging pollutants in the urban water cycle in Latin America: a review of the current literature. J. Environ. Manage. 237, 408–423. doi:10.1016/j.jenvman.2019.02.100. Used with permission of Elsevier.

7.3 Route of entry of emerging pollutants into aquatic systems

The routes of entry into aquatic environments are influenced by the discharge mechanism and the physicochemical properties of the emerging pollutants. Industrial, municipal, aquaculture, mining, and concentrated animal feeding operations effluent often result in the direct discharge of emerging pollutants in aquatic systems. This type of aquatic pollution is called point-source pollution because emerging pollutants originate from a single discharge point. In contrast, nonpoint source pollution occurs when pollutants enter the environment through diffuse sources. Examples of nonpoint source pollution include agriculture runoff, aerial deposition, seepage, landfill leachate, and vehicle emissions. Point source pollution is easier to regulate, monitor, or mitigate compared to nonpoint source pollution (Malkoske et al., 2016). Environmental regulators often set maximum acceptable concentrations in industrial and municipal effluent. However, emerging pollutants are often not included in the list of regulated contaminants. Understanding the transport of pollutants in aquatic systems is essential for the development of effective aquatic pollution mitigation and monitoring strategies.

Aerial transport and deposition are the major pathways by which volatile and light emerging pollutants discharged from combustion, industrial flue gas, and pesticide spraying are transported into aquatic systems. The atmospheric deposition also known as aerial deposition involves the movement of emerging pollutants from the atmosphere directly to aquatic environments. Lake Ontario, Canada found aerial deposition was the dominant loading pathway for polychlorinated biphenyls (PCBs) contributing 66% of the total loadings (Melymuk et al., 2014). A flux of emerging pollutants from the atmosphere can be via dry or wet deposition. A wet deposition involves the deposition of particulate or dissolved particles in an aerial plume following precipitation. A study in France found deposition of microplastics increased five-fold following a precipitation event (Dris et al., 2015). In contrast, dry deposition occurs when particles in the aerial plume settle in aquatic environments due to gravity. In Los Angeles, dry deposition dominated the total potentially toxic elements that entered urban stormwater, with wet deposition accounting for 1–10% of the total aerial deposition (Sabin et al., 2005). The distance traveled by a pollutant is influenced by its volatility, atmospheric half-life, and molecular weight or density. Compounds with high volatility and long half-life can undergo long-range transport. For example, previous studies in France and China found aerial transport of microplastics could reach a maximum distance of 95 km (Allen et al., 2019). These results suggested aerial transport of microplastics could contribute to the pollution of remote freshwater or marine environments far from anthropogenic activities. Previous studies have shown that the accumulation of emerging pollutants such as lead and microplastics in the Arctic is mainly due to the Icelandic Low, North American High, Aleutian Low, and the Siberian High air masses (Outridge et al., 2008). A study in Lake Michigan found that deposition of particle-bound PCBs decreased by 90% when aerially transported for 40 km (Wethington and Hornbuckle, 2005). The high molecular weight of the PBDEs and PCBs favored gravitational sedimentation rather than aerial transport.

7.4 Processes influencing emerging pollutant fate and transport

Emerging pollutants often enter aquatic water bodies such as rivers, lakes, and the sea through surface water and groundwater. Surface waters include tributaries, agricultural runoff, and urban stormwater where emerging pollutants are in dissolved, suspended, or particle-associated phases. The profile of emerging pollutants transported by runoff or groundwater leaching is influenced by landscape ecology and physicochemical properties of the pollutant (Willis and McDowell, 1982). Briefly, high concentrations of pharmaceuticals and personal care products are often detected in aquatic systems proximal to urban areas while pesticides and antibiotics are frequently detected in agricultural areas (Müller et al., 2020; Patel et al., 2019). Previous studies demonstrated that pesticides with high solubility are transported in the aqueous phase by agricultural runoff into aquatic systems while compounds with low solubility are transported as sediments (Willis and McDowell, 1982). Emerging pollutants with a high octanol–water partition coefficient ($\log K_{OW} > 5.0$) readily partition from the aqueous phase to the solid particles. Hence, the influx of suspended particles and sediments into aquatic environments is an important loading pathway for hydrophobic substances. Additionally, microplastics are an important vector for the transport of organic pollutants in aquatic environments (Shi et al., 2020). In Lake Ontario, tributaries were more dominant ($1600 \pm 280\,\mathrm{kg\ y^{-1}}$, 71%) than aerial deposition (<10%) suggesting urban surface runoff was the main pathway for PAH loading (Melymuk et al., 2014).

The occurrence of emerging pollutants in aquatic systems is influenced by their discharge patterns and mechanisms, environmental transport, and transformation mechanisms, and biological uptake processes (Gavrilescu, 2005). Discharge patterns of emerging pollutants from domestic sources are often influenced by chemical usage patterns, precipitation patterns, wastewater treatment efficiency, water consumption, and population characteristics (Zhao et al., 2018). Overall, the processes that facilitate the delivery of emerging pollutants into aquatic systems control the discharge profiles while processes that facilitate the movement of emerging pollutants from the water column to solids (suspended particles and sediment) or aquatic biota control the removal and accumulation profiles (Gavrilescu, 2005). The persistence and mobility of emerging pollutants in aquatic systems are controlled by the following environmental processes: (i) transport processes; (ii) transfer processes; and (iii) transformation processes (Gavrilescu, 2005). The distribution (transfer and transport processes) of emerging pollutants in aquatic systems is primarily governed by the physical processes (Table 7.2). In contrast, the transformation of emerging pollutants is governed by the physicochemical and biological properties of the aquatic system (Table 7.3).

Biological uptake processes such as bioaccumulation in aquatic organisms (e.g., fish, mussels, and frogs) and plant uptake and translocation play a key role in the transfer of emerging pollutants from the water or sediment phase to biota. Aquatic biota such as bacteria and plants are important in the removal of emerging pollutants. In contrast, uptake in fish, frogs, and other higher-order organisms indicates the potential ecological risk by the emerging pollutants. Depending on the physicochemical properties of the pollutant, uptake processes are often followed by metabolism and elimination (reintroduction of the parent emerging pollutant or fresh introduction of transformation products). In recent years, this phenomenon has been leveraged in situ bioremediation techniques; for example, the use of constructed wetlands for removing emerging pollutants (Bi et al., 2019). There are four processes by which emerging pollutants are removed from aquatic systems by constructed wetlands: i) direct uptake of dissolved compounds via the cell membrane of vascular plant roots, bacteria, or algae followed by plant metabolism; ii) microbial transformation in the rhizosphere followed by the uptake of the transformation products; iii) sorption to biofilm; and iv) direct photolysis (Bi et al., 2019).

Biological uptake processes are influenced by the physicochemical properties of the emerging pollutant (e.g., lipophilicity, water-solubility, chemical stability, and polarity), the local environmental conditions (e.g., acidity, salinity, temperature, nutrients, suspended solids, and organic carbon content), and biological traits (e.g., feeding ecology, lipid content, depuration, and size). However, a hydroponic study comprising of free-floating and submerged plant species found that there was no significant relationship between the bioaccumulation behavior of 19 pharmaceuticals and endocrine-disrupting chemicals with their physicochemical properties (Pi et al., 2017). Triclosan and diphenhydramine readily bioaccumulated in the plant species while bisphenol A, warfarin, estrone, and 17β-estradiol had the lowest bioaccumulation potential (Pi et al., 2017). A field study investigating the removal of pharmaceuticals, plasticizers, perfluorinated compounds, illicit drugs, and metabolites found that only perfluorinated compounds had a significant relationship between physicochemical properties of the pollutant (i.e., hydrophobicity and alkyl chain length) and bioaccumulation behavior (Wilkinson et al., 2018). The observed trends are probably because perfluorinated compounds as analogs share similar functional groups and structural configurations.

7.5 Influence of physicochemical properties on the fate of emerging pollutants

7.5.1 Poly- and perfluorinated compounds

Poly- and perfluorinated compounds are ubiquitous in aquatic systems. They are widely used in industrial and domestic products due to their high thermal, solvent, and chemical stability. The chemical structure of poly- and perfluorinated compounds comprise hydrophilic functional groups such as sulfonates, sulfonamides, alcohol, or carboxylates and hydrophobic fluorinated alkyl chain. Fluorine substitutions shield the alkyl chain from chemical oxidation or reduction, hydrolysis, photolysis, acid–base reactions, and biotransformation. Hence, highly fluorinated poly- and perfluorinated compounds are more recalcitrant in aquatic systems than the less fluorinated poly- and perfluorinated compounds. Poly- and perfluorinated compounds with carboxylate groups have higher vapor pressure than those with sulfonate groups. Aerial deposition accounted for up to 10 times perfluorooctanoic acid discharge in seas compared to perfluorooctanesulfonic acid while perfluorooctanesulfonic acid accounted for up to 30 times riverine discharges to seas (Lindim et al., 2016). Hence, the ratio of perfluorooctanoic acid and perfluorooctanesulfonic acid concentrations is often used as a chemical marker of long-range transport of PFCs in the Arctic.

7.5.2 Brominated flame retardants

Physicochemical properties of brominated flame retardants vary widely among congeners due to differences in the degree of bromination and aromaticity. Highly brominated congeners have low volatility and solubility; thus, do not

TABLE 7.2 Factors influencing the transport and transfer processes of emerging pollutants in aquatic systems (Ding and Peijnenburg, 2013; Jinde, 1994; Pereira et al., 2016).

Property	Description	Environmental significance	Factors affecting the property		Examples	Reference
Solubility S, $\mu g\,L^{-1}$	Measure the number of emerging pollutants that can potentially dissolve in water	• Highly soluble chemicals readily partition to the aqueous phase. • Highly soluble chemicals have a low tendency to sorb on solids or bioaccumulate in aquatic organisms. • Highly soluble and volatile chemicals readily vaporize and undergo aerial transportation.	Polarity	Polar chemicals tend to dissolve readily in aqueous media while non-polar chemicals readily partition to non-polar media such as organic matter	Increasing the degree of bromination results in a decrease in the aqueous solubility of the PBDE congener	Kuramochi et al. (2007), Tittlemier et al. (2002)
			Hydrogen bonding	Helps less polar chemicals to be water-soluble due to the formation of the hydrogen bonds	About 1.3% DDT ($S=0.003$ ppm) partitions to the water column compared to 60.6% for lindane ($S=10$ ppm)	Jinde (1994)
			Molecular size	When molecules have the same polarity, an increase in size result in a decrease in solubility	Increasing the molecular size of C_{10}-C_{19} alkanes resulted in a decrease in water solubility due to an increase in the free energy penalty for the formation of a cavity in water	Tolls et al. (2002)
			Temperature, pH	An increase in temperature often increases solubility Changes in pH often affect the solubility of ionogenic compounds	Aqueous solubility of five anthranilic acid derivative drugs ($2.27 \leq pKa \leq 5.70$) increased with pH and temperature	Pobudkowska and Domańska (2014)
Octanol/water partition coefficient, log K_{OW}	Measures the tendency of a pollutant to the partition between an organic phase (e.g., fish tissue, suspended particle, soil, or sediment) and an aqueous phase	• Hydrophobic contaminants bioaccumulate and biomagnify in aquatic biota • Emerging pollutants with log $K_{OW} \geq 5.0$ are considered highly hydrophobic	Polarity	Polar molecules are often highly soluble and have a low tendency to partition to octanol; thus, have low log K_{OW}.	Most pesticides have lower polarity than water and tend to accumulate in sediment and biota.	Jinde (1994)
			General rule	An increase in molecular surface area, molecular weight, density, boiling point, and molar volume often increases log K_{OW}	Log K_{OW} values of perfluoroalkyl carboxylates are ~2 orders of magnitude higher than those of corresponding alkyl carboxylates with similar carbon chain lengths	Ding and Peijnenburg (2013)

Organic carbon/water partition coefficient, log K_{OC}	Measures the distribution of pollutants between an organic phase (soil, sediment, and organic matter) and the aqueous phase It is obtained by dividing the soil/sediment-water partition coefficient (log K_d) by the total organic carbon content	• Non-polar pollutants (high log K_{OC}) sorbed to sediments are less mobile than polar substances • Runoff and leaching occur when a pollutant does not strongly sorb to the soil • Organic matter plays a key role in the vertical transport of emerging pollutants in aquatic systems	Organic carbon content	Increase in organic carbon content may result in an increase in log K_{OC}	Sediment organic carbon was shown to be the dominant sediment-parameter affecting sorption of per and polyfluorinated alkyl substances	Ding and Peijnenburg (2013)
			Dissolved or suspended organic matter	An increase in organic matter increases in the number of sites available for sorption	Seasonal increase in discharge of suspended particles in estuaries is associated with an increase in loading of hydrophobic pollutants	Turner and Millward (2002)
			Polarity	Variations in the polarity of emerging pollutants are often due to functional groups	Sulfonate moieties in PFAS and PFOS added 0.23 log units to log K_{OC} compared to the carboxylate analogs	Ding and Peijnenburg (2013)
			Salinity	Salinity dependency of log K_{OC} is due to the competing and complexing effects between salts and pollutants and the salting-out of neutral solute	The log K_{OC} of metals often decreases with an increase in salinity, particularly in marine and coastal environments	Turner and Millward (2002)
Volatilization, flux, or half-life	It is the transport of a pollutant from water or a wet or dry surface into the atmosphere		Wind	Wind direction and intensity facilitate the aerial transport of volatile and semi-volatile pollutants	In the Yangtze River estuary, wind speed negatively correlated with PAH volatilization in winter but positively in summer	Jiang et al. (2018)
			Fetch	The presence of forests and buildings that slow airflow can reduce the aerial transport range of emerging pollutants	Air concentration of PBDEs, PCBs, and PAHs was lower in forest areas than in clearing. The filter effect is more pronounced for semi-volatile pollutants with $7 < \log K_{OA} < 11$ and $\log K_{AW} > -6$ compared to volatile pollutants	Barrett et al. (2019), Mclachlan and Horstmann (1998), Su et al. (2007)

Continued

TABLE 7.2 Factors influencing the transport and transfer processes of emerging pollutants in aquatic systems (Ding and Peijnenburg, 2013; Jinde, 1994; Pereira et al., 2016)—cont'd

Property	Description	Environmental significance	Factors affecting the property		Examples	Reference
			Temperature	An increase in temperature increases the vapor pressure of pollutants increasing volatilization	Selenium volatilization from a reservoir in California demonstrated significant seasonal variations, peaking during the summer months	Flury et al. (1997)
					Mercury volatilization in Swedish forest lakes increased by 2.5-times on average during daytime compared to night-time	Schroeder et al. (1992)
			Molecular properties	An increase in molecular weight often results in a decrease in volatility	TBECH and TBCO (molecular weight=427.8) have high vapor pressure than HBCD (molecular weight=641.7)	Marvin et al. (2011)
			Concentration	At high concentrations, more molecules are available to escape the water phase increasing volatility	Volatilization of low molecular weight PAHs (which had a higher concentration in water column compared to high molecular weight PAHs) in the Yangtze River Estuary was higher than that of the high molecular weight PAHs	Jiang et al. (2018)
Bioconcentration factor (BCF), log BCF	It determines the bioaccumulation potential by measuring the distribution of emerging pollutants between an aquatic organism and the aqueous phase	BCFs offer a quantitative approach for assessing the potential of a pollutant to be transported through the food chain	Polarity and solubility	Polar chemicals have low solubility in tissue while non-polar chemicals bioaccumulate	Bioaccumulation of PFSAs in rainbow trout was higher than PFCAs of the same perfluoroalkyl chain length suggesting the presence of the acid functional group affected the bioaccumulation potential	Martin et al. (2003)
			Lipid content	Hydrophobic pollutants accumulate in lipid-rich tissue	Hydrophobic organic contaminants readily bioaccumulate in lipid-rich blubber of cetaceans	Sanganyado et al. (2018, 2020a)
			Metabolism	Aquatic organisms metabolize xenobiotic compounds to increase their polarity to enhance elimination	Carp preferred meta-debromination of PBDEs, while trout and salmon equally meta- and para-debrominated the PBDEs	Roberts et al. (2011)
			Habitat	Environmental factors (e.g., salinity, pH, temperature, and concentration) influence the bioaccumulation of emerging pollutants in aquatic organisms	Increasing temperature from 7°C to 19°C increased the relative distribution of PFOS increased in blood, liver, and brain of adult rainbow trout while decreasing in muscle	Vidal et al. (2019)

TABLE 7.3 Factors influencing the transformation processes of emerging pollutants in aquatic systems (Ding and Peijnenburg, 2013; Jinde, 1994; Pereira et al., 2016).

Property	Description	Environmental significance	Factors affecting the property		Examples	Reference
Microbial transformation	• Biological processes whereby emerging pollutants are broken down by aerobic or anaerobic microbes to lower-molecular-weight chemicals	Is an important natural attenuation mechanism for emerging pollutants. It may result in the formation of more persistent or more toxic transformation products	Environmental factors	Physicochemical properties of the aquatic system influence the composition, abundance, and diversity of microorganisms involved in transforming emerging pollutants. Environmental factors also influence the speciation of emerging pollutants	Pharmaceuticals transformed rapidly in eutrophic waters but slowly in estuarine and coastal seawater	Benotti and Brownawell (2009)
			Molecular properties	Compounds with a high degree of halogenation and conjugation tend to be more recalcitrant	Microbial transformation of azo dyes by microorganisms isolated from coastal sediment was influenced by molecular weight and steric hindrance. The transformation rate of Methyl Orange (95%) was more than double that of the more sterically hindered and heavier Reactive Yellow 84 (<40%)	Zhuang et al. (2020a, b)
			Bioavailability	If a compound is strongly bound to sediments or particulates, it is less bioavailable for microbial transformation. Bioavailability is influenced by organic carbon content and log K_{OW} of the pollutant	Local environmental factors such as pH, redox potential, and salinity, and the molecular properties of a pollutant can influence their desorption, partitioning, microbial transformation, and oxidation of sediments	Eggleton and Thomas (2004), Fu et al. (2016)
Hydrolysis	• Involves the reaction of an emerging pollutant with water or another anion	This results in the formation of transformation products that are more susceptible to dissolution or biotransformation	Functional groups	Hydrolysis readily occurs when highly electronegative substituents are present	Alcohol groups that result from proton abstraction on N-mono substituted carbamate pesticides hydrolyze at significant rates	Stangroom et al. (2000)
			Temperature	An increase in temperature increases the rotational and translational energy of the pollutant molecules, thus increasing the hydrolysis rate	Hydrolysis rates for β-lactam antibiotics increased 2.5- to 3.9-times following a 10°C temperature increase	Mitchell et al. (2014)
			Particulates	Minerals and metals in aquatic systems can act as catalysts for the hydrolysis of emerging pollutants	The catalytic activity of minerals is associated with the identity of the cation as well as the charge of layers on the clay mineral. Mg-, Ca-, and Cu-hectorites and Cu-montmorillonite catalyzed the hydrolysis of azinphosmethyl while no catalytic activity was observed for Ca-nontronite and Ca montmorillonites	Stangroom et al. (2000)
			pH	Changes in pH affect the ionization of the pollutants	Increasing pH from 5 to 9 results in a significant increase in the	Jinde (1994)

Continued

TABLE 7.3 Factors influencing the transformation processes of emerging pollutants in aquatic systems (Ding and Peijnenburg, 2013; Jinde, 1994; Pereira et al., 2016)—cont'd

Property	Description	Environmental significance	Factors affecting the property		Examples	Reference
				which in turn affects the deprotonation or dehydroxylation reactions	hydrolysis of carbaryl (contains an amide linkage) from a half-life of 1230 d to 0.134 d	
					Hydrolysis rates for β-lactam antibiotics that were base-catalyzed were significantly higher than those that were acid-catalyzed or occurred at neutral pH	Mitchell et al. (2014)
Photolysis	• The breakdown of a chemical due to exposure to sunlight • Occurs in surface water, air, and sediments	Photolysis controls the emerging pollutants that are loaded to aquatic systems through the aerial deposition. Photolysis can result in the mineralization or transformation of the emerging pollutants. However, sometimes the transformation products are more toxic	Molar absorption properties	The presence and ability of functional groups or chemical structures to absorb solar radiation influences the degree of photolysis	Aromatic rings, conjugated π systems, heteroatoms, and other functional groups in pharmaceuticals promote the direct absorption of solar radiation in the UV-C, UV-B, or UV-A range, in descending order of prominence	Challis et al. (2014)
			pH and polarity	Changes in water pH altered the protonation state, absorbance spectrum, and ultimately the reactivity of ionogenic compounds.	Sulfamethoxazole underwent rapid photolysis in neutral, sulfamethizole and sulfathiazole preferred the anionic forms, and sulfisoxazole preferred the cationic form.	(Boreen et al., 2004)
			Meteorological factors	The light intensity can be influenced by time of the day, cloud cover, or water depth. Higher light intensities result in higher solar absorption	Climate change can affect photolysis by increasing surface water browning, alkalinity, summer stratification in lakes, flow velocity in rivers, and photobleaching. It can also reduce the ice cover period	Vione and Scozzaro (2019)
					Direct photolysis of bentazone was more prominent at a water depth of 0.015 m than at 3 m in natural surface waters	Carena et al. (2020)
			Particulates	Particulates are complex and dynamic and can cause photosensitize (indirect photolysis), screen light, scavenge, or oxidatively inhibit emerging pollutants in aquatic systems	Dissolved organic matter increased the photolysis rate of sulfonamides. However, aquatic DOM primarily mediated photolysis via DOM intermediates while terrestrial DOM promoted photolysis via reactive oxygen species	Challis et al. (2014), Remucal (2014)
					River Po had higher concentrations of hydroxyl and carbonate radicals due to agricultural activities in the watershed, and this contributed to higher pesticide photolysis rates	Carena et al. (2021)

favor partitioning to the atmosphere from aquatic systems. In addition, highly brominated congeners often have log $K_{OW} > 7.0$ suggesting a tendency to sorb to solids such as sediments or suspended particles. In addition, brominated flame retardants can bioaccumulate and bio-magnify aquatic organisms. For example, the log BCF of hexabromocyclododecane is 3.9–4.3 while for tetrabromoethylcyclohexane and tetrabromocyclooctane is 3.3 suggesting the latter are slightly within the regulatory threshold of 3.7 (Marvin et al., 2011). Brominated flame retardants undergo microbially mediated debromination in aquatic systems. The rate of debromination is often influenced by the degree of bromination, molecular weight, functional groups, bioavailability, and local environmental conditions.

7.5.3 Pharmaceuticals

Pharmaceuticals are a diverse group of compounds that are ubiquitous in aquatic systems. They are considered pseudo-persistent because despite normally having short half-lives ranging from days to months in freshwater and marine environments, pharmaceuticals are continuously discharged into the environment rendering them pseudo-persistent (Sanganyado et al., 2017). Pharmaceuticals often have low volatilities indicating that they distribute in the environment primarily through aqueous phase and food chain transport (Caliman and Gavrilescu, 2009). Many antibiotics such as sulfonamides have photoactive functional groups and conjugated structures that make them susceptible to photolysis. Ionogenic compounds such as β-blockers are mainly removed by biotransformation in sediment-water systems with sorption playing a minor role (Ramil et al., 2010; Sanganyado et al., 2016). However, the biotransformation rates are often influenced by the intrinsic properties (polarity, p*K*a, log K_{OW}, and functional groups) of the compound and external environmental conditions (e.g., pH, salinity, and temperature) (Patel et al., 2019). Natural attenuation of 14 neuro-active pharmaceuticals in streams showed that fluoxetine transformed rapidly with a half-life of 3.6 ± 0.3 h compared to carbamazepine (21 ± 4.5 h), while parent compounds were more persistent than their corresponding metabolites (Writer et al., 2013). Analysis of the pharmaceuticals and their metabolites in sediments and water column revealed natural attenuation was primarily due to the interactions between the pharmaceuticals and sediment bed or biofilm (Writer et al., 2013).

7.5.4 Personal care products

Personal care products are a diverse group of bioactive compounds that are used for improving the quality of life such as UV filters, synthetic musk fragrances, disinfectants, biocides, and cosmetics. Benzophenones are the most widely used and frequently detected UV filters in the aquatic environment. The presence of the methoxy group on benzophenones decreases their solubility from $1905\,\mathrm{mg\,L^{-1}}$ to $30.5\,\mathrm{mg\,L^{-1}}$ for 4,4′-dihydroxybenzophenone and BP-6, respectively (Mao et al., 2019). As expected, the log K_{OW} correspondingly increase from 2.19 to 3.90. Benzophenones are less likely to be lost through volatilization as they have high boiling points (around 400°C) and low vapor pressures (around 3.44×10^{-10} to 6.62×10^{-6} mmHg) (Mao et al., 2019). Indirect photolysis, mediated by photosensitizers (e.g., NO_3^-/NO_2^-, co-solutes, and natural organic matter), plays a key role in the natural attenuation of benzophenones in aquatic systems. Besides cashmeran, which has a solubility of $5.94\,\mathrm{mg\,L^{-1}}$, synthetic musks are generally slightly soluble with solubilities below $1.0\,\mathrm{mg\,L^{-1}}$ (Liu et al., 2020). Synthetic musks are semi-volatile and can partition to air from aquatic systems (Liu et al., 2020). They have a low potential for long-range transport since they rapidly undergo photolysis with half-lives within the tens of hours range (Wong et al., 2019). Synthetic musks are highly hydrophobic compounds and have been shown to have a high potential to partition to sediments and suspended particles or accumulate in biota.

7.5.5 Geogenic and natural pollutants

Although geogenic elements occur naturally in the environment, anthropogenic activities increase their discharge into aquatic environments. Numerous studies have detected metals, metalloids, radionuclides, and rare earth elements (potentially toxic elements) in sediments, suspended particles, and surface waters above natural levels (Gwenzi et al., 2018; Ma et al., 2019; Zhuang et al., 2019). Potential toxic elements in aquatic systems are distributed in pore water, weakly adsorbed, associated with carbonates, oxides, and sulfides, complexed by organics, and in mineral lattices (Väänänen et al., 2018). These potential toxic elements exist as free ions, inorganic complexes, organic complexes, and chelates. The nature of the metal speciation or association influences their mobility. Lattice-associated elements are the least mobile while free ions are the most mobile. However, organic elements such as methyl mercury have a higher potential to bioaccumulate in aquatic organisms. In addition, complexation with organic matter enhances the bioaccumulation potential of potentially toxic elements (Fernando, 1995). Besides inorganic pollutants, there hundreds of organic pollutants of natural origin that have been detected in aquatic environments. Examples of natural organic pollutants include methoxylated PBDEs that have been detected in marine sediments (Aznar-Alemany et al., 2019).

7.5.6 Engineered nanomaterials

Nanomaterials are increasingly used for industrial, domestic, agricultural, and medical applications. They are classified as nanoparticles, nanofibers, and nanoplates and comprise metals, metal oxides, carbonaceous nanomaterials, semiconductors, nanopolymers, emulsions, and nanoclays. The mobility and persistence of nanomaterials in aquatic systems are governed by physical, chemical, and biological processes as shown in Fig. 7.2 (Batley et al., 2013). Examples of the physical processes include surface coating formation and wear, aggregation, agglomeration, deposition, and resuspension while chemical processes include complexation, redox reactions, and sulfidation (Peijnenburg et al., 2015). Uptake of nanomaterials has been reported in several aquatic species such as mussels (Petersen et al., 2009), daphnia (Petersen et al., 2009), freshwater algae (Rhiem et al., 2015), and fish (Laux et al., 2018). A previous study found that CeO_2 nanomaterials adsorbed to phytoplankton via electrostatic attraction between the pollutant and phytoplankton cell wall and not via active uptake (Bacchetta et al., 2017). Since nanomaterials tend to undergo aggregation and agglomeration and sink to the sediments, they present a greater risk to benthic organisms rather than pelagic organisms (Laux et al., 2018). Additionally, inorganic nanomaterials often occur in aquatic systems as charged or neutral compounds which might influence the proportion that undergoes bioaccumulation. A previous study on uptake of ZnO nanoparticles in freshwater crustaceans (*Ceriodaphnia dubia*) showed that charged nanomaterials contributed less to toxicity and bioaccumulation than the uncharged fraction (Bhuvaneshwari et al., 2016). Microbial transformation of nanomaterials involves the breakdown of capping agents or their phase transfer. Since nanomaterials have high adsorption capacities, they often act as vectors for organic pollutants which sorb on their surfaces (Peijnenburg et al., 2015). However, the adsorption of organic pollutants on nanomaterials alters the hydrophobicity and surface charge of the nanomaterials. Such physicochemical changes affect the mobility and fate of the nanomaterials in aquatic systems.

7.5.7 Implications of chirality on fate and transport

More than 50% of pharmaceuticals and 30% of pesticides are chiral compounds (Sanganyado, 2020). Enantiomers of chiral compounds often have different properties in chiral environments such as biological systems. Hence, previous

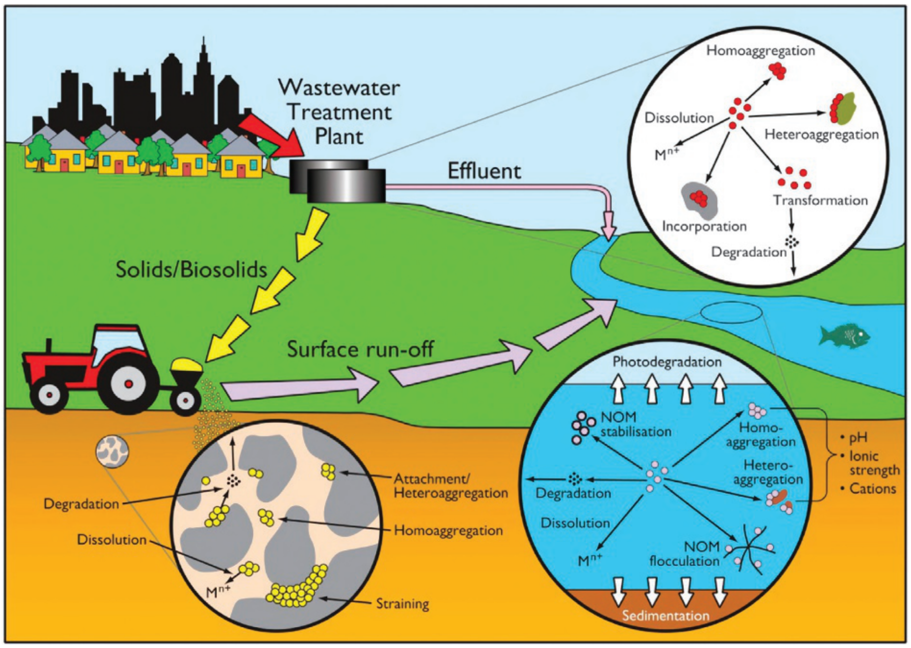

FIG. 7.2 Pathways and transformations of nanomaterials in the environment. *From Batley, G.E., Kirby, J.K., McLaughlin, M.J., 2013. Fate and risks of nanomaterials in aquatic and terrestrial environments. Acc. Chem. Res. 46, 854–862. doi:10.1021/ar2003368. Copyright 2012 by the American Chemical Society.*

studies have shown that the microbial degradation of chiral pollutants in aquatic systems often favors one enantiomer over the other (enantioselectivity) (Petrie et al., 2018). It was previously assumed that adsorption in aquatic systems was not enantioselective (Kasprzyk-Hordern, 2010; Wong, 2006). However, few studies have shown that the adsorption of pharmaceuticals and estrogen compounds on organic matter and chiral mineral surfaces was enantioselective (Sanganyado et al., 2016). A previous hydroponic study found that the plant metabolism of the pesticides tebuconazole and imazalil in *Phragmites australis* (a plant species widely used in constructed wetlands) was enantioselective while only the plant translocation of imazalil was enantioselective (Lv et al., 2017). However, plant uptake was found to be not enantioselective for both pesticides. Understanding the role of chirality on the mobility and persistence of emerging pollutants is imperative because enantiomers often exhibit different toxicities. For example, (*R*)-atenolol exhibited higher toxicity to *Tetrahymena thermophile* (protozoan) while its antipode (*S*)-atenolol had higher toxicity to *Pseudokirchneriella subcapitata* (microalgae) (De Andrés et al., 2009).

7.6 Current approaches in assessing the fate of emerging pollutants

Quantitative assessment of the environmental fate of emerging pollutants is a crucial step in environmental risk assessment. Environmental fate in aquatic systems is often determined using field studies or laboratory microcosm experiments. In field studies, samples are collected over time and space to determine the transfer and transformation of the emerging pollutants. For example, previous studies evaluated the removal of emerging pollutants in a river by determining the levels of the contaminants along the river. Sometimes the changes in concentration of emerging pollutants in a specific parcel of water in a river can be sampled using Lagrangian sampling design (Brown et al., 2009; Writer et al., 2013). Lagrangian sampling allows for accurate quantification of the reactivity of the emerging pollutants along with the various segments of the river. Laboratory experiments are more controlled and can be used to determine the mechanisms of fate processes as well as assess the influence of several factors such as local environmental factors, biological traits, or physicochemical characteristics of the pollutants (Schwientek et al., 2016). In recent years, the chiral nature of pollutants has been leveraged as a marker of biological transformation since oftentimes abiotic processes are not enantioselective. Changes in enantiomeric composition over time and space were considered to indicate the presence of microbially mediated transformation (Sanganyado et al., 2017). However, such use of enantioselective analysis requires validation to determine whether abiotic fate processes are indeed not enantioselective (Sanganyado et al., 2020b). Since the physicochemical properties play a critical role in the emerging of pollutants, in silico approaches using quantitative structure-activity relationships have been developed for estimating environmental fate in aquatic systems. The United States of America Environmental Protection Agency developed the EPI (Estimation Programs Interface) Suite while the OECD has the QSAR Toolbox.

7.7 Conclusion and outlook

The discharge of emerging pollutants in aquatic environments continues to increase globally due to increases in urbanization and industrialization. The mobility and transformation in aquatic environments are influenced by the physicochemical properties of the emerging pollutants and the local environmental conditions. Emerging pollutants are highly diverse and include highly volatile compounds such as industrial solvents, polar such as pharmaceuticals, hydrophobic such as PBDEs, and slightly soluble such as organic UV filters. Hence, understanding the environmental behavior and fate of emerging pollutants should remain a priority to improve environmental risk assessment.

Hundreds of unregulated new chemicals are introduced to the market each year. The environmental fate, transport, and toxicity of these chemicals are often unknown (see Tavengwa et al., 2022, Chapter 20). Quantitative structure–activity relationships are a valuable tool for predicting the fate and transport of contaminants. Future studies should incorporate machine learning to better predict the behavior of new chemicals. In addition, there has been an increase in the use of nanomaterials in the past two decades. However, the effect of nanomaterials on the mobility and persistence of chemical pollutants remains poorly understood.

The development of high-resolution mass spectrometers and multi-dimensional chromatography has made it possible to identify non-target and suspect contaminants in complex environmental matrices. At present, non-target and suspect screening is used to identify transformation products in aqueous systems. However, the technique has the potential to identify the transformation pathways of emerging pollutants. Understanding the transformation pathway is essential for determining if the fate processes result in detoxification of the emerging pollutants or otherwise. Overall, predicting the environmental behavior and fate of emerging pollutants and determining their transformation pathways will help in developing pollution mitigation strategies. This chapter falls under the section on fate and occurrence of emerging pollutants within aquatic ecosystems with other chapters, e.g., Ajayi et al. (2022), Cristale (2022), Vizioli et al. (2022), Galhardi et al. (2022), Hashemi and Kaykhaii (2022), Madikizela et al. (2021), Mashile et al. (2022), Montagner et al. (2022), Moodley et al. (2022), Ntshani and Tavengwa (2022), Sanganyando and Kajau (2022), and Yardy et al. (2022).

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CHAPTER

8

Remediation of emerging pollutants through various wastewater treatment processes

Geaneth P. Mashile, Shirley K. Selahle, Anele Mpupa, Azile Nqombolo, and Philiswa N. Nomngongo

8.1 Introduction

Over the years, the major interest has been on the impact that chemicals have on the environment with an emphasis on; heavy metals, polycyclic aromatic hydrocarbon, flame retardants (Cristale, 2022, Chapter 16), pesticide product active ingredients (Montagner et al., 2022, Chapter 12) and other emerging organic pollutants (Boxall et al., 2012; Vizioli et al., 2022, Chapter 14; Galhardi et al., 2022, Chapter 17; Hashemi and Kaykhaii, 2022, Chapter 15; Madikizela et al., 2022, Chapter 10; Moodley et al., 2022, Chapter 13; Ntshani and Tavengwa, 2022, Chapter 11; Sanganyando and Kajau, 2022, Chapter 7; Yardy et al., 2022, Chapter 9). Emerging organic pollutants (EOPs) is a term used to classify a group of chemicals that fall out of the standard monitoring and regulatory programs (Glassmeyer et al., 2008; Tavengwa and Dalu, 2022, Chapter 1). These chemicals have a wide range of water solubilities and environmental persistence (Glassmeyer et al., 2008). The word “emerging” usually leads to a misinterpretation that indicates that the chemicals’ present in the environment is new, whereas it is an indication that the chemical has recently gained the interest of scientific communities (Alvarez et al., 2005). These pollutants often include mixtures of a new generation of surfactants, pesticides, dyes, pharmaceuticals, and personal care products (Alvarez et al., 2005).

Per- and polyfluoroalkyl substances (PFAS) represent a group of organic anthropogenic compounds which were first produced in the late 1940s (Ivanković and Hrenović, 2010). Perfluorooctane sulfonate (PFOS) and perfluoroctanoic acid (PFOA) are the two most well studied PFAS (Ghisi et al., 2019), which have been detected worldwide in a variety of environmental compartments, such as surface water, drinking and groundwater, soils and sediments (Ivanković and Hrenović, 2010; Rahman et al., 2014; Kucharzyk et al., 2017; Feng et al., 2019; Gagliano et al., 2020; Pan et al., 2020). Due to their amphiphilic properties and preferential binding to proteins, PFAS have also been found to be the most prevalent contaminants in wildlife throughout the world, presenting clear, potential hazards to human health (Jardak et al., 2016; Banks et al., 2020). These compounds are considered highly toxic, extremely persistent in the environment, and with the potential to bioaccumulate and bio-magnify through the food chain (Palmer and Hatley, 2018). Results from in vivo and in vitro studies showed that PFAS can exhibit reproductive, developmental, hepatic, neurological, immunosuppressive, and endocrine disruptive toxicity in laboratory animals (Letcher et al., 2020). Although studies of toxicological effects on humans are still limited, they have been linked to obesity, cancer, and immune suppression in children (Palmer and Hatley, 2018; Kaczerewska et al., 2020).

There are over 500 known different pesticide formulations used as agrochemicals (Malik et al., 2017). The term pesticide refers to any substance or mixture whose primary use is to repel or destroy or pest (Sindhu et al., 2016). Usage of pesticides has aided the agricultural industry with increasing crop production and protection. The discovery of pesticides in the environment however has caused concern over the use of pesticides. This is because; pesticides have been overused in aquatic environments which lead to serious hazard to the organism such as fish (Mahmoud et al., 2016). Ineffective administering of agricultural processes can lead to contamination of soil and groundwater by nutrients and pesticides (Ntow and Botwe, 2012). Pesticides are widely used in agriculture because of their effective ability to control

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pests and they are usually transported into soil and groundwater, where they go through a variety of conversions that give a complex pattern of metabolites. The percolation of pesticides into the soil and groundwater can be reached by adsorption and infiltration (Feo et al., 2010). The latter is more conventional and exemplifies a strong source of environmental contamination (Tiryaki and Temur, 2010). Therefore, due to the toxicity of pesticides and their ability to accumulate in soil and groundwater, they have been connected to an extensive variety of human wellbeing dangers, varying from short-term impacts such as headaches and nausea to chronic impacts like cancer, reproductive harm, and endocrine disruption (Bedendo and Carasek, 2010).

The main source of organic and synthetic dyes in wastewater is the textile industries as they generate high concentrations of dyes, organic matter, and suspended solids and, these products are said to have toxic effects in both humans and aquatic organisms (Kaykhaii et al., 2018). Dyes can be categorized as either basic, reactive, acidic, direct, or as metal complexes. These organic dyes are not easily degradable due to their xenobiotic properties, and complex structure like MB dye which is used in dying cotton, silk, and wool but it turns to be harmful to human beings as it causes mental confusion, nausea, and eye damage (Widodo et al., 2018).

Pharmaceutical and personal care products (PPCPs) are a class of emerging micro-pollutants that are environmentally persistent, bioactive, and can accumulate in aquatic life (Juliano and Magrini, 2017). They are classified as emergent contaminants despite being present in our daily lives for decades (Bernal et al., 2019). However, a few years ago their presence in nature was specifically confirmed in aqueous environments (Arrubla et al., 2016). PPCPs may include drugs, cosmetic ingredients, dietary supplements, and products for metabolism (Esplugas et al., 2007). Thus, diverse types of PPCPs have been detected in various water bodies, which have raised global concern concerning environmental and human health complications (Al Aukidy et al., 2012). The major source of these micro-pollutant emissions into the environment are sewages, aquaculture facilities, runoff from fields, and soils through sludge and manure applications. They are often detected at ranges from ng/L to μg/L in WWTP effluents and downstream surface waters (Kasprzyk-Hordern et al., 2009). Moreover, the number of PPCPs discharged into receiving waters is dependent on factors such as WWTPs processes, physicochemical properties of the substances, and climatic conditions (Juliano and Magrini, 2017).

Mechanisms such as sorption, biodegradation, volatilization, and photooxidation (Carballa et al., 2005) have been used as conventional methods in WWTPs. However, their effectiveness depends highly on the properties and chemical structure of each substance (Ternes et al., 2004). In addition, the use of conventional methods like coagulation and filtration used for drinking water processes are not effective in the removal of emerging pollutants from the source water (Zwiener and Frimmel, 2000). The disinfectants used in the drinking water treatment such as chlorine, monochloramine, permanganate, ozone, and UV can only remove some and not all EOPs (Benotti and Brownawell, 2009). One example is the use of chlorination which degrades sulfamethoxazole almost completely but cannot do the same to carbamazepine (Stackelberg et al., 2004).

Though shown to be detected in surface waters throughout the world, relatively little is known about the fate and full toxicity of EOPs (Juliano and Magrini, 2017). Therefore, there is a need for more studies on their occurrences, persistence, distribution, and especially the mitigation of EOPs in wastewater. This is most important because the majority of wastewater treatment plants release their effluents into neighboring water systems.

8.2 Occurrence and impacts emerging pollutants

Municipal wastewaters around the globe contain many organic compounds which include active ingredients surfactants, pesticides, dyes, pharmaceuticals, and personal care products utilized in large quantities worldwide (Arrubla et al., 2016). Thus, thenceforth these groups of chemicals are collectively referred to as EOPs (Bartelt-Hunt et al., 2009). Due to their continuous release into the aquatic environment as they are being utilized in large amounts, EOPs are environmentally persistent, bioactive, and can bioaccumulate (Brausch and Rand, 2011). These EOPs are introduced directly or indirectly into water systems through anthropogenic sources that include but are not limited to wastewater effluents, treated sewage sludge, industrial effluents, aquaculture, and animal feedlots (Luo et al., 2014). Thus the top priority globally concerning these pollutants has been their safety toward the environment and aquatic life (Zulaikha et al., 2015).

Even though these emerging pollutants occur in trace concentrations which range from ng/L to several μg/L, their diversity and low concentrations not only complicate their associated detection and analysis but also pose problems to the water and wastewater treatment processes (Luo et al., 2014). This is because current wastewater treatment plants (WWTPs) are not properly equipped or designed to eliminate emerging micro-pollutants (Floer Miller, 2011). Due to such circumstances, many types of EOPs can infiltrate through wastewater treatment processes by their persistency/continued introduction (Bartelt-Hunt et al., 2009). The amount and type of EOPs discharged depends on the affluence of the society as the wealthier the society, the higher the consumption thereof (Archer et al., 2017). Moreover, those EOPs which resist the treatment processes commonly used in WWTPs or any other transformation which can occur in the environment can end up in surface and groundwater as well as in sediments and rocks (Liu and Wong, 2013).

Wastewater treatment plants are the main source of EOPs residues (Miege et al., 2010) as a result of them generally designed to remove only organic matter and nutrients and the use of conventional activated sludge (CAS) without taking into account emerging organic pollutants (Andrade-Eiroa et al., 2016; Al Aukidy et al., 2012). As a result, these compounds are not eliminated from the treated wastewater (Park et al., 2017). The biological treatment method is the most common and inexpensive method used in wastewater treatment (Subedi et al., 2015). In this treatment, the substances are biodegraded by bacteria and fungi contained in "activated sludge" cultivated to break down organic matter (Park et al., 2017; Pawe et al., 2017). However, the rate of biodegradation in activated sludge is low for most compounds, despite being the most effective process for removing EOPs in wastewater (Chen et al., 2015). Besides the biodegradation methods which are biological processes, other chemical methods are also involved in the goal to eliminate EOPs from wastewater such as sorption, coagulation coupled with dissolved air flotation (DAF) (El-Gohary et al., 2010), advanced oxidation processes (AOPs) (Paucar et al., 2019; Wang and Wang, 2016), volatilization, and photo-transformation (de Melo et al., 2013). However, volatilization and photo-transformation are not considered in WWTPs (Stevens-Garmon et al., 2011; Trinh et al., 2016). In addition to the treatment processes, other advanced biological methods introduced over the years include membrane reactors (Friha et al., 2014), mixed anaerobic-aerobic processes (Nie et al., 2012), anaerobic reactors (Puyol et al., 2011), and membrane bioreactors (Park et al., 2017).

8.3 Wastewater treatment processes for the removal of emerging pollutants

Promising alternatives for the elimination of PPCPs, dyes, surfactants, and pesticides in WWTPs include the membrane filtration processes such as nanofiltration (NF), reverse osmosis (RO) (Yoon et al., 2010), ultrafiltration (UF), and microfiltration (Yoon et al., 2006; Yang et al., 2017b). Despite these processes' proven abilities, their removal performance is relatively poor due to the pore size which is considerably larger than the PPCPs molecules (Yang et al., 2017b). Consequently, the adsorption method offers better removal performance due to the wide range of adsorbents used with high surface areas (provide more active sites).

8.3.1 Adsorption technology

Adsorption makes us of adsorbent materials such as carbonaceous materials (Rodriguez et al., 2016), zeolites (Sun et al., 2017), metal-organic frameworks (Yang et al., 2017a), and bio-sorbents (Xu et al., 2009). The most used materials for EOP adsorption are carbon-based materials. This is because they have been shown to have high adsorption capacities for emerging pollutants (Ek et al., 2014). Adsorption is effective for the adsorption of a multiclass of emerging pollutants. For example, Varga et al. (2019) showed the use of activated carbon for the removal of pharmaceuticals with adsorption capacities between 50 and 80 $\mathrm{mg\,g^{-1}}$. Granular activated carbon has been explored by Delgado et al. (2017) for the adsorptive removal of pharmaceuticals and personal care products with adsorption capacity 142 and 323 $\mathrm{mg\,g^{-1}}$ and adsorption time of 168 h. Carbon-based adsorbents have also been used for various emerging pollutants such as surfactants (Wang et al., 2018), dyes (Munagapati et al., 2020), and pesticides (Suo et al., 2019). The versatility of adsorptive removal is primarily based on the different sorbent materials. These include the use of cross-linked β-cyclodextrin-containing (β-CD) polymer adsorbents for the removal of PFAS and PFOA. The results obtained by Yang and colleagues (Yang et al., 2020a) showed that amine-based adsorbents were superior in the removal of 10 anionic PFAS and perfluoro(2-methyl-2-oxahexanoic) acid (GenX) while amido-based sorbent showed high affinity toward the removal of PFOA. The adsorption capacities of the amido based adsorbent toward GenX and PFOA were 222 $\mathrm{mg\,g^{-1}}$ and 457 $\mathrm{mg\,g^{-1}}$, respectively. Up to 96% removal of PFAS were achieved and the residual concentrations in solution were below the established health advisory level for PFOA and PFOS set by the EPA (70 ng/L). Lastly, the authors observed that the removal efficiency of longer chain derivatives was between 60% and 75%. Another study reported by Ateia et al. (2019), in the poly(ethylenimine)-functionalized cellulose microcrystals sorbent for the removal of different classes of PFAS. The results obtained showed that the adsorbent was more suitable for the removal of longer chain PFAS. Further studies on the removal of PPCPs, surfactants, organic dyes, and pesticides are summarized in Table 8.1, the reported adsorbents showed high adsorption capacities for the targeted analytes.

8.3.2 Advanced oxidation processes (AOP)

Advanced oxidation processes (AOP) include processes, such as ozonation, UV, photocatalysis, and Fenton reaction (Yang et al., 2017b). These have been used for the treatment of drinking water (e.g., odor/taste control and disinfection) and sometimes in wastewater disinfection (Klavarioti et al., 2009; Gerrity et al., 2010). However, AOPs can change the polarity and functional groups of some target pollutants (Papageorgiou et al., 2014; Margot et al., 2013). Therefore,

TABLE 8.1 Summary of removal of EOPs by various sorbents.

Analytes	Adsorbent	Adsorption capacity ($mg\,g^{-1}$) or removal efficiency (%)	References
Ibuprofen (IBP)	Carbon cloth (CO)	492	Guedidi et al. (2017)
Carbamazepine (CBZ), Paroxetiro, Sulfamethoxazole	Magnetic AC from paper mill sludge	209, 407, 47–407	Silva (2019)
Carbamazepine	AC biochar from pomelo peel	287	Chen et al. (2017a)
Carbamazepine	Magnetic Activated carbon	183	Baghdadi et al. (2016)
Carbamazepine (CBZ) and Ciprofloxacin (CPX)	AC-F400, MWCNTs, carbon nanofibers	242, 264	Álvarez-Torrellas et al. (2017)
Atenolol	Granular activated carbon	4.0	Haro et al. (2017)
Methyl-, ethyl-, and propyl-paraben	MG-mSiO_2-Ph composites	98.4–106	Feng et al. (2016)
Atenolol	Graphene oxide	55.49	Kyzas et al. (2015)
Propranolol	Graphene oxide	42.48	Kyzas et al. (2015)
Tetracyclines, quinolones, and penicillin	Activated carbon	1341, 639, and 570	Ahmed (2017)
Naproxen, gembrozil, ibuprofen	Magnetic nanoparticles coated zeolites	95	Salem Attia et al. (2013)
Reactive Red 141 and Reactive Yellow 14	Magnetic chitosan	98.8 and 89.7	Jaafari et al. (2020)
Basic blue 41	Pistachio shell	41.77	Şentürk and Alzein (2020)
Alizarin dye	Maghemite iron oxide	23.2	Badran and Khalaf (2020)
Reactive Black 5	Chemically modified banana peel powder	211.8	Munagapati et al. (2020)
Rhodamine B	MOF-MBC	55	Navarathna et al. (2020)
PFOS	Magnetic fluorinated Vermiculite	166–1127; 98	Du et al. (2017)
Monocrotophos	PEI-modified cotton and PEI-modified wool	333.3 and 500	Abdelhameed et al. (2018)
Prothiofos and ethion	ZIF-8 and ZIF-67	366.7 and 261.1 279.3 and 210.8	Abdelhameed et al. (2019)
Profenofos	Roasted date pits, activated date pits and nano-activated date pits	14.49, 4.38, 370.4	Hassan et al. (2020)
Pentachlorophenol	Chitosan (CHT) (I) with 2-hydroxy-1-naphthaldehyde. Functionalized chitosan CHTA was $CuCl_2$ to prepare CHTAC	39.1, 35.4, 24.4	Shankar et al. (2020)
Pyraclostrobin	Mesoporous activated carbon	66.2	Suo et al. (2019)

AOPs are preferred for recycled water purposes that include direct contact with humans, i.e., household wastewater reuse applications (Leal, 2010). For instance, Xu et al. (2020b) developed an AOP system based on a carbon sphere modified with bismuth phosphate composite photocatalyst (BiOHP/CS) for the removal of PFOA in water. The effectiveness of the BiOHP/CS indicated 200 μg/L of PFOA was adsorbed completely in 2 h and full in situ decomposition of the adsorbed PFOA with over 32.5% of fluorine converted to fluoride. Qanbarzadeh et al. (2020) reported the efficiency of UV/$Bi_3O(OH)(PO_4)_2$ photocatalyst on the degradation of perfluoro carboxylic acid. The results showed that up to 99% degradation of long-chain PFCAs was achieved within 60 min. Sahu et al. (2018) reported the application of novel $Bi_3O(OH)(PO_4)_2$(BOHP) catalyst for degradation and mineralization of PFOA under UV radiation.

Other studies have indicated WWTPs designed with AOP systems can further emerging and caffeine, were removal efficiencies of 84.2%, 92.2%, and 89.5%, respectively (Lin et al., 2016). A pilot-scale study performed in a WWTP was previously conducted (Borikar et al., 2015). The results revealed that conventional WWTPs that had either ozone/H_2O_2 or UV/H_2O_2 showed great improvement for PPCP removal from 26% to 97% or 92%, respectively. Among tested PPCPs, naproxen, carbamazepine, gemfibrozil, fluoxetine, and TCS showed almost complete removal. Moreover, ibuprofen and diclofenac removal were also up to 98% and 97% respectively. Despite this, some pharmaceuticals showed some resistance; 88% of atorvastatin was the highest removal that could be achieved. An investigation performed by Fast (2015) for holistic analysis involving a ranking system, was used to determine the performance of various AOPs. This report showed H_2O_2/ozone to have the highest average ranking in decreasing the amounts of PPCPs. Furthermore, the performance was significantly enhanced when oxidation processes were coupled with other unit processes. An investigation by Česen et al. (2015) showed that removal rates of up to 94% for ifosfamide (IF) and 99% for cyclophosphamide (CP) were obtained by utilizing UV/O_3/H_2O_2 system with 5 g/L of H_2O_2 for 120 min. A combination of AOPs with treatments such as biological treatment further enhanced the removal rates of CP and IF to ˃99%. A study conducted by Česen et al. (2015) showed that coupled processes where UV radiation with specific parameters and nanofiltration were combined were highly effective, with removal rates of >80% in most experiments being achieved. However, certain reports recently noted significant concern with regards to the use of AOPs for the removal of PPCPs. These were noted by Huang and Liu (2015) where they proved that certain PPCPs products formed from oxidation products like ibuprofen produced significantly high risks for acute toxicity than the concerned parent chemical. Moreover, Yang et al. (2016) analyzed the performance of UV/chlorine and UV/H_2O_2 processes for degradation of PPCP residues in water purification after they had been filtered by sand. Other AOP systems have been developed for the photo-degradation of dyes and surfactants. Oxidation processes for various pollutants (PPCPs, dyes, surfactants, and pesticides) and their corresponding performances are summarized in Table 8.2.

8.3.3 Removal by biological technologies

The removal of PPCPs by biological technologies has been considered as an ideal approach due to ease in operation and less energy consumption during the process (Onesios et al., 2009). This process requires that for the biological transformation of PPCPs using microbes for removal, a primary substrate must be present for the corresponding bacteria to grow on (Miege et al., 2010). In some instances, PPCPs are used by the bacteria as an energy or carbon source, therefore, mineralizing them completely. PPCPs removal in biological systems is based on treatment performance, efficiency, and the use of processes such as sorption, biological degradation, plant uptake, among others. Moreover, the efficiency of conventional biological treatment processes in degrading PPCPs is highly dependent on seasonal variations. Furthermore, biological treatment processes where sludge is used are said to cause secondary contamination (Banerjee et al., 1997). Therefore, treatment of secondary pollution is a significant step when using biological technologies for the removal of PPCPs (Banerjee et al., 1997). In addition, it does not show reasonable performance where persistent contaminants are involved due to certain persistent contaminants being highly toxic to microorganisms and have high resistance.

Biological removal of emerging pollutants is considered as another approach, this is due to its reduced energy consumption and ease of operation (Onesios et al., 2009). This treatment method is based on the biological transformation of EOPs using microbes and is dependent on a suitable growth substrate for the bacteria (Miege et al., 2010). Generally, the pollutants are used as an energy or carbon source b the growing microbes, thus mineralizing them (Banerjee et al., 1997). Biological processes are not only based on microbe degradation, but it also includes processes such as sorption, plant uptake among others (Banerjee et al., 1997). The major disadvantage of biological treatment is the possibility of causing secondary contamination. In addition, the process can be affected by season variations and highly toxic contaminants can affect the microorganisms (Banerjee et al., 1997). For example, pesticides are reported to be toxic to various bacteria and fungi making their digestion difficult (Goodwin et al., 2017).

TABLE 8.2 Summary of advanced oxidation processes (degradation).

Analytes	Catalyst and methods	Efficiency	References
Bisphenol AF	Montmorillonite KSF dispersions-Photo-catalytic technology	78%	Liu et al. (2010)
Carbamazepine	Magnetic cobalt ferrite-Photo-Fenton oxidation	96% removal	He et al. (2017)
Salicylic acid	Zero-valent iron-Fenton-like oxidation	100% removal, 48% removal of TOC	Savun-Hekimoğlu and Ince (2017)
Phenazone, ibuprofen	Ozone oxidation	70.0% removal; 90.0% removal	Yang et al. (2009)
Antipyrine, caffeine, metoprolol, bisphenol A	$TiO_2/SiO_2/Fe_3O_4$-Photo-Fenton oxidation	$k_{HO} = 5.2 \times 109\,M^{-1}\,S^{-1}$, $k_{HO} = 5.9 \times 109\,M^{-1}\,S^{-1}$, $k_{HO} = 6.8 \times 109\,M^{-1}\,S^{-1}$, $k_{HO} = 10.2 \times 109\,M^{-1}\,S^{-1}$	Álvarez et al. (2010)
17a-Ethinylestradiol	TiO_2 doped zeolites-Photo-catalytic technology	$K_{app} = 0.1\,min^{-1}$	Pan et al. (2014)
Amoxicillin, cloxacillin	Ferrihydrite-Fenton oxidation	73.0%–81.2%	Affam and Chaudhuri (2014)
Diclofenac	Fe-MCM-41-Ozone oxidation	76.3%	Chen et al. (2016)
Ciprofloxacin	MnO_x/MWCNT-Ozone oxidation	90.5%	Sui et al. (2012)
Caffeine	Goethite-Photo-catalytic technology	94.0%	Wang et al. (2017)
Phenazone, ibuprofen, diphenhydramine	MnO_x/MA-Ozone oxidation	70.0%–90.0%	Yang et al. (2009)
Norfloxacin	MnO_x/SBA-15-Ozone oxidation	54.0%	Chen et al. (2017c)
Acetaminophen	TiO_2/ZSM-5-Photocatalytic technology	96.6%	Chang et al. (2015)
Perfluorooctanoic acid (PFOA)	Ga_2O_3/UV assisted peroxymonosulfate	100%	Xu et al. (2020a)
Perfluorooctanoic acid	Fe/TNTs@AC	>90%	Li et al. (2020)
Perfluorooctanoic acid	Iron (hydr)oxides/carbon sphere composite	95.2%	Xu et al. (2020b)
Dimethoate, Triazophos, and Malathion	UV/Fenton and Microwave electrodeless, Ultraviolet (MWEUV)/Fenton	Complete removal	Cheng et al. (2015)
Acetamiprid	UV/TiO_2; $UV/H_2O_2/Fe$; $UV/Na_2S_2O_8$; and $UV/Na_2S_2O_8/Fe$	Complete removal	Carra et al. (2016)
Atrazine	UV/TiO_2 and UV/Pt-TiO_2	76%	Chen et al. (2017b)
Direct Blue 86 (DB-86) dye	O_3 combined with UV	98%	Hassaan et al. (2017)
Yellow Acid 36	TiO_2 p-25 catalyst	97.6%	Nokandeh and Khoshmanesh (2019)
Disperse Red-60	$ZnO/UV/H_2O_2$	97%	Jamil et al. (2020)
MB	$Fe_3O_4@MnO_2$	99.0%	Kang et al. (2019)

To overcome challenges caused by the independent use of biological processes or AOPs, more attention was then paid to the combination of AOPs and biological methods over the years where the pretreatment process is performed by chemical methods such that all persistent pollutants were transformed into their biodegradable intermediates. Thereafter, the intermediates are completely degraded using biological methods (Wang and Wang, 2016). Studies analyzing the removal of EOPs by the combination of chemical and biological methods were performed.

TABLE 8.3 Summary of the removal of PPCPs by biological separation.

Analytes	Biological process	Removal efficiency (%)	References
Paracetamol	Modified Bardenpho process	98	Yu et al. (2013)
Atenolol	Grit tanks þ primary sedimentation þ bioreactor þ clarifiers	47.1	Roberts et al. (2016)
Propranolol	Anaerobic sludge digestion	60	Narumiya et al. (2013)
Methylparaben	Primary treatment þ conventional activated sludge þ tertiary treatment (ultrafiltration and ozonation)	98.8	Li et al. (2015)
Propylparaben	Primary treatment þ conventional activated sludge þ tertiary treatment (ultrafiltration and ozonation)	99.8	Li et al. (2015)
Ketoprofen	Primary treatment conventional activated sludge þ tertiary treatment (ultrafiltration and ozonation)	−30 to 80	Sun et al. (2014)
Aspirin	Modified Bardenpho process	92	Yu et al. (2013)
Triclosan	Grit tanks þ primary sedimentation þ bioreactor þ clarifiers	99.8	Roberts et al. (2016)
Chlorpyrifos	Aerobic activated sludge þ photocatalysis	88.2	Becerra et al. (2020)
Glyphosate	Activated sludge	80	Carboneras et al. (2018)
Fungicides	Bioaugmentation		Murillo-Zamora et al. (2017)
Glyphosate	Unacclimated activated sludge		Tazdaït et al. (2018)
Herbicides	Bacterial consortium	$<$99	Zhang et al. (2018)

Due to their toxicity, tetracyclines are hardly eliminated by single biodegradation, thus Gómez-Pacheco et al. (2011) used the integrated process of ozone AOP and biological treatments to remove tetracyclines. The report indicated the degradation of tetracycline was completed after ozonation for 10 min, but the mineralization degree was low. However, when biological treatment preceded ozone, mineralization was remarkably increased with reduced demand for chemical oxygen. Therefore, this demonstrated the effectiveness of the integrated process in the removal of tetracycline. It was reported by Keen et al. (2012) that carbamazepine which is a persistent pharmaceutical compound, could be mineralized by UV/H_2O_2 thereafter, by a mixed bacterial inoculum, thus indicating the potential of the coupled methods to mineralize persistent PPCPs. A further summary of biological technologies is provided in Table 8.3.

Pesticide digestion can occur in two ways, namely aerobic and anaerobic treatments, Javaid et al. reported the use of aerobic treatment for di-chlorinated pesticides (Javaid et al., 2016). The process includes the oxidation of the ether bond and formation of chloro-catechol followed by digestion once the aromatic ring is open (Javaid et al., 2016; Saleh et al., 2020). Similar to PPCPs, pretreatment using advanced oxidation can be necessary for the biological treatment of pesticides as reported by Huang et al. (2018) and Zhao et al. (2017) where 82.18% of norfloxacin in wastewater was digested in 25 min. Table 8.3 shows the digestion of other emerging pollutants using biological methods.

Notably, the combination of AOPs and biological treatment technologies demonstrated high removal efficiency for EOPs along with their by-products produced during AOPs. As a result, coupling these methods presents options for offsetting the drawbacks caused by single biological treatments or advanced oxidation treatments. However, more studies are required to determine the optimum conditions for each unit. In addition, for different compositions of EOPs, different parameters namely: temperature, pH, hydraulic retention time, reactor configuration, redox conditions, and the concentration of the catalyst are needed for the combination treatment to achieve optimal performance for both removal efficiency and cost.

8.3.4 Removal by membrane technology processes

Various removal processes by membranes, such as nano-filtration (NF) (Yoon et al., 2007), ultra-filtration (UF) (Sheng et al., 2016), micro-filtration (MF) (Yoon et al., 2006) have been readily applied in the area of wastewater treatment. The removal of PPCPs via membrane technology has been limited because most PPCPs can pass through membranes, as a result, the MF and UF processes can only be effectively used for pretreatment. Thus far, NF also known as

TABLE 8.4 Summary of the removal of EOPs by membrane filtration.

Analytes	Membrane	Performance	References
Atrazine and diazinon	TFC NF	98.8% rejection	Huang et al. (2011)
Carbamazepine	MIEX-UF	Only UF 13%, Hybrid 74%, adsorption rejection	Chen et al. (2019)
Perfluorohexanoic acid	RO-XLE Filmtec, RO-BW30, Filmtec, RO-SW30XLE Filmtec	97%–99%, 96%–99%, 96%–98%, Size exclusion and electrostatic interaction	Soriano et al. (2019)
Methylparaben, ethyl paraben, propylparaben, benzyl paraben, sulfadiazine, sulfamethoxazole, sulfamethazine, trimethoprim, norfloxacin, ofloxacin	NF270-Filmtec	26%–98%, 33%–98%, 42.6%–97%, 33%–99%, 26%–98.5%, hydrophobic interaction	Guo et al. (2017)
Bisphenol A, carbamazepine, and acetaminophen	ROESPA1-2521 Hydranautics	30%–67%, Steric effect	Baransi-Karkaby et al. (2019)
Atenolol, Carbamazepine, and Ibuprofen	NF	76%–89%, Donnan exclusion and steric hindrance	Ouyang et al. (2019)
Betamethasone, fluconazole, phenylbutazone, prednisone, and metformin	TFC-ROBW30 Filmtec, GE Osmonics SG	Size exclusion and hydrophobic interaction	Foureaux et al. (2019)
Rhodamine B and methylene blue	Sm-MOF/GO/PVDF	91%	Yang et al. (2020b)
Acid black 210	PPSU-PES	99.65%	Al-Ani et al. (2021)
CR and MB	GO NF membrane	98.8% and 92.9%	Kang et al. (2020)
Yellow disperse dye	high-impact polystyrene membrane	99.8%	Khoshnevisan and Bazgir (2021)
Direct-red-75	$FeAl_2O_4$ membrane	90%	Kunde and Sehgal (2020)
Glyphosate	SPEEK-PES	90%	Song et al. (2013)
Carbofuran	8YSZ-NF	82%	Qin et al. (2020)

reverse osmosis (NF/RO) has been effectively used for the removal of PPCPs from wastewater due to their size and molecular weight (MW) which also matches the separation dimension of NF/RO (Nghiem et al., 2005; Kimura et al., 2009).

A study by Rana et al. (2012) on prepared membranes were one NF membrane had charged surface modifying macromolecule (SMM) additives and another had hydrophilic SMM additives. The NF membrane with charged SMM demonstrated that it had a high and longer-term performance in separating ibuprofen owing to the charge repulsion. However, a drawback of this technique was the membrane fouling and the need for proper disposal of the rejected concentrate. Thus, a combination of membrane filtration with other technologies may provide more effective solutions to the removal of water pollutants as indicated in some of the examples provided in Table 8.4. In this table, it can be observed that different membrane technologies are more effective in the removal of dyes and surfactants as compared to other emerging contaminants. This might be due to the molecular sizes of dyes and surfactants as compared to other emerging contaminants.

8.4 Summary and future perspectives

Various studies on sorbents materials including activated carbon, agricultural solid waste, biochar, industrial by-products, nanomaterials, natural clay minerals, and bio-sorbents have indicated promising results in the adsorptive removal of PPCPs, surfactants, dyes, and pesticides in aqueous environments. However, due to the diverse chemical structures of PPCPs and their unique properties especially when in contact with environmental factors, the adsorption process becomes more complex for application in the real environment. Thus, more attention is required on novel sorbent synthesis that will be suitable for natural aqueous environmental conditions. Moreover, single-use sorbent material can become highly ineffective. Thus, combining the physicochemical properties of different sorbent materials for effective adsorption removal of these pollutants is required. Also, the use of activated sludge systems by current wastewater treatment processes is ineffective in the removal of certain pollutant residues which are persistently present in the effluent. Recent interests in some advanced technologies such as AOPs, membrane filtration, and the combination of different removal technologies have proved to be effective. However, factors such as cost, and performance of the individual processes vary greatly based on each case. Thus, there is a need to analyze the effects of these pollutants on the treatment performance, the stability of the process as well as the structure of the microbial community for biological processes of the WWTPs. The analysis of such factors would provide a standard base from which treatment technology can be integrated into currently existing treatment processes for water purification.

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CHAPTER

9

Microplastics in freshwater ecosystems with special reference to tropical systems: Detection, impact, and management

Lewis D. Yardy, Rana Al-Jaibachi, and Amanda Callaghan

9.1 Introduction

As a result of poor waste management and improper disposal, plastic waste has dramatically accumulated in the environment (Derraik, 2002; Thompson et al., 2009; Mashile et al., 2022, Chapter 8; Tavengwa and Dalu, 2022, Chapter 1). As early as the 1960s, plastic debris was recorded in the oceans and a growing awareness of environmental issues was developing (Ryan et al., 2009). Although it is easy to focus on the larger and more evident plastic debris, by number, most plastic waste is microscopic, including much of the plastic found in the Great Pacific Garbage Patch (Howell et al., 2012). Microplastics (MP) are most commonly defined as plastics <5 mm (Auta et al., 2017; Li et al., 2017). This definition is not universal and has been refined by some to include nanoparticles ≤ 0.1 mm; MPs ≤ 1 mm to >0.1 mm; "mesoplastic" for particles between ≤ 5 to >1 mm and "macroplastics" as >5 mm (Moore, 2008; Fendall and Sewell, 2009; Gigault et al., 2018).

Under environmental influences such as ultraviolet light and physical abrasion, the degradation of larger plastic particles leads to the production of MPs (Wagner et al., 2014). Consequently, much of the plastic pollution found on the ocean surface is dominated by particles smaller than 4.8 mm in diameter (Hidalgo-ruz et al., 2012). However, not all MPs are the result of the degradation of larger particles. Many are released into the environment in this form, particularly from domestic wastewater. Although most of the research to date has focused on the pollution of the world's oceans, plastic debris has been found in numerous aquatic systems, including rivers (Lechner et al., 2014; Morritt et al., 2014), lakes (Horton et al., 2017), mangrove swamps (Kukulka et al., 2012) and even groundwater (Panno et al., 2019). Waste emanating from domestic sewage is often released into freshwaters where a multitude of organisms are exposed to the pollution. Despite the widespread presence of MP worldwide little research had focused specifically on tropical freshwater, especially in low economic value regions. This chapter will discuss the sources and types of MP, their occurrence within freshwater systems and organisms, and the impact of waste-water and waste-water treatment plants in controlling MP release. Finally, we provide some practical advice for anyone wishing to pursue studies in this field.

9.1.1 Source and types of microplastics in freshwaters

Microplastics can be fibers, films, foams, fragments, or pellets (Rochman et al., 2019) (Fig. 9.1). Fibers are defined differently by individual studies, but as a rule, they are more than twice as long as they are thick, threadlike, and very thin (Cole et al., 2011); they can be found individually or as a bundle where individual fibers cannot be separated (Rochman et al., 2019). Fragments are hard, irregular, and angular pieces, often resulting from the breakdown of larger plastic pieces. Films are very thin and flat fragments, which commonly result from the degradation of plastic bags. Foams are usually thick, soft, and compressible and can be smooth or angular. Pellets such as nurdles (small, colored

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Shape	Example	Description
Fibre		Long, thin and threadlike Found individually or as a bundle
Fragment		Solid, hard and angular
Film		Thin and flat, often irregular
Foam		Thick, soft and compressible
Pellet		Solid, hard and regular, can be spherical

FIG. 9.1 The most common types of microplastics found in aquatic environments.

plastic pellets used in the manufacturing of plastic products) are regular and smooth and are often cylindrical or spherical (Kalogerakis et al., 2017; Quecholac-Piña et al., 2017).

Microplastics are further defined as primary or secondary depending on their origin. Primary MPs are found in the environment in the same size and shape that they were manufactured. These MPs are mostly made of polyethylene but may also be made of polypropylene, polyamide, Teflon, or any other plastic polymers (Rochman, 2016). They are often added to consumer care products such as toothpaste or facial scrubs which can pass through filtration systems of the wastewater treatment plants (WWTP) and enter aquatic environments (Browne et al., 2007; Napper et al., 2015; Horton et al., 2017). A UK investigation into MP beads in cosmetic products found that a single use of a facewash containing MP beads could release up to 94,500 MPs into the wastewater system (Napper et al., 2015). Following on from campaigns from nongovernmental organizations, many countries have now banned, or are proposing to ban, the sale of products that contain primary microbeads, including many European countries, Taiwan, Australia, India, and South Korea (Xanthos and Walker, 2017).

Secondary MPs are formed by the mechanical or environmental breakdown of larger pieces of plastics, a common example is polyethylene terephthalate (PET) bottles (Duis and Coors, 2016; Jaikumar et al., 2019; El Hadri et al., 2020). Many secondary MPs originate from roads. There are more than a billion cars on the road worldwide with tires that shed plastic particles every time they are driven; tires are arguably the main source of aquatic pollution, with particles in the range of 1–1000 μm (Baensch-Baltruschat et al., 2020). Once these particles have been produced, they enter the aquatic and terrestrial environment through surface runoff and aerial deposition. Surface runoff is the process where material gathered on surfaces (particularly in an urban environment) are washed towards other environments, such as fields on the side of roads, or more often into drains which then discharge into waterways or WWTPs (Lambert and Wagner, 2018; Pariatamby et al., 2020).

In Denmark and Norway, tire wear accounts for >50% of microplastics in the water (Sundt et al., 2014; Lassen et al., 2015). Throughout Europe, it is estimated that 1.3 million tons of MPs per year are released into the environment this way (Wagner et al., 2018). Since 90% of new roads are being built in tropical and subtropical regions (Dulac, 2013) and these areas are susceptible to flooding (Alamgir et al., 2017), tropical freshwater environments will be increasingly vulnerable.

Degradation of polymers by environmental conditions takes place through several routes including thermo-oxidative, photo, and biological degradation. Thermo-oxidative degradation is a slow oxidative degradation under moderate temperatures (Andrady, 2011); photo-degradation results from the exposure to sunlight over time, in which large polymer molecular weight is decreased and oxygen-rich functional groups are released (Browne et al., 2007; Andrady, 2011) and biodegradation refers to degradation by living organisms, such as microorganisms, which can convert the polymers to carbon dioxide, although for most polymers only partial breakdown occurs (Andrady, 2011). All these processes can affect the plastic materials and cause continuous breakdown of polymers over time until they become tiny in size (Ryan et al., 2009). Due to these biotic and abiotic factors, plastics in different environments will degrade at different rates; this is evident in the marine environment, where degradation occurs much faster in epipelagic regions (Wang et al., 2021). The key factors associated with plastic degradation are UV exposure, temperature, moisture, pH, and presence of microorganisms, except for pH, all other factors are more conducive to the plastic breakdown in freshwater (Wang et al., 2021). This is especially relevant to tropical regions which experience much higher UV exposure, temperatures, and humidity, and so even the terrestrial environment has ideal conditions for degradation (Arias-Villamizar and Vázquez-Morillas, 2018).

Unfortunately, many plastics are nondegradable meaning they may fragment into secondary plastics but do not chemically degrade, and as such are extremely persistent within the environment. Biodegradable "plastics" that are broken down by microbes are often cellulose rather than petroleum-based. Whilst switching to biodegradable plastics is seemingly an ideal solution, degradable and biodegradable plastics have limitations, as they are not suitable for exterior use where they encounter degrading conditions. These conditions are often limited within the environment, for example, only surface water has sufficient ultraviolet concentrations for photodegradation, and the microbes required for biodegradation can have specific requirements. Ultimately degradable and biodegradable plastics do not negate the need for waste treatment as they do not reliably degrade, and when they do the result is still to produce secondary MPs (Song et al., 2009; Iwata, 2015; Nauendorf et al., 2016; Rujnić-Sokele and Pilipović, 2017).

An aerial deposition is where MPs are lifted into the atmosphere, then transported by air currents to fall out of the atmosphere elsewhere; this is facilitated by their small size and relatively low density (Allen et al., 2019). There is little data on the distance MPs travel in the air, or how high up they are in the air column. It is likely to be difficult to predict since the shape and type of MP are so variable. No significant differences were found in the concentration of MPs collected at 1.7 and 80 m above ground level (Chen et al., 2020a). While the distance MPs are transported in the atmosphere is unknown, studies from the French Pyrenees (Allen et al., 2019) and Swiss Alps (Bergmann et al., 2019) suggest at least 95 km. While not a true source of MP, aerial deposition is an important transport mechanism within tropical freshwater because it explains the presence of MP in remote areas away from obvious sources of MP pollution.

Most MPs that are transported aerially are fibers; in Paris, over 90% of MPs collected from atmospheric fallout on the roof of a university were fibers (Dris et al., 2015), a result replicated in London with 92% being fibers (Wright et al., 2020). In Dongguan, China, aerial samples of fibers were more often from nonsynthetic textiles (84.6%), and yet the abundance of plastic fibers was still an order of magnitude higher than any other type of MP (Cai et al., 2017). Samples from Hamburg, Germany, however, showed that most MPs were fragments (95%), likely to be secondary MPs (Klein and Fischer, 2019).

9.2 Occurrence of microplastics in freshwaters worldwide

The past ten years have seen a rapid increase in research looking at the presence of MPs in the water and sediment of freshwater environments including rivers, lakes, ponds, and reservoirs (Lambert and Wagner, 2018). Surveys have demonstrated alarming quantities of MPs in these ecosystems, including within tropical regions (Table 9.1). Even a remote mountain lake in Mongolia has been contaminated with MPs (Free et al., 2014). Similarly, MP particles have been detected in the surface water of the Laurentian Great Lakes in the USA (Eriksen et al., 2013), and Canada (Zbyszewski and Corcoran, 2011). Almost 99.9% of the microbeads found in the North American studies were particles less than 2 mm in diameter, spherical, and with a polyethylene (PE) composition, resembling those used in facial products, suggesting this as the source. In Africa, Lake Victoria, bordered by Kenya, Uganda, and Tanzania, is threatened by the input of raw sewage and the dumping of domestic and industrial waste. A survey of MPs in the surface waters of Northern Lake Victoria found that most appeared to be secondary MPs generated from larger plastic debris that may have resulted from poor waste management (Egessa et al., 2020b).

The concentrations of MPs reported in the various freshwater studies are difficult to compare since they used different sampling methods and units for quantifications (Horton et al., 2017). To compound the issue of comparability, studies vary enormously in the type of MP (e.g., size, shape, density, and composition) recorded as well as the abiotic factors (e.g., weather, season and equipment used) that may influence MP distribution (Lattin et al., 2004; Hidalgo-ruz et al., 2012).

Rainfall and storm disturbances can increase the presence of MPs in the water column, particularly in shallow lakes and estuaries (Lattin et al., 2004; Yonkos et al., 2014). The fate of MPs in natural freshwater ecosystems will to some extent depend on their partitioning between the water column and sediment. High-density MPs, such as polyvinyl chloride (PVC) and polyesters (PES) settle into the sediment and may be less prevalent in the water column due to their negative buoyancy (Kowalski et al., 2016; Lozoya et al., 2016). However low-density MPs, such as PE and polystyrene (PS) are positively buoyant and more likely to persist in the water column, making them accessible to filter

TABLE 9.1 Microplastics pollution in tropical freshwater ecosystems.

Location	Average abundance	Reference
USA		
Californian rivers, USA	30–109 particles m^{-3}	Moore et al. (2011)
Los Angeles river, USA	12,000 particles m^{-3}	Moore et al. (2011)
South America		
La Salada Lake, Argentina	Summer: 180 MPs m^{-3} Spring: 140 MPs m^{-3}	Alfonso et al. (2020)
Amazon, Brazil	Sediment: 417–8178 pieces kg^{-1}	Gerolin et al. (2020)
Pantanal wetlands, Brazil	Urban: $19.9 \pm 5.8 \times 100\,\text{L}^{-1}$ Rural: $4.5 \pm 2.5 \times 100\,\text{L}^{-1}$	de Faria et al. (2021)
Asia		
Netravathi River, India	Water: 288 pieces m^{-3} Sediment: 96 pieces kg^{-1} Soil: 84.5 pieces kg^{-1}	Amrutha and Warrier (2020)
Vembanad Lake, Kerala, India	Sediment: 96–496 particles m^{-2}	Sruthy and Ramasamy (2017)
Veeranam Lake, India	Water: 28 items km^{-2} Sediment: 309 items kg^{-1}	Bharath et al. (2021)
Red Hills Lake, Chennai, India	Water: 5.9 particles L^{-1} Sediment: 27 particles kg^{-1}	Gopinath et al. (2020)
Sambarmati River, India	Sediment: 135 particles kg^{-1}	Patel et al. (2020)
Poyang Lake, China	Water: 1064 ± 90 MP m^{-3}	Jian et al. (2020)
Wei River, China	Water: 3.67 to 10.7 items L^{-1}	Ding et al. (2019)
Pearl River, Guangzhou City, China	Water: 19860 items m^{-3}	Yan et al. (2019)
Urban lakes in Changsha, China	Water: 2425 ± 248 to 7050 ± 1061 items m^{-3}	Yin et al. (2019)
Xiangxi River of Three Gorges Reservoir, China	Surface water: 80–864 particles m^{-2} Sediment: 0.55×10^5–342×10^5 items km^{-2}	Zhang et al. (2017)
Taihu Lake, China	Water: 3.4–25.8 particles L^{-1} Sediment: 11–35 particles kg^{-1}	Su et al. (2016)
Africa		
Lake Victoria, Uganda	Surface water: 0.02–2.17 pieces m^{-3} Sediment: 0.8–240 pieces kg^{-1}	Egessa et al. (2020b)
Lake Naivasha, Kenya	Surface water: 0.407 ± 0.135 pieces m^{-3}	Migwi et al. (2020)
Ox-bow Lake, Yenagoa, Nigeria	Surface water: 1000–8330 pieces m^{-3} Sediment: 347–4030 pieces kg^{-1}	Oni et al. (2020)
Braamfontein Spruit, South Africa	Surface water: 705 pieces m^{-3} Sediment: 167 pieces kg^{-1}	Dahms et al. (2020)

feeders for accidental ingestion, and increasing their potential distribution range (Cole et al., 2013; Eerkes-Medrano et al., 2015; Avio et al., 2017).

Rivers have historically, and continue to be, essential to human communities globally; they are relied upon for food, transport, industry, and tourism. It is therefore unsurprising that rivers have been highly impacted by plastic pollution. While previous studies on MP contamination had been largely limited to temperate, developed areas, in recent years studies have expanded to include tropical and lower- and middle-income countries. This new research is significant because the majority of continental (rather than oceanic) MPs that enter the marine environment come from Asian rivers (Lebreton et al., 2017; Ta and Babel, 2020), and of the top 20 plastic polluting countries only Turkey (14th) and North Korea (19th) are neither tropical, or sub-tropical; China (1st) and USA (20th) are both partially subtropical (Jambeck et al., 2015).

A study of the Netravathi River in Southwest India investigated both macro and MP pollution in sediment and water samples and found that plastic abundance in the water column ranged from 56 pieces m^{-3} to 288 pieces m^{-3} (Amrutha and Warrier, 2020). The amount of plastic increased downstream of towns with high populations but it was also higher upstream compared to uninhabited regions downstream, suggesting small to moderate populations are a detectable source. Likewise, the sediment results showed a range between 253 pieces kg^{-1} and 9.4 pieces kg^{-1}, with the lowest values sourced from regions with low anthropomorphic pressure. Surprisingly, the region with the highest water pollution had a low sediment pollution of 17.6 pieces kg^{-1}. This anomaly can be explained by the resuspension of MPs from sediment into the water column by turbulent currents caused by wind, rain, and monsoon (Amrutha and Warrier, 2020).

Plastic pollution in canals connected to the Saigon River in Vietnam was predominantly generated from plastic bags (37%), followed by food containers (14%), of which 79% were PE (Lahens et al., 2018). The yearly mass of land-based plastic that entered the river per inhabitant was calculated to be 350–7270 g $inhabitant^{-1}$ yr^{-1}. Microplastics were also identified as either fibers or fragments; the smallest size group (50–250 μm and 0.5–50 10^3 μm^2) accounted for half of the MPs collected. The vast majority of these MP were fibers, up to 519,000 fibers m^{-3}, compared with a maximum of 23 fragments m^{-3}; while both fibers and fragments were lowest upstream and highest downstream, the difference was less than expected, given the difference in population between the sites (Lahens et al., 2018).

In many countries, lakes are essential to the local communities and supply not only food and water but also transport and recreation. Lakes typically have a much lower flow rate than rivers and therefore have the potential to act as a sink for many pollutants, including MPs. Lake Victoria is the largest tropical freshwater lake, bordered by Tanzania, Uganda, and Kenya, and it is estimated that 4 million people are dependent upon the fishing industry alone (Mkumbo and Marshall, 2015). When the surface waters were studied, all samples were found to have MPs ranging from 0.02 pieces m^{-3} to 2.19 pieces m^{-3} with an average of 0.73 pieces m^{-3} (Egessa et al., 2020b). This was within the same range as the Great Lakes of America, but lower than large lakes such as Lake Taihu in China (Dongting and Hong; Su et al., 2016; Wang et al., 2018). Another study on Lake Victoria focused upon MPs in the sediment and found a mean abundance of 0.9 to 239.8 pieces kg^{-1} in shoreline sediment and 0 to 14.5 pieces kg^{-1} in lakebed sediment. (Egessa et al., 2020a). Films were the dominant plastic polluting the shoreline whereas fibers were dominant in the lake sediment.

Lake Vembanad in Kerala, Southwest India is a freshwater estuarine system, with higher salinity north of the lake (4.5) and very low salinity (0.42) in the south. The north is fed by Kochi, the commercial capital of the state, whereas the south is fed by smaller populated centers. A study of various sites across the lake found an average MP contamination of 253 pieces m^{-2} throughout with higher concentrations (496 pieces m^{-2}) in the north; this was attributed in part to pollution from Kochi but also to the marine influence the north experienced (Sruthy and Ramasamy, 2017). Higher salinity influencing MP pollution has been recorded in the Gulf of Mexico (Wessel et al., 2016). Here the locations that were more exposed to tides and currents were shown to have a greater abundance of MPs. There are several explanations for this: tidal action increases plastic degradation into secondary fragments by mechanical wear producing more MPs (Wessel et al., 2016); it also increases the residence time of plastics within the region as the water column moves in and out (Wessel et al., 2016). The higher salinity produces a higher density which enables larger and denser MP to stay in suspension rather than become sequestered into the sediment, further explaining the increase in MP typically found in these regions. Salinity was a proposed factor for MP levels in a Spanish River Delta where the estuarine sediments are significant sink areas for MPs, particularly fibers (Simon-Sánchez et al., 2019).

9.3 Ingestion and impact of microplastics in freshwater fish

There is a plethora of evidence in the literature showing that different animal taxa ingest plastics; this can be divided into intentional and unintentional, with unintentional being subdivided into incidental and trophic. Intentional is when an organism deliberately ingests plastic believing it to be a food source, while incidental is when an organism accidentally ingests plastic alongside their normal food source. Trophic is when an organism ingests another organism that itself has ingested plastic, thereby allowing the MP to transfer between trophic levels and can result in bioaccumulation in predators (Cole et al., 2011; Cedervall et al., 2012; Peters and Bratton, 2016).

Fish ingestion of MPs is a worldwide environmental issue that has been widely reported (Wang et al., 2019). Freshwater fish ingest MPs intentionally, mistaking them for food particles, or accidentally, where they are mixed with food (Roch et al., 2020). Fish feeding behavior is linked to MP intake (Jabeen et al., 2017; Silva et al., 2018), with fish foraging on the sediment bed exposed to higher concentrations than predatory and omnivorous fish feeding in the water column (Mizraji et al., 2017; McNeish et al., 2018; Roch et al., 2020). In the tropical Goiana Estuary in South America, MP fiber consumption found in different fish life stages is linked to their feeding preference over a seasonal cycle (Silva et al., 2018). As discussed previously, salinity in estuarine systems is present as a gradient from marine to freshwaters and so the concentration of MPs will vary by location as well as by seasonality of the fish and their prey. Juveniles of Haemulidae species feed in the water column targeting zooplankton, but switch to feeding on benthic invertebrates such as polychaetes or mollusks as subadults, thus increasing their exposure to fibers (Ferreira et al., 2018; Silva et al., 2018).

In Northeast Brazil, 83% of *Hoplosternum littorale*, a common and regularly consumed riverine fish, contained plastics, most of which were MPs (Silva-Cavalcanti et al., 2017). The most common type of MP was fiber (46%) and the authors found plastic load in the guts was correlated with a lower diversity of food type. Similar percentages have been found in South East Asia; a study looking into eight species from the Chi River in Thailand found between 50% and 86.7% of fish had ingested MPs with an average of 1.7 pieces per fish, and once again it was fibers that represented 86.9% of MPs (Kasamesiri and Thaimuangpho, 2020). A study from Malaysia in the Skudai River had greater variation, with MP ingestion between 19% and 100% for six species with an overall average of 40%.

In Lake Victoria, only 20% of Nile perch (*Lates niloticus*) and Nile tilapia (*Oreochromis niloticus*) were found to have ingested MPs, which is lower than found elsewhere, probably because they were limited to detecting MPs larger than 0.5 mm (Biginagwa et al., 2016). A more recent study investigated *O. niloticus* and a catfish *Bagrus bayad*, with the same limit of >0.5 mm and found that 79.5% of the Tilapia and 78.6% of the catfish had ingested MPs, consuming an average of 7.5 ± 4.9 and 4.7 ± 1.7 pieces respectively (Khan et al., 2020). Again, fibers were the most frequent MP, followed by films.

Whilst early studies were focused on proving that fish were eating the plastics (Sanchez et al., 2014; Lambert and Wagner, 2018), research soon began to search for negative effects from MP ingestion. Physical effects reported include blockages in the alimentary system, inflammation, and damage to the gastrointestinal tissues, and associated impacts on nutrient absorption (Jabeen et al., 2018; Lei et al., 2018). There have now been many studies, mostly in the laboratory, looking at ecotoxicological effects of MPs on fish and there is some evidence that MPs may have various toxicological effects. For example, PS MPs had a negative impact on the activity of neurotransmitter enzymes in the brains of red tilapia (*Oreochromis niloticus*) (Ding et al., 2018) and zebrafish (*Danio rerio*), they were associated with oxidative liver damage and reductions in lipid and energy metabolism (Lu et al., 2016). These impacts, if also observed in the wild, would likely impact predator-prey interactions and organism growth and reproduction. There are concerns that some MPs, which have a large surface area and due to their hydrophobicity are known to bind to toxins, will concentrate toxic chemicals such as hydrophobic organic compounds, thereby magnifying their effect (Wang et al., 2020). The degree to which MP harm aquatic animals have been questioned, with several studies finding negligible to no impact (Cole et al., 2011; Li et al., 2020; Xu et al., 2020), the risk of overfishing and climate change are suggested to be far greater than any risk posed by MP (Cunningham et al., 2020). It is also worth considering the role publication bias has to play in the proportion of publications finding significant impacts.

9.4 Ingestion and impact of microplastic on freshwater invertebrates

As with early fish studies, research on freshwater invertebrates initially focused on detection and loading, an example being a study of a riverine valley in South Wales, the UK, downstream from a WWTP, where half of the macroinvertebrates tested (Baetidae, Heptageniidae and Hydropsychidae) contained multiple fragments of plastic (Windsor et al., 2019). A large-scale survey of Asian clam, *Corbicula fluminea*, in the Yangtze river basin which included lakes, rivers, and estuaries, demonstrated that levels of MP pollution (mostly fibers) in the sediment were closely correlated with MP load in the clam (Su et al., 2018). The authors have suggested that it could be used as an indicator species for MPs in freshwaters.

Most published research on freshwater invertebrates has been in the laboratory using model species, including the mollusk *Sphaerium corneum*, *Daphnia*, *Lumbriculus*, *Gammarus*, and *Tubifex* species, answering questions related to ingestion, uptake, depuration, and ecotoxicological effect (Anbumani and Kakkar, 2018). Generally, research has revealed that MP uptake is concentration and time-dependent (Rehse et al., 2016; Bruck and Ford, 2018; Canniff and Hoang, 2018; Lambert and Wagner, 2018).

The ingestion of MPs is likely to have varied impacts on an organism depending on the size, shape, concentrations and exposure period, and the feeding method of the organism (Redondo-Hasselerharm et al., 2018). Very small PS MPs (20 and 1000 nm) can cross the *D. magna* gut epithelium where they are accumulated in lipid storage droplets (Rosenkranz et al., 2009). Although some studies have not confirmed this observation (Lambert and Wagner, 2018), work on *Daphnia galeata* exposed to PS nanoparticles (52 nm) recorded the transfer of particles from the external body to the internal organs as well as storage in lipid droplets (Cui et al., 2017).

Likewise, small PS MPs (2 μm) were found to transfer ontogenically from larvae to adult *Culex pipiens* mosquitoes, whereas larger MPs (15 μm) were not. The smaller PS MPs accumulated in the mosquito renal excretion system, where they stayed throughout the metamorphosis to pupae and then to adults, thereby transferring plastics from the freshwater to the terrestrial food webs (Al-Jaibachi et al., 2018). Despite the retention of the PS MPs, there was no impact on the mosquito development or eclosion (Al-Jaibachi et al., 2019).

Although PS MPs (20–500 μm) decreased growth rates in *Gammarus pulex* (Redondo-Hasselerharm et al., 2018), several studies have examined the ecotoxicological effect of MPs on mortality, reproduction, and growth rate and found that any effect was more related to the availability of food rather than toxicity of MPs (Ogonowski et al., 2016; Aljaibachi and Callaghan, 2018). However, it could depend on the type or size of plastic used; fibers were more toxic than spherical MPs to *D. magna*, a result which could be due to fibers obstructing the gut system (Jemec et al., 2016). Immobilization of *D. magna* is a parameter measured in ecotoxicology and smaller sized MPs (1 μm) were shown to have a concentration- and time-dependent immobilization effect (Rehse et al., 2016) while the deceased growth rate and induced stress defenses were reported in *Daphnia pulex* (Liu et al., 2019b). The trophic transfer of MPs from two standard ecotoxicological invertebrate models (*Daphnia magna* and *Chironomus riparius* larvae) with and without a toxic pollutant chemical to zebrafish (*Danio rerio*) found no impact on liver enzymes as a measure of stress (Hanslik et al., 2020).

The lack of information outside of the standard ecotoxicology models extends to studies of community responses and effects in a more natural field environment where predator-prey interactions and competition exist. Here MPs are more likely to be fibers or nonspherical shapes generated from primary MPs, making it difficult to extrapolate from studies using single species and virgin MPs (Rummel et al., 2016).

9.5 Management of water waste systems and microplastics

Microplastics are known to enter the WWTPs through domestic products; clothes washing (Browne et al., 2011; Napper and Thompson, 2016), personal care products (Fendall and Sewell, 2009; Duis and Coors, 2016; Kalčíková et al., 2017), toothpaste (Leslie, 2014), and have recently been found in human stools (Schwabl et al., 2019). Microplastics, including microbeads, washed down domestic drains are transported in the raw effluent to the WWTPs. Studies suggest that this is the main source of MP pollution in freshwater ecosystems (McCormick et al., 2014; Horton et al., 2017; Windsor et al., 2019). The wastewater treatment processes currently used in the European Union are not specifically designed to capture MPs but where some form of tertiary treatment is operating efficiently, the removal of MPs from the water can be effective. However, if sludge is retained and spread onto agricultural land as a fertilizer, any MPs that it contains will be available for pollution of the natural habitat (de Sá et al., 2018). Sewage sludge is used for landfilling and as fertilizer in agriculture that may increase the possibility to transfer the MPs to the rivers, lakes, and seas through surface runoff (Wagner et al., 2014; Nizzetto et al., 2016).

In studies from subtropical regions with high-value economies (USA, South Korea, and Australia), the majority of MPs in both the incoming waste and effluent are fibers (Ziajahromi et al., 2016; Lasee et al., 2017; Ziajahromi et al., 2017; Conley et al., 2019; Hidayaturrahman and Lee, 2019). Whenever textiles are washed, they release fibers, hence the presence within the incoming waste, and when compared to particles fibers do not settle as readily, due to greater surface area to volume ratio, and their ability to pass through pores more easily (a 100 μm long fiber will pass through a 25 μm pore). Samples from a textile manufacturing area in Eastern China showed that most fibers in both surface water and sediment were in the range of 0.1–1 mm with the average size within surface water being smaller than in the sediment (Deng et al., 2020).

A recent survey on the regulation of WWTPs and MPs found that worldwide there are no regulations that specify the maximum levels of MPs permitted in discharged wastewater (Freeman et al., 2020).

In tropical regions, including countries in South America, wastewater treatment is often limited and awareness of the issue with MPs has trailed other areas of the world. In Ecuador, the lack of effective enforcement of wastewater management policies along with poor management of solid waste and general water resources has resulted in exceptionally high levels of MP pollution (Donoso and Rios-Touma, 2020). Less than 10% of wastewater from the capital city Quito is treated through WWTPs and many major Andean cities are found on the headwaters of basins that drain into the Pacific or the Amazon-Atlantic basin (Donoso and Rios-Touma, 2020). In their 2020 study, Donoso and Rios-Touma (Donoso and Rios-Touma, 2020) found exceptionally high concentrations of MPs in wastewater samples, mostly fibers from clothing, that far exceeded those in countries such as Germany with effective wastewater treatment. The WWTPs are an essential tool in limiting MPs entering the environment because they can be up to 100% effective in

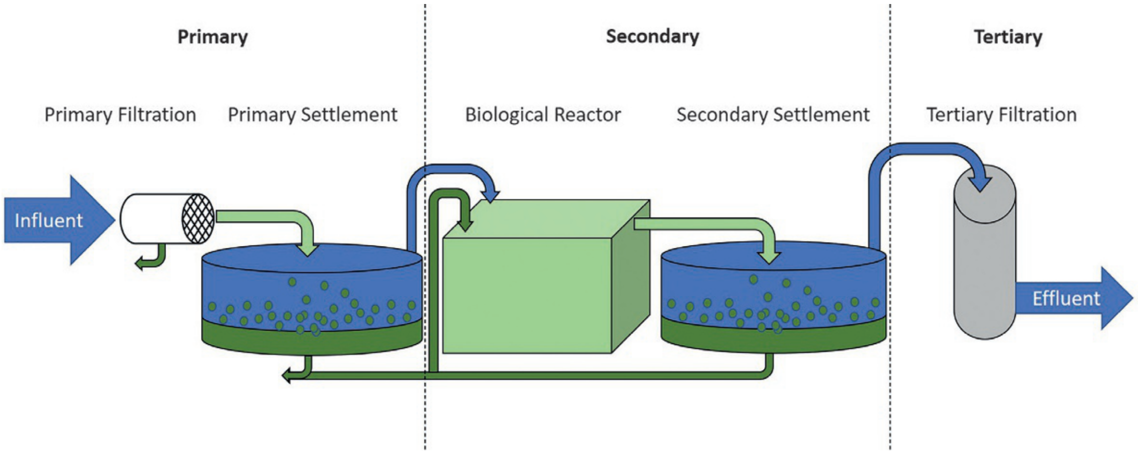

FIG. 9.2 Wastewater treatment plant showing primary, secondary and tertiary stages.

TABLE 9.2 Microplastic removal rate from WWTPs in the tropics.

Country	Treatment Stage	Removal efficiency	Microplastics in effluent	Reference
Thailand	Secondary	84%	2 pieces L^{-1}	Hongprasith et al. (2020)
South Korea	Tertiary	98.9%–99.2%	33–297 pieces L^{-1}	Hidayaturrahman and Lee (2019)
South Korea	Secondary	75%–91.9%	433–7863 pieces L^{-1}	Hidayaturrahman and Lee (2019)
South Korea	Primary	56.8%–64.4%	1568–12,580 pieces L^{-1}	Hidayaturrahman and Lee (2019)
Australia	Secondary	76.6%	2.76 ± 0.11 pieces L^{-1}	Raju et al. (2020)
China	Tertiary	64.4%	28.4 pieces L^{-1}	Liu et al. (2019a)
China	Tertiary	89.17%–97.15%	0–447 pieces L^{-1}	Sun et al. (2019)
Turkey	Secondary	73%–79%	4.1–6.9 pieces L^{-1}	Gündoğdu et al. (2018)

removing MPs from wastewater (Ziajahromi et al., 2017). While well-designed and maintained plants can achieve these levels of efficiency, not all plants are created equal (Fig. 9.2).

The most basic plants are a mesh screen which removes large solid matter from wastewater, the smaller the mesh the more efficient it will be in removing solids; however, it requires a more advanced and expensive clearing mechanism. Clarification tanks improve MP removal efficiency by allowing suspended matter to settle out from the water. Dissolved solids will not be removed by clarifiers, they require either biological or chemical treatment. The effluent from a biological reactor must then go through another clarifier to remove the microbes and suspended solids into a sludge, some of this sludge is disposed of as waste-activated sludge with the remainder being pumped back into the biological reactor. The effluent from this secondary clarifier can be discharged into the environment or go through a tertiary treatment. Tertiary treatment can include further filtration through sand filters, chemical treatment, or reverse osmosis. Plants with these clarifiers, biological reactors, and tertiary treatments have been shown to achieve >90% efficiency, whereas plants with simple mesh screening having a far lower efficiency (Ziajahromi et al., 2016; Ziajahromi et al., 2017) (Table 9.2).

9.6 Practical approaches to microplastic studies

9.6.1 Microplastic collection and separation

9.6.1.1 Water

There are two main methods for sampling water, in situ, and ex situ. The optimum method depends on several factors including sample size required, equipment available, time available, nature of water body, type, and size of MP targeted (Prata et al., 2019). Ex situ sampling involves collecting a defined volume of water from the test site and processing it in a laboratory by passing it through sieves of the required size or a filter with vacuum filtration. The advantage of this approach is that MPs of all sizes can be collected and little specialized equipment is needed. However, the processing can take time and the sample volume is limited by the amount that can be transported from the sampling site to the laboratory (Dubaish and Liebezeit, 2013). When conducting in situ sampling, MPs are removed from the water at the sample site; this is most often achieved using nets, although sieves can also be used. Specialized nets such as manta nets allow a large volume of water to be sampled rapidly, however they require a boat, and the mesh size imposes limits on which MP can be sampled. Nets with a finer mesh such as plankton nets allow smaller MP to be collected, but they are prone to clogging and so typically cannot be used to sample large volumes, as such a greater number of replicates are required to sample the same total volume (Prata et al., 2019). Microplastic fibers are selectively recovered depending on mesh size; an 80 μm mesh captured 250 times more fibers than a 333 μm mesh (Dris et al., 2018). A pump system allows water from a known depth to be sampled, and a set of metal sieves allow a greater volume to be sampled, by separating particulates across a range of mesh sizes. (Lenz and Labrenz, 2018).

The method used to collect MPs can have a significant impact on the estimate of MP abundance. A study based in Guangxi in China collected MPs from the Lijiang river using two collection methods: pumping 90 L over a 25 μm sieve and plankton nets (mesh sizes 75 and 300 μm) fitted with flow meters (Zhang et al., 2021). The abundance of MPs was 100-fold higher using the pumping method, due to the smaller mesh size. However, the total volume sampled using the pump was three orders of magnitude lower than the nets, possibly resulting in an overestimation of MP abundance (Zhang et al., 2021).

To separate MP, water samples are passed through a 5 mm sieve to remove large matter and then a finer sieve to remove suspended solids from the water, it is common to use a 0.3 mm sieve in this final stage, however, many nano plastics and fibers will pass through (Dris et al., 2018), if these are of importance then a sieve of 20 μm should be used. The contents of the sieves are then transferred to a beaker and dried in an oven to remove the water; this allows the mass of suspended solids to be calculated.

Once dried a substance is added to the solids to remove the organic matter, this can be an oxidizing agent, an acid, an alkali, or an enzyme. While acids and alkali will digest organic matter, they can degrade or discolor MP (Catarino et al., 2017; Karami et al., 2017). The risk of degradation is much lower using oxidizing agents, most commonly hydrogen peroxide (Karami et al., 2017; Matthew and Richard, 2017). Enzymes have an even lower risk of damaging MP and do not require the same safety precautions as other methods (Maes et al., 2017), however, they are expensive, which limits their use.

A compound is added to the solution to achieve a density of 1.15 g mL^{-1} or greater, the solution is vigorously stirred to release MPs from the sediment and then transferred to a density separator (Masura et al., 2015). Sodium Chloride (NaCl) is the most common compound because it is cheap and environmentally safe, however, it is less effective at separating denser MPs such as High-Density Poly Ethylene (HDPE), PVC or, PET, for that Zinc Bromide (1.7 g cm^{-3}) is the most effective (Quinn et al., 2017). Once the separation is complete the denser sediment can be discarded, allowing the solution with the floating MPs to be run through a sieve or filter from which individual MPs can be identified and classified.

9.6.1.2 Sediment

Sediment from the lakeshore can simply be collected with a shovel or trowel and kept in a glass container, but if submerged samples are needed, they must be collected using a sediment grab or corer (Shruti et al., 2019). Most studies investigating MP in sediment transport samples back to a laboratory, with only a few conducting a full field sieve, however, some do prescreen samples using a 2–3 mm sieve that can remove large material (Hanvey et al., 2017). Many studies have taken the depth of samples into account, rather than a simple 2-dimensional quadrat sampling regime, to allow for the differential settlement of various MPs (Hanvey et al., 2017).

A similar separation process is used for sediment samples; however, additional density separation is conducted to remove the majority of the sediment before oven drying, this is again most often performed with NaCl (Hanvey et al., 2017).

If using gut contents or tissue samples, density separation may not be necessary as there is unlikely to be much sediment, and depending on the amount of material in the gut simply sieving and manually sorting may be sufficient (Silva-Cavalcanti et al., 2017) Studies using tissue samples or gut contents with a high organic load have used digestion processes, followed by sieving (Thiele et al., 2019). The increased time and temperature required to digest large volumes of organic matter can make MPs more prone to damage (Thiele et al., 2019). The use of enzymes alongside other agents, or using lower temperatures has helped reduce this damage (Catarino et al., 2017; Thiele et al., 2019).

9.6.1.3 Microplastic experiments involving organisms

To reliably expose organisms to MPs, their route into the organism must be established; this could be through ingestion or respiration. If through ingestion, then the functional feeding group of the organism must be identified and MPs suitably incorporated into their food source (Kampfraath et al., 2012; Yardy and Callaghan, 2020). Where the organism is a filter feeder such as *Daphnia* spp. and bivalves, MPs can be simply suspended in water at known concentrations and organisms left to ingest them, (Aljaibachi and Callaghan, 2018; Thomas et al., 2020).

Where the organisms are scrapers and grazers such as snails, the preferred method is to allow the MPs to settle onto food so that they are ingested as the animal feeds (Song et al., 2020). If the food is plant material, the MP may adsorb onto the plant surface, allowing trophic transfer to be investigated (Mateos-Cárdenas et al., 2019).

MPs have been directly incorporated into the food in known concentrations, for example using agar or algal waters mixed with the MP or tissues of an organism that has been previously exposed to the MPs (Kampfraath et al., 2012; Farrell and Nelson, 2013; Yardy and Callaghan, 2020). The advantage of this approach is that it ensures the MP is taken up as a result of feeding rather than MPs adhering to the body. Food does not have to be artificial to achieve this; live organisms exposed to MPs previously can be used as a source of MP exposure to following trophic transference. Chae et al. (2018) exposed an alga, *Chlamydomonas reinhardtii* to nanoplastic (NP) beads and demonstrated that the NPs were transferred into the invertebrate filter-feeder *D. magna*. The authors continued with the trophic study by feeding the NP exposed individuals to a secondary-consumer Chinese rice fish, *Oryzias sinensis* which was itself then fed on to an end-consumer dark chub fish *Zacco temminckii* (Chae et al., 2018). The NPs were transferred from the alga to the end consumer in the food chain. However, the study was more of a proof-of-concept paper, using concentrations that are much higher than those found in the environment and without the animals having a choice of food.

When MPs are being deliberately fed to organisms it is prudent to make them easily identifiable to the experimenter. This has been done simply and cheaply by choosing an easily recognizable shape or color, which is distinct from the rest of the food source. This was achieved in a study of *Gammarus* ingestion by using black fibers which were easily distinguished from the green algal food (Yardy and Callaghan, 2020). Another method is to use fluorescent dye to stain MPs, allowing clear visualization under a fluorescent microscope, however, a low-cost alternative can be an ultraviolet torch which also allows real-time observation of fluorescent MPs through tissue (Ehlers et al., 2020). Although using fluorescent dyes is a more expensive option it allows smaller MPs to be easily identified and differentiated from non-MP particles.

Once exposed, MPs in organisms can be studied in either the tissue of the organism or in the gut only. If small organisms are being investigated then the whole individual can be used, for larger organisms, a tissue sample is likely to be the best approach (Silva-Cavalcanti et al., 2017). If the gut is being investigated then there are two options, the gut can be dissected out and investigated alongside its contents (Steer et al., 2017), alternatively the gut contents can be removed and investigated separately (Grigorakis et al., 2017; Ory et al., 2018). Gut contents can be removed physically, or the animal can be left to defecate; either way, this has the advantage that the organisms do not necessarily need to be killed (Reynolds and Ryan, 2018; Coppock et al., 2019). If animals have been deliberately exposed to fluorescent MPs, they can be identified easily using fluorescent microscopy and to date studies using this approach have been conducted with MPs of various materials and sizes with several freshwater invertebrates (Table 9.3).

Microplastics (from the environment, or deliberately exposed to the organism) can be separated using a similar method as for sediment samples. If using gut contents or tissue samples, density separation may not be necessary as there is unlikely to be much sediment, and depending on the amount of material in the gut simply sieving and manually sorting may be sufficient (Silva-Cavalcanti et al., 2017) Studies using tissue samples or gut contents with a high organic load have used digestion processes, followed by sieving (Thiele et al., 2019). The increased time and temperature required to digest large volumes of organic matter can make MPs more prone to damage (Thiele et al., 2019). The use of enzymes alongside other agents, or using lower temperatures has helped reduce this damage (Catarino et al., 2017; Thiele et al., 2019).

9.6.2 Detection methods

Once MPs have been isolated for study, a sample, or all of the material recovered, must be analyzed to allow sample identification and quantification. Manual methods include visually inspecting each piece under 40 × magnification to look, e.g., homogenous texture, straight lines, and unnatural shapes or colors (Shim et al., 2017; Wagner, 2018; Prata et al., 2019; Elkhatib and Oyanedel-Craver, 2020). Alternatively, a “hot needle test” can identify plastic since holding an extremely hot needle close to the suspected item will melt or deform the MP (Karlsson et al., 2017). Similarly, the “break test” is also used, where the suspected MP is poked and bent with forceps and a needle to see if it will bend and not

TABLE 9.3 Fluorescent MPs exposed to freshwater invertebrates.

Species	MP	Peak Fluorescence	MP Concentration	MP size/μm	Ingested	Which organ	Reference
Gammarus duebeni	PE	605 nm	60,000 mL^{-1}	10–45	Yes	Gut	Mateos-Cárdenas et al. (2020)
Gammarus pulex	PET	465–495 nm	4000 mL^{-1}	10–150	Yes	Gut	(Weber et al. (2018)
Gammarus pulex	PS beads	441 nm	3000 mL^{-1}	1	Yes	Gut	Scherer et al. (2017)
Gammarus pulex	PS beads	441 nm	3000 mL^{-1}	10	Yes	Gut	Scherer et al. (2017)
Gammarus pulex	PS beads	441 nm	300 mL^{-1}	90	Yes	Gut	Scherer et al. (2017)
Daphnia magna	PS beads	441 nm	3000 mL^{-1}	1	Yes	Gut	Scherer et al. (2017)
Daphnia magna	PS beads	441 nm	3000 mL^{-1}	10	Yes	Gut	Scherer et al. (2017)
Daphnia magna	PS beads	441 nm	300 mL^{-1}	90	No	Gut	Scherer et al. (2017)
Chironomus riparius	PS beads	441 nm	3000 mL^{-1}	1	Yes	Gut	Scherer et al. (2017)
Chironomus riparius	PS beads	441 nm	3000 mL^{-1}	10	Yes	Gut	Scherer et al. (2017)
Chironomus riparius	PS beads	441 nm	300 mL^{-1}	90	Yes	Gut	Scherer et al. (2017)
Physella acuta	PS beads	441 nm	3000 mL^{-1}	1	Yes	Gut	Scherer et al. (2017)
Physella acuta	PS beads	441 nm	3000 mL^{-1}	10	Yes	Gut	Scherer et al. (2017)
Physella acuta	PS beads	441 nm	300 mL^{-1}	90	Yes	Gut	Scherer et al. (2017)
Lumbriculus variegatus	PS beads	441 nm	300 mL^{-1}	1	Yes	Gut	Scherer et al. (2017)
Lumbriculus variegatus	PS beads	441 nm	300 mL^{-1}	10	Yes	Gut	Scherer et al. (2017)
Lumbriculus variegatus	PS beads	441 nm	300 mL^{-1}	90	No	Gut	Scherer et al. (2017)
Eriocheir sinensis	PS beads	488 nm	40,000 $\mu g\ L^{-1}$	5	Yes	Gill Liver Gut	Yu et al. (2018)
Lumbriculus variegatus	Acrylic	Red range	1:10 Ratio MP: food	29.5 ± 26	Yes	Gut	Imhof et al. (2013)
Daphnia magna	Acrylic	Red range	1:10 Ratio MP: food	29.5 ± 26	Yes	Gut	Imhof et al. (2013)
Notodromas monacha	Acrylic	Red range	1:1 Ratio MP: food	29.5 ± 26	Yes	Gut	Imhof et al. (2013)
Potamopyrgus antipodarum	Acrylic	Red range	1:10 Ratio MP: food	29.5 ± 26	Yes	Gut	Imhof et al. (2013)
Gammarus pulex	Acrylic	Red range	1:10 Ratio MP: food	29.5 ± 26	Yes	Gut	Imhof et al. (2013)
Culex pipiens	PS Beads	470 nm	8×10^5 mL^{-1}	2	Yes	Malpighian tubules	Al-Jaibachi et al. (2018)
Culex pipiens	PS Beads	480 nm	8×10^2 mL^{-1}	15	Yes	Malpighian tubules	Al-Jaibachi et al. (2018)

break (Hidalgo-ruz et al., 2012). While these methods allow reliable identification, they are highly time-consuming and result in the destruction of the particles sampled. The preferred method to identify and quantify MPs uses one of several spectroscopic methods.

Fourier-Transform InfraRed (FTIR) spectroscopy measures the infrared adsorption and emission of a sample which is compared to a database of known materials. This can not only differentiate between plastics and nonplastics but it can also identify the specific type of plastic. While this method is the "gold-standard" for identification, it requires examples of different plastics to be in its database, and it can also take several hours to analyze a 5 × 5 cm sample. Purchasing an FTIR microscope is expensive, and is not suitable for identifying particles $<20\,\mu\text{m}$ (Wesch et al., 2016). As such many studies manually sort through samples and then analyze a sub-sample of their suspected MPs with FTIR for quality assurance (Hanvey et al., 2017; Prata et al., 2019).

Scanning Electron Microscopy (SEM) can identify particles using their physical structure, and can be used to confirm findings from standard microscopy (Eriksen et al., 2013), however, is time-consuming and does not give information on polymer type.

Raman spectroscopy uses the interaction of the sample with monochromatic light; it will provide reliable data on the polymer type, yet has been used less than FTIR (Sun et al., 2019). This may be because while it provides resolution of MPs down to 1 μm (Ribeiro-Claro et al., 2017) and does not suffer disturbance from polar environmental compounds (Schymanski et al., 2018), it is disturbed by fluorescence (both organic and inorganic) (Elert et al., 2017) and the filters needed are hugely expensive (Prata et al., 2019).

Few studies have used gas chromatography/mass spectrometry (GS/MS) (Sun et al., 2019), because while it instantly gives data on polymer types and relative abundance (Zhang et al., 2020), it gives no data on the number, size, or shape of individual MP (Prata et al., 2019; Sun et al., 2019) and are destructive. A more advanced method includes the addition of a thermo-extraction and desorption process, enabling products from plastic thermal degradation to be analyzed separately, which allows a sample to be analyzed without MP having to be presorted (Dümichen et al., 2017; Elert et al., 2017).

9.7 Summary

Despite the ever-increasing number of studies of the effects of MPs on aquatic biota, individual studies have been biased towards a particular type of polymer MP, with widespread use of laboratory over field studies, and overwhelming use of fish and crustaceans as model organisms (de Sá et al., 2018; Tavengwa et al., 2022, Chapter 20). It can be argued that in countries where research of the abundance and impact of MP is in its infancy, there is limited value in examining whether a novel species will ingest a novel polymer; the wealth of available data suggests that depending on the MP size, it will eat it accidentally or through confusion with food particles. Identification of polymer type and origin along with understanding its fate and transport will help to predict loadings in sediment and water.

A 2020 systematic analysis of global data identified seven main categories of MP in the environment: polyethylene terephthalate, polyethylene, polyvinyl chloride, polypropylene, polystyrene, polyurethane, and miscellaneous plastic (Jones et al., 2020). The type of MP found in waters around the globe varied considerably between countries and research mostly concentrated on measuring total abundance with little evidence of any links of sources to particles in the environment. However, the prevalence of fibers from clothing points to a failure of WWTPs to remove the MPs and prevent them from entering the ocean.

In tropical regions, wastewater treatment may be unable to cope with the removal of MPs and a heightened awareness and better wastewater management may help reduce the release of MPs, particularly fibers, into the environment. The WWTPs are an essential tool in limiting MPs entering the environment because they can be up to 100% effective in removing MPs from wastewater.

Before worldwide research can be pulled together in a meta-analysis, there is a need for standardized MP characterization methods and collection methods, using the types of guidelines already developed for chemical pollutants. We urgently need more studies looking at the behavior of MPs in a variety of habitats, including partitioning and availability to organisms and the food chain. It is essential that studies can be effectively and informatively compared, and at the moment very few studies can identify the smallest MP, which we know to be the most abundant, and there is limited value in comparing them with studies with a less sensitive methodology.

A consistent and comprehensive method for identifying the MP present in an ecosystem should form the basis for further investigations into the impact of these MP at both the individual, population, and community levels. The key to making these investigations environmentally relevant would be to not only use relevant MP shapes and polymers but to use them in environmentally relevant concentrations. By using consistent methods to base the experimental parameters, the impacts to different ecosystems would be more reasonably compared.

This chapter falls under the section on fate and occurrence of emerging pollutants within aquatic ecosystems with other chapters, e.g., Ajayi et al. (2022), Cristale (2022), Vizioli et al. (2022), Galhardi et al. (2022), Hashemi and Kaykhaii (2022), Madikizela et al. (2022), Mashile et al. (2022), Montagner et al. (2022), Moodley et al. (2022), Ntshani and Tavengwa (2022) and Sanganyando and Kajau (2022) that aims to make an understanding of the different emerging pollutants within the aquatic environment.

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CHAPTER

10

Pharmaceuticals and personal care products

Lawrence M. Madikizela, Cornelius Rimayi, Sinegugu Khulu, Somandla Ncube, and Luke Chimuka

10.1 Introduction

The global production, as well as use of pharmaceuticals and personal care products (PPCPs), is growing at an exponential rate worldwide (Madikizela and Chimuka, 2017a). PPCPs are now ubiquitously detected in many effluents impacted freshwater bodies at pseudo-persistent concentrations in developed and emerging countries due to their constant discharge into urban waters (Bu et al. , 2016; Gu et al., 2019; Liu et al., 2019; Wang et al., 2015a, b). PPCPs are an emerging class of compounds that include, but not limited to human and veterinary medicines, illegal drugs, disinfectants, hormones, fragrances, sunscreen agents, preservatives, additives, and insect repellents (Brausch and Rand, 2011; Cizmas et al., 2015; Dai et al., 2015a; Liu and Wong, 2013). As the use of PPCPs in the contemporary world has become indispensable for maintaining good hygiene, health, and improving quality of life, their presence in the environment has become a concern for water resource managers (Fekadu et al., 2019; Vanessa et al., 2018). With conventional wastewater and drinking water treatment processes having inefficient PPCPs removal efficiencies, there are concerns about the quality of drinking water worldwide (Madikizela et al., 2017b). Biodegradation, advanced oxidation, adsorption, membrane separation, and adsorption are some of the technologies utilized for the removal of PPCPs from wastewater and drinking water, but when used alone they are inefficient for removal of the entire spectrum of mid-polar to polar PPCPs (Yao et al., 2019). Many wastewater treatment plants (WWTPs) in developing countries (mostly activated sludge and waste stabilization ponds) are either poorly performing or overwhelmed by influent due to uncontrolled influent volumes, power failures, and insufficient funding to support and maintain the operations (Nikiema et al., 2013). As a result, they release untreated or partially treated sewage into freshwater bodies. The detection of 10 pharmaceuticals in 13 different fish species tested in Spain indicates that PPCPs in freshwater can bioconcentrate in aquatic animals, leading to further exposure to animals higher up the food chain (Peña-Herrera et al., 2020).

The presence of PPCPs at low concentrations in freshwater resources is a concern as they can cause unintended chronic effects in non-target aquatic organisms (Kallenborn et al., 2018; Tiwari et al., 2017). The presence of a plethora of different pharmaceutical classes can potentially cause synergistic effects with elevated biological effects in aquatic species that might exceed the magnitude of the therapeutic dose of a single pharmaceutical (Cizmas et al., 2015; Osorio et al., 2016; Rimayi et al., 2019). With considerations that access to medication can be critical to life and for the prevention of illnesses and outbreaks with devastating and debilitating effects, the World Health Organization (WHO) has published a list of essential medicines containing more than 400 medications (Engler and Skosana, 2016). The provision of pharmaceuticals globally is critically important as the illness has been identified as a major cause of poverty in different regions of the world (Jan et al., 2018; Liu et al., 2017). Under the theme of health promotion, the health sector has been aggressively marketing drugs competitively, offering novel pharmaceuticals and doses as well as a choice of a cocktail of active ingredients in a single dose (Gerardi et al., 2016; Greenway and Ross, 2017; Tiwari et al., 2017). As such, critics have accused pharmaceutical companies of colluding with health practitioners in inventing new diseases to match existing drugs (Wolinsky, 2005), unnecessarily contributing to the large spectrum of PPCPs detected in the environment. The extensive use and testing of new medicines especially in developing countries

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have led to their detection in drinking water sources at elevated concentrations. This in turn has overshadowed the therapeutic success story of pharmaceuticals.

To date, there has been considerably more research on pharmaceuticals in the environment than PCPs (Brausch and Rand, 2011). The first mention of PPCPs in surface water was in a technical report about pollution of the Missouri River, the USA published in 1970 (Tabak and Bunch, 1970). Europe followed up in the 1990s (Halling-Sørensen et al., 1998) but it was not until over 20 years later in 2012 when the first report in Africa was published (K'oreje et al., 2012). Due to their considerable resources, Europe and North America currently conduct the majority of the freshwater PPCP research globally, accounting for up to 80% of the total research (Birch et al., 2015). With extensive monitoring of PPCPs done mostly in industrialized countries, the current priority watch lists for PPCPs have been established for Europe, the USA, and Canada (Ebele et al., 2017). Except for China, Brazil, and South Africa, PPCPs monitoring in most developing countries remains minimal or non-existent owing to the lack of highly sensitive and high-tech analytical instrumentation required to adequately determine PPCPs at low levels found in the environment (Inam et al., 2015; Matongo et al., 2015; Offiong et al., 2019; Rimayi et al., 2019). However, lately, PPCP monitoring in developing countries has been gradually increasing. Therefore, in this chapter, we have critically evaluated the sources of PPCPs present in freshwater bodies of developing countries. The analytical methods for environmental analysis, the occurrence of PPCPs in freshwaters of the developed countries, health effects associated with unintentional consumption of PPCPs, and regulations currently in place in the developing countries were also reviewed.

10.2 Sources of PPCPs in freshwaters of the developing countries

PPCPs enter the freshwater resources through various pathways (Fig. 10.1). In literature, WWTPs have been noted as the major source of PPCPs found in the aquatic environment (Ebele et al., 2017). Pharmaceuticals are not completely metabolized in the human body or animals which leads to their excretion and release into the sewage system (Mlunguza et al., 2019). On the other hand, several groups of personal care products (PCPs) are insoluble in water to slightly soluble. Some of these chemicals are used in fragrances and as UV filters in sunscreen products while some are additives in the household products such as detergents. Therefore, these PCPs are easily washed down the drains with the assistance of detergents and get transferred into sewage or domestic waste. PPCPs are transferred into WWTPs as part of the domestic or industrial waste. Some PPCPs possess polar functional groups; therefore, they are not easily eliminated from water during the water purification processes. Also, pharmaceuticals are often discharged as soluble metabolites (e.g., glucoside or glutathione metabolites) which are then hydrolyzed in WWTPs back to the parent drugs resulting in higher concentrations in the effluents than influents. Hence, the availability of scientific data reporting the negative removal efficiencies for these compounds (Kermia et al., 2016; Kosma et al., 2014). The compounds released as part of effluent from WWTPs are discharged into freshwater (rivers and dams) and seawater.

The removal of PPCPs from wastewater is partly driven by the adsorption of these compounds into the sewage sludge. The sludge is used as an organic fertilizer in agricultural fields and/or ameliorants in landfills therefore PPCPs may migrate into the freshwater through leaching. Also, the application of animal waste as fertilizer on agricultural fields is common in developing countries due to the high costs of manure. This practice introduces veterinary drugs into the agricultural fields where they can be absorbed and distributed throughout different parts of edible plants and become available to humans (Chen et al., 2017). These pharmaceuticals can enter the freshwater systems and leach into groundwater (Ebele et al., 2017). Also, in the developing countries mostly in rural communities, livestock (cattle, sheep, horses, etc.) look for food sources along the rivers and directly excrete their waste into the surface water which is used as drinking water without any form of purification. This is likely to introduce veterinary drugs directly into the drinking water.

Developing countries mainly those in Africa have a high number of citizens residing in rural communities with poor sanitation, limited availability of modern ablution facilities (flushing toilets) that can be flushed with water to direct the human waste into WWTPs (Madikizela et al., 2020). Therefore, they mainly make use of open-air defecation (mainly children) and pit latrines (Jombo et al., 2010). The majority of people from these communities mostly consume those pharmaceuticals belonging to NSAIDs and analgesics as general medications for most pains. But due to affordability, the consumption rates are much less than in urban communities. Fragrances and triclosan are also easily accessible to rural communities. Groundwater, particularly in low aquifers is often infiltrated by pit latrine waste and as a result, several pharmaceuticals including NSAIDs and carbamazepine have been detected in contaminated groundwater in Cameroon (Branchet et al., 2019). People in rural areas tend to discard their unused or expired medications in pit

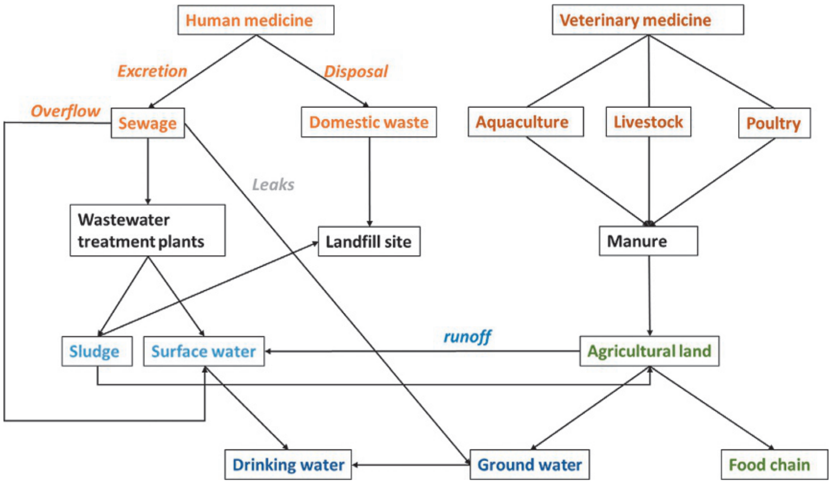


FIG. 10.1 Illustration of sources of environmental contamination with PPCPs. *Modified from Ebele, A.J., Abdallah, M.A., Harrad, S., 2017. Pharmaceuticals and personal care products (PPCPs) in the freshwater aquatic environment. Emerg. Contam. 3, 1–16.*

latrines or dug up rubbish pits for incineration. As described by Phaswana-Mafuya (2006) in a case study for a rural South African community, water used for cleaning and bathing which could contain a significant amount of PCPs is usually discarded by throwing onto the ground (Phaswana-Mafuya, 2006). Contamination of the aquatic environment in rural communities is mostly due to the leaching of PPCPs from the ground through surface run-off or seepage into the nearby rivers.

10.3 Overview of analytical methods for PPCPs in freshwaters of the developing countries

With most PPCPs detected in the ng—μg L^{-1} concentration levels in surface water samples, proper sample preparation techniques for their isolation and pre-concentration are needed to be followed by determination using sensitive chromatographic instrumentation. For developing countries that do not have the capacity for advanced extraction techniques, the commercial Oasis HLB-based SPE remains the most reported sample preparation technique (Madikizela et al., 2017b; Offiong et al., 2019). MIPs as alternative SPE sorbents have also been introduced with a large number of articles coming from China and South Africa. Researchers in China have contributed immensely in advanced applications of MIPs for environmental analysis (Chen et al., 2016; Dai et al., 2015b) while in South Africa the MIPs have been utilized to enhance the detectability of pharmaceuticals using HPLC-DAD (Madikizela and Chimuka, 2016, 2017b; Zunngu et al., 2017). Other extraction techniques that have been used by researchers from developing countries include membrane-based techniques such as HF-LPME reported mainly in South Africa, and China (Mlunguza et al., 2020; Zhang et al., 2013).

Among the developing countries, BRICS (Brazil, Russia, India, China, and South Africa) are better developed economically and have the infrastructure and institutional capacity to source state-of-the-art instrumentation such as ultra-high performance liquid chromatography (UHPLC) and gas chromatography (GC) coupled to mass spectrometry (MS) or high-resolution mass spectrometry (HRMS). Generally, China as the biggest developing country is also the most technologically advanced while South Africa is the cradle of development in Africa. In this regard, various reviews have observed that the extent of research in South Africa remains non-comparable with other African countries (aus der Beek et al., 2016; Madikizela et al., 2017a,b), the same with China in Asia (Philip et al., 2018). In Latin America, Brazil seems to be the most active country in the determination of PPCPs in freshwater sources (Llorca et al., 2017; Quadra et al., 2017). BRICS countries have also financially supported the research on environmental monitoring of PPCPs. The research in these countries continues to surge forward with articles reporting MS and HRMS as detectors. However, while the developed countries have shifted towards the development of automated online techniques and green analytical techniques such as sorbent-based micro-extractions (SPME and SBSE) and solvent-less materials (nanosorbents and ionic liquids) (Patel et al., 2019; Perez-Fernandez et al., 2017), as of now only China has managed to achieve this fit for analysis of PPCPs in environmental samples (Pan et al., 2014). With recent calls for international cooperation and knowledge transfer (aus der Beek et al., 2016), a few researchers in developing countries without the research capacity notably in Kenya (K'oreje et al., 2016; Ngumba et al., 2016) and Uganda (Nantaba et al., 2020) have collaborated with European institutions to provide reliable data about PPCPs pollution in their countries.

Regarding the monitoring of steroid hormones, enzyme-linked immunosorbent assay has been described as the best technique for water analysis (Fang et al., 2016). This technique has been applied in environmental monitoring conducted in South Africa (Manickum and John, 2014). However, other researchers in developing countries have opted for the application of LC–MS during the monitoring of steroid hormones in water (Mnguni et al., 2018; Sodré et al., 2010). In this case, LC–MS remains a preferred analytical tool when pharmaceuticals belonging to different therapeutic classes are monitored in the same investigation (Farounbi and Ngqwala, 2020; Kim et al., 2007).

10.4 Occurrence of pharmaceuticals in freshwater

In Africa, the information on the contamination of environmental waters only emerged after 2012 (Fekadu et al., 2019), with the recent literature review indicating that environmental monitoring has been conducted in less than 50% of African countries (Koreje et al., 2020; Madikizela et al., 2020). The surge in the quantities of PPCPs detected in the environment in recent years can be attributed in part to the rising global population and emergence of new communicable and non-communicable diseases for which aggressive research is continuously being made to find more and better pharmaceuticals for treatment (K'oreje et al., 2018). Despite the recent availability of environmental monitoring data in Africa, Fekadu et al. (2019) observed that the concentrations found in the African freshwaters are nearly 20,000 times higher than those reported in Europe (Fekadu et al., 2019). When focusing on antibiotics alone, a recent review article reported higher concentrations of antibiotics in freshwaters of Africa and Asian-pacific countries reaching 50 and 450 $\mu g\,L^{-1}$, respectively (Danner et al., 2019). The levels of antibiotics in freshwaters of the European and American countries reported in the same article were only up to 10 and 15 $\mu g\,L^{-1}$, respectively. Saari et al. (2017) reviewed the occurrence of calcium channel blockers in the environment and observed the lack and nonexistence of scientific data on monitoring of these pharmaceuticals in environmental waters of South America and Africa (Saari et al., 2017). Also, the monitoring data on the occurrence of antihistamines in water is lacking in developing countries (Kristofco and Brooks, 2017) with one case reported in China for diphenhydramine with the highest concentration of 3 $ng\,L^{-1}$ in Yangtze River (Wu et al., 2014).

Although data is limited, Fig. 10.2 shows that various pharmaceuticals belonging to different therapeutic classes including NSAIDs, ARVDs, antibiotics, β-blockers, antidiabetics, lipid regulators, antidepressants, antipsychotics, muscle relaxants, and anti-epileptics have been detected in freshwaters of the developing countries. While the monitoring of pharmaceuticals in freshwater bodies of the developing countries may still be considered as a new research

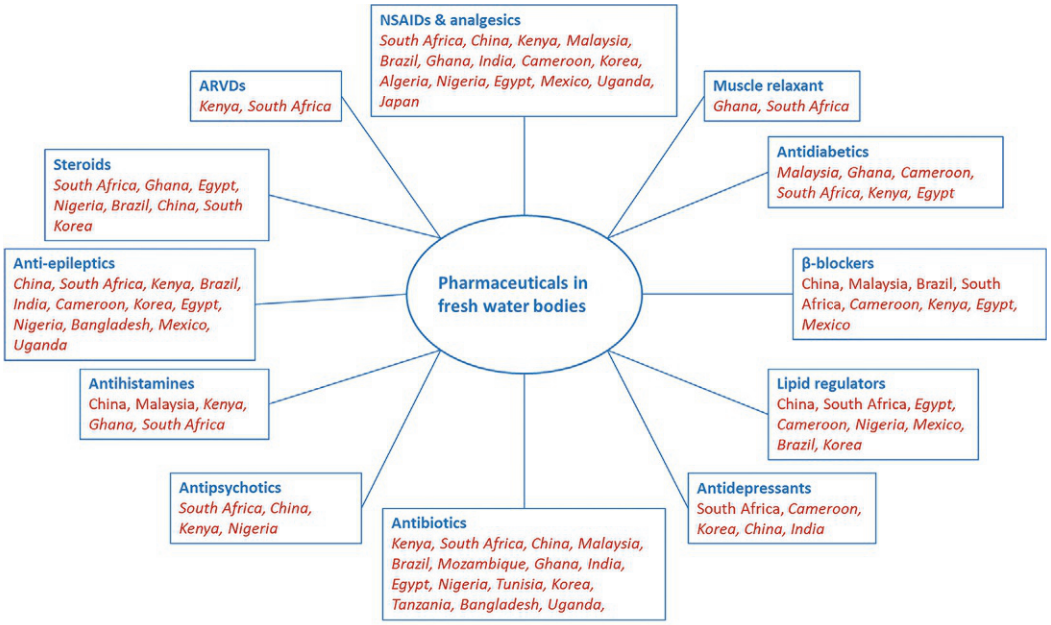


FIG. 10.2 Classes of pharmaceuticals detected in freshwaters of the developing countries. The countries where detection is observed are given in italics.

niche area, researchers from China started to investigate the environmental occurrence of pharmaceuticals over a decade ago (Fatta-kassinos et al., 2011), while in Brazil this started in the 1990s (Stumpf et al., 1999). As a result, review articles on contamination of water bodies by PPCPs in China have been presented (Bu et al., 2013; Liu and Wong, 2013; Richardson et al., 2005; Yidong et al., 2017; Zhao et al., 2016). Extensive environmental monitoring of PPCPs in China could be a result of the high production and consumption of these drugs (Liu and Wong, 2013). Due to similar reasons, the occurrence of PPCPs has also been reviewed in Indian water bodies (Balakrishna et al., 2017).

10.4.1 Nonsteroidal anti-inflammatory drugs and analgesics

NSAIDs and analgesics are available in pharmacies as over-the-counter drugs that one can access without any referral from a medical practitioner. This contributes to the increase in the sales rate for these drugs. Therefore, pharmaceuticals belonging to NSAIDs and analgesics are likely to dominate as environmental pollutants. Hence, they are mostly monitored in the aquatic environment and have been detected in freshwaters of numerous developing countries (Fig. 10.2). Their detection in freshwaters is further influenced by their physicochemical properties which include high water solubility and the presence of polar functional groups in their chemical structures which result in them by-passing most of the WWTP processes. In developed countries, pharmaceutical levels in freshwaters are mostly lesser than the quantities found in domestic WWTPs. This is in accordance with the fact that WWTPs have been labeled as the main source of pharmaceuticals in freshwater. In a South African case, the detection of NSAIDs in river water at higher concentrations than those found in WWTPs was reported (Madikizela et al., 2017a). This observation was linked to the lack of water treatment facilities which is likely to contribute to the direct disposal of pharmaceuticals in the environment through the excretion of human waste into the ground or improper disposal of unused or expired medications.

Our research group has published review articles where the analytical data from African countries published from 2012 to 2016 (Madikizela et al., 2017b) and 2017 to 2019 (Madikizela et al., 2020) was critically reviewed. These review articles showed naproxen, ibuprofen, diclofenac, and meclofenamic acid as the major NSAIDs that are mostly detected in the African surface waters. As shown in Table 10.1, over 10 pharmaceuticals belonging to NSAIDs and analgesics have been detected in freshwaters of the developing countries. Overall, naproxen, ibuprofen, diclofenac, and acetaminophen are the most common NSAIDs detected in developing countries. Generally, ibuprofen is one of the commonly studied pharmaceuticals globally with studies showing that 15% of this drug is excreted unaltered while hydroxyl and carboxylic acid conjugates make up the majority of the excreted metabolites (Ferrando-climent et al., 2012; Mills et al., 1973). The data on the occurrence of NSAIDs from China is dominant (Table 10.1). In general, the detected concentrations of NSAIDs and analgesics in freshwaters are relatively high in the African countries (Nigeria and Kenya) and Brazil (Table 10.1). Acetaminophen showed the highest concentrations in this group of pharmaceuticals with its levels reaching 30,421, 31,003, and 12,430 $\mathrm{ng\,L^{-1}}$ in freshwaters from Kenya, Nigeria, and Brazil, respectively. The technologically advanced developing countries such as China and Korea in Asia have reported the occurrence of trace amounts of etodolac, phenazone, and hydrocodone in important water resources. The levels of these pharmaceuticals (and other pharmaceutical groups given in Table 10.1) in freshwaters vary across different samples and regions. The reported concentrations could be influenced by consumption patterns across different countries, availability of toilets that can be flushed, and the disposal mechanisms of unused or expired medications. This is an indication that each country should conduct its countrywide survey to determine the extent of water pollution caused by pharmaceuticals.

African data published from 2012 to 2019 that has been previously reviewed (Madikizela et al., 2017b, 2020) by our research group is excluded in Table 10.1. Korean surface waters include several lakes (Paldang and Dongbok lakes) and rivers (Han River, Nakdong River, and Youngsan River). Indian rivers—Kaveri, Vellar, and Tamiraparani Rivers.

10.4.2 Antibiotics

Antibiotics are the most prescribed medication all over the world with numbers estimated at 100000 tons per year (Danner et al., 2019). In this regard, environmental antibiotic pollution is expected to be elevated. Hence, the number of antibiotics detected in freshwaters across different developing countries is higher than any other group of pharmaceuticals (Table 10.1). While in the Western world so much quantitative and mitigation work has been done (Carvalho and Santos, 2016; Szymańska et al., 2019), the challenge remains with developing countries due to limited capacity to carry out such decisive steps to protect the human population from potential adverse consequences such as drug resistance. Most of the studies on antibiotics in the developing countries are therefore limited to a few countries compared to

TABLE 10.1 Concentrations (ng$\,L^{-1}$) of common pharmaceuticals found in freshwaters of the developing countries.

Therapeutic group	Pharmaceutical	Concentration	Location	Reference
NSAIDs and analgesics	Naproxen	4	Urban rivers, China	Wang et al. (2015b)
		11	Dianshan Lake, China	Duan et al. (2013)
		328	Pearl River Delta, China	Peng et al. (2008)
		118	Pearl River, China	Zhao et al. (2009)
		41	Liao River, China	Wang et al. (2010)
		18	Korean surface water	Kim et al. (2007)
		100	Han River, Korea	Yoon et al. (2010)
		26	Indian rivers, India	Shanmugam and Sampath (2014)
		50	Paraiba do Sul River, Brazil	Stumpf et al. (1999)
		655	Monjolinho River, Brazil	Campanha et al. (2015)
		100	Lobo reservoir, Brazil	Pompei et al. (2019)
		2120	Lagos surface water, Nigeria	Ebele et al. (2020)
	Ibuprofen	145	Dianshan Lake, China	Duan et al. (2013)
		1417	Pearl River Delta, China	Peng et al. (2008)
		490	Pearl River, China	Zhao et al. (2009)
		99	Yangtze River, China	Wu et al. (2014)
		416	Yellow River, China	Wang et al. (2010)
		38	Korean surface water	Kim et al. (2007)
		51	Han River, Korea	Yoon et al. (2010)
		200	Indian rivers, India	Shanmugam and Sampath (2014)
		743	Monjolinho River, Brazil	Campanha et al. (2015)
		130	Lobo reservoir, Brazil	Pompei et al., 2019)
		780	Lake Victoria, Uganda	Nantaba et al. (2020)
		2740	Lagos surface water, Nigeria	Ebele et al. (2020)
	Diclofenac	124	Dianshan Lake, China	Duan et al. (2013)
		717	Liao River, China	Wang et al. (2010)
		147	Pearl River, China	Zhao et al. (2009)
		7	Korean surface water	Kim et al. (2007)
		30	Han River, Korea	Yoon et al. (2010)
		103	Indian rivers, India	Shanmugam and Sampath (2014)
		60	Paraiba do Sul River, Brazil	Stumpf et al. (1999)
		386	Monjolinho River, Brazil	Campanha et al. (2015)
		50	Lobo reservoir, Brazil	Pompei et al., 2019)
		160	Lake Victoria, Uganda	Nantaba et al. (2020)
		200	Lagos surface water, Nigeria	Ebele et al. (2020)
		188	Langat River, Malaysia	Al-odaini et al. (2013)
		15	Selangor River, Malaysia	Praveena et al. (2018)
	Ketoprofen	6	Dianshan Lake, China	Duan et al. (2013)
		100	Indian rivers, India	Shanmugam and Sampath (2014)
	Indomethacin	1800	Funan River, China	Yang et al. (2008)
		200	Urban rivers, China	Wang et al. (2015b)
		0.7	Naruo-shin River, Japan	Hoshina et al. (2011)
	Etodolac	0.3	Naruo-shin River, Japan	Hoshina et al. (2011)
	Phenazone	26	Urban rivers, China	Wang et al. (2015b)
	Propyphenazone	3	Urban rivers, China	Wang et al. (2015b)
	Mefenamic acid	0.4	Naruo-shin River, Japan	Hoshina et al. (2011)
		64	Langat River, Malaysia	Al-odaini et al. (2013)
		140	Yellow River, China	Wang et al. (2010)
		22	Pearl River, China	Zhao et al. (2009)
	Acetaminophen	30,421	Monjolinho River, Brazil	Campanha et al. (2015)
		130	Lobo reservoir, Brazil	Pompei et al. (2019)
		185	Langat River, Malaysia	Al-odaini et al. (2013)
		85	Chao Lake, China	Wu et al. (2014)
		73	Korean surface water	Kim et al. (2007)
		27	Lake Victoria, Uganda	Nantaba et al. (2020)

TABLE 10.1 Concentrations ($ng L^{-1}$) of common pharmaceuticals found in freshwaters of the developing countries—cont'd

Therapeutic group	Pharmaceutical	Concentration	Location	Reference
		31,003	Nairobi River catchment, Kenya	Bagnis et al. (2020)
		12,430	Lagos surface water, Nigeria	Ebele et al. (2020)
	Aspirin	660	Indian rivers, India	Shanmugam and Sampath, 2014)
	Codeine	2440	Lagos ground water, Nigeria	Ebele et al. (2020)
	Hydrocodone	2	Korean surface water	Kim et al. (2007)
	Tramadol	883	Lagos ground water, Nigeria	Ebele et al. (2020)
	Meclofenamic acid	2000	Lagos surface water, Nigeria	Ebele et al. (2020)
Antibiotics	Sulfamethoxazole	79	Urban rivers, China	Wang et al. (2015b)
		52	Water reservoir, China	Cui et al. (2018)
		190	Haihe River, China	Luo et al. (2011)
		19	Chao Lake, China	Wu et al. (2014)
		0.5	Tap water, China	Qiao et al. (2011)
		114	Selangor River, Malaysia	Praveena et al. (2018)
		36	Korean surface water	Choi et al. (2008)
		61	Han River, Korea	Yoon et al. (2010)
		5600	Lake Victoria, Uganda	Nantaba et al. (2020)
		11,250	Nairobi River catchment, Kenya	Bagnis et al. (2020)
		3180	Lagos surface water, Nigeria	Ebele et al. (2020)
	Trimethoprim	156	Urban rivers, China	Wang et al. (2015b)
		4	Water reservoir, China	Cui et al. (2018)
		106	Ba River, China	Jia et al. (2018)
		140	Haihe River, China	Luo et al. (2011)
		26	Chao Lake, China	Wu et al. (2014)
		5	Korean surface water	Kim et al. (2007)
		17	Han River, Korea	Yoon et al. (2010)
		89	Lake Victoria, Uganda	Nantaba et al. (2020)
		3346	Nairobi River catchment, Kenya	Bagnis et al. (2020)
		388	Lagos surface water, Nigeria	Ebele et al. (2020)
	Azithromycin	129	Urban rivers, China	Wang et al. (2015b)
		60	Lake Victoria, Uganda	Nantaba et al. (2020)
	Clarithromycin	123	Urban rivers, China	Wang et al. (2015b)
		103	Yangtze River, China	Wu et al. (2014)
	Erythromycin	22	Urban rivers, China	Wang et al. (2015b)
		808	Yangtze River, China	Wu et al. (2014)
		38	Haihe River, China	Luo et al. (2011)
		300	Ba River, China	Jia et al. (2018)
		5	Korean surface water	Kim et al. (2007)
		66	Lake Victoria, Uganda	Nantaba et al. (2020)
		275	Lagos surface water, Nigeria	Ebele et al. (2020)
	Roxithromycin	206	Urban rivers, China	Wang et al. (2015b)
		2	Water reservoir, China	Cui et al. (2018)
		37	Haihe River, China	Luo et al. (2011)
	Levofloxacin	213	Urban rivers, China	Wang et al. (2015b)
		29	Lake Victoria, Uganda	Nantaba et al. (2020)
	Lincomycin	180	Urban rivers, China	Wang et al. (2015b)
		357	Tai lake, China	Wu et al. (2014)
	QCA	26	Urban rivers, China	Wang et al. (2015b)
	Giseofulvin	16	Urban rivers, China	Wang et al. (2015b)
	Tiamulin	3	Urban rivers, China	Wang et al. (2015b)
	Sulfadimethoxine	344	Urban rivers, China	Wang et al. (2015b)

Continued

TABLE 10.1 Concentrations ($ng\,L^{-1}$) of common pharmaceuticals found in freshwaters of the developing countries—cont'd

Therapeutic group	Pharmaceutical	Concentration	Location	Reference
	Sulfamethazine	3	Urban rivers, China	Wang et al. (2015b)
		15	Water reservoir, China	Cui et al. (2018)
		464	Ba River, China	Jia et al. (2018)
		38	Yangtze River, China	Wu et al. (2014)
		50	Lake Victoria, Uganda	Nantaba et al. (2020)
	Clindamycin	503	Tai lake, China	Wu et al. (2014)
	Sulfapyridine	61	Urban rivers, China	Wang et al. (2015b)
	Sulfadiazine	21	Water reservoir, China	Cui et al. (2018)
		39	Ba River, China	Jia et al. (2018)
		170	Haihe River, China	Luo et al. (2011)
	Sulfachloropyridazine	3	Water reservoir, China	Cui et al. (2018)
		210	Haihe River, China	Luo et al. (2011)
	Enrofloxacin	19	Water reservoir, China	Cui et al. (2018)
	Ofloxacin	19	Water reservoir, China	Cui et al. (2018)
		180	Haihe River, China	Luo et al. (2011)
	Norfloxacin	48	Water reservoir, China	Cui et al. (2018)
		122	Ba River, China	Jia et al. (2018)
		26	Lake Victoria, Uganda	Nantaba et al. (2020)
	Ciprofloxacin	176	Water reservoir, China	Cui et al. (2018)
		130	Haihe River, China	Luo et al. (2011)
		29	Ba River, China	Jia et al. (2018)
		300	Gombak River, Malaysia	Praveena et al. (2018)
		41	Lake Victoria, Uganda	Nantaba et al. (2020)
		168	Nairobi River catchment, Kenya	Bagnis et al. (2020)
	Tetracycline	95	Water reservoir, China	Cui et al. (2018)
		27	Haihe River, China	Luo et al. (2011)
		854	Ba River, China	Jia et al. (2018)
		70	Lake Victoria, Uganda	Nantaba et al. (2020)
	Oxytetracycline	241	Water reservoir, China	Cui et al. (2018)
		41	Haihe River, China	Luo et al. (2011)
		164	Ba River, China	Jia et al. (2018)
		300	Lake Victoria, Uganda	Nantaba et al. (2020)
	Enoxacin	51	Lake Victoria, Uganda	Nantaba et al. (2020)
	Chlortetracycline	272	Ba River, China	Jia et al. (2018)
	Cefotaxime	18	Ba River, China	Jia et al. (2018)
	Cefazolin	33	Ba River, China	Jia et al. (2018)
	Chloramphenicol	33	Ba River, China	Jia et al. (2018)
		24	Selangor River, Malaysia	Praveena et al. (2018)
	Amoxicillin	4	Lui River, Malaysia	Praveena et al. (2018)
		272,150	Lagos surface water, Nigeria	Ebele et al. (2020)
	Sulfacetamide	13	Lake Victoria, Uganda	Nantaba et al. (2020)
ARVDs	Efavirenz	37,300	Springfield, South Africa	Mlunguza et al. (2020)
	Emtricitabine	220	Springfield, South Africa	Mlunguza et al. (2020)
	Tenofovir disoproxil	110	Hartbeespoort dam, South Africa	Mlunguza et al. (2020)
β-Blockers	Atenolol	181	Urban rivers, China	Wang et al. (2015b)
		0.2	Tap water, China	Qiao et al. (2011)
		80	Langat River, Malaysia	Al-odaini et al. (2013)

TABLE 10.1 Concentrations ($ng L^{-1}$) of common pharmaceuticals found in freshwaters of the developing countries—cont'd

Therapeutic group	Pharmaceutical	Concentration	Location	Reference
		150	Han River, Korea	Yoon et al. (2010)
		8199	Monjolinho River, Brazil	Campanha et al. (2015)
		380	Lake Victoria, Uganda	Nantaba et al. (2020)
	Metoprolol	134	Urban rivers, China	Wang et al. (2015b)
		173	Langat River, Malaysia	Al-odaini et al. (2013)
		21	Lake Victoria, Uganda	Nantaba et al. (2020)
		168	Lagos surface water, Nigeria	Ebele et al. (2020)
	Diltiazem	6	Urban rivers, China	Wang et al. (2015b)
		0.3	Yangtze River, China	Wu et al. (2014)
	Disopyramide	13	Urban rivers, China	Wang et al. (2015b)
	Propranolol	77	Monjolinho River, Brazil	Campanha et al. (2015)
		12	Lagos surface water, Nigeria	Ebele et al. (2020)
Lipid-regulators	Bezafibrate	7	Urban rivers, China	Wang et al. (2015b)
	Gemfibrozil	9	Korean surface water	Kim et al. (2007)
		13	Han River, Korea	Yoon et al. (2010)
		87	Hai River, China	Wang et al. (2010)
		17	Pearl River, China	Zhao et al. (2009)
		730	Lagos groundwater, Nigeria	Ebele et al. (2020)
	Atorvastatin	6	Han River, Korea	Yoon et al. (2010)
Antipsychotics	Sulpiride	200	Urban rivers, China	Wang et al. (2015b)
		0.1	Tap water, China	Qiao et al. (2011)
Anti-epileptics	Carbamazepine	21	Urban rivers, China	Wang et al. (2015b)
		3	Chao Lake, China	Wu et al. (2014)
		61	Korean surface water	Kim et al. (2007)
		68	Han River, Korea	Yoon et al. (2010)
		215	Monjolinho River, Brazil	Campanha et al. (2015)
		72	Lake Victoria, Uganda	Nantaba et al. (2020)
		172	Nairobi River catchment, Kenya	Bagnis et al. (2020)
		342	Lagos surface water, Nigeria	Ebele et al. (2020)
	Gabapentin	67	Lagos surface water, Nigeria	Ebele et al. (2020)
	Dilantin	9	Korean surface water	Kim et al. (2007)
		17	Han River, Korea	Yoon et al. (2010)
Antidiabetics	Metformin	132	Langat River, Malaysia	Al-odaini et al. (2013)
		1760	Lagos surface water, Nigeria	Ebele et al. (2020)
	Glyburide	326	Lagos surface water, Nigeria	Ebele et al. (2020)
	Gliclazide	7	Langat River, Malaysia	Al-odaini et al. (2013)

developed countries with Danner et al., 2019 observing that they have been reported in Brazil, China, Vietnam, Korea, Iran, Kenya, Mozambique, Nigeria, Ghana and South Africa (Danner et al., 2019). In China as the technologically based country and most resourceful in comparison with other developing countries, the monitoring of antibiotics have been conducted in most useful freshwater resources such as lakes (Wang et al., 2018), groundwater (Yang et al., 2017), water reservoirs (Cui et al., 2018) and rivers (Wu et al., 2014). In African countries, the analytical data is dominated by the work conducted in rivers (Madikizela et al., 2017b, 2020). In addition, while in Europe the reported concentrations are only as high as $10\,ng\,mL^{-1}$, among the developing countries in Africa and Asia the concentrations are as high as 50 and $450\,ng\,mL^{-1}$ respectively (Danner et al., 2019). For example, Fekadu et al., 2019 observed that some antibiotics such as ciprofloxacin and sulfamethoxazole have been detected in Africa at levels more than 100 times those reported in Europe (Fekadu et al., 2019).

Sulfamethoxazole, trimethoprim, erythromycin, sulfamethazine, and ciprofloxacin are the most common antibiotics in freshwaters from developing countries (Table 10.1). As was the case in the African WWTPs which are considered as the main feed of antibiotics in the surface water (Madikizela et al., 2020), sulfamethoxazole appeared most prominently in freshwater from developing countries with a maximum concentration of 11,250 ng L^{-1} recorded in Kenya (Bagnis et al., 2020). However, amoxicillin which was only measured in freshwaters from Nigeria (Ebele et al., 2020) and Malaysia (Praveena et al., 2018) had the highest concentration of 272,150 ng L^{-1} among other detected antibiotics. The occurrence of antibiotics in water and their environmental quantities are likely to be influenced by multiple prescriptions from healthcare professionals as some of these pharmaceuticals are only accessible through medical prescriptions.

10.4.3 Antiretroviral drugs

HIV/AIDS mostly affects people from developing countries with recent information indicating South Africa as the country with the biggest antiretroviral treatment (Ncube et al., 2018). As a result, the recent literature shows that the environmental monitoring of ARVDs is more noticeable in African countries particularly South Africa and Kenya (Madikizela et al., 2017b, 2020). ARVDs have also been reported in drinking surface water sources of Germany, the USA, France, Poland, and Finland (Ncube et al., 2018). The concentrations of ARVDs found in African freshwaters have been reviewed elsewhere (Madikizela et al., 2017b, 2020; Ncube et al., 2018), except for newly published research from South Africa (data included in Table 10.1) (Mlunguza et al., 2020). Previous work shows nevirapine and efavirenz as the most monitored drugs in the environment, while lamivudine has been found with the highest concentration of 167,100 ng L^{-1} in Kenyan freshwaters (K'oreje et al., 2016). High levels of lamivudine in freshwaters, when compared to its counterparts (nevirapine and efavirenz), could be related to its higher solubility in water, while consumption and excretion rates have the potential to influence the environmental trends. Water solubility given in the literature for lamivudine, efavirenz, and nevirapine is 70, 0.00855, and 0.7046 mg mL^{-1}, respectively (Ncube et al., 2018). Furthermore, the environmental concentrations of ARVDs found in African waters have been reported to be higher than in any other continent.

10.4.4 Beta-blockers

The distribution of β-blockers in freshwaters from the developing countries has been observed (Table 10.1). Related research has been conducted in China, Malaysia, Korea, Brazil, Uganda, and Nigeria. The reviewed literature (Table 10.1) showed atenolol as the most plentiful drug of this therapeutic class in freshwater with a maximum concentration of 8199 ng L^{-1} detected in Monjolinho River, Brazil (Campanha et al., 2015). In comparison with the developed world, the highest recorded concentration for atenolol in Lake Ontario (Canada) was 28 ng L^{-1} (Li et al., 2010). The highest concentration of metoprolol found in the same lake was 5 ng L^{-1} (Li et al., 2010). These levels are lower than those found in a lake in Uganda (a developing country) where 380 and 21 ng L^{-1} were recorded for atenolol and metoprolol respectively (Nantaba et al., 2020). Three β-blockers (metoprolol, propranolol, and atenolol) have been detected in surface waters of Egypt and Cameroon at concentrations not exceeding 17 ng L^{-1} (Madikizela et al., 2020). These concentrations are viewed as an indication that intensive monitoring for these drugs is required in developing countries. The variations across different countries and sampling sites are influenced by the differences in consumption patterns and the time of sampling. Also, the employed analytical methods can influence the analytical data, taking into consideration passive sampling was utilized in the measurement of β-blockers in Canada (Li et al., 2010) as opposed to the grab sampling applied in the cited work from the developing countries.

10.4.5 Lipid-regulators

Reviewed literature shows gemfibrozil as the most studied/detected lipid-regulator in freshwaters of the developing countries with its highest concentration of 730 ng L^{-1} reported in groundwater of Lagos, Nigeria (Table 10.1). This is almost two times higher than the 368 ng L^{-1} concentration reported in surface water from Morelos, Mexico (Rivera-jaimes et al., 2018). Although there is only one reported case of bezafibrate in urban rivers of China with a concentration of 7 ng L^{-1} (Wang et al., 2015b), this pharmaceutical has reached 233 ng L^{-1} in the Msunduzi River of South Africa (data not tabulated) (Agunbiade and Moodley, 2016). More research work on the occurrence of lipid regulators in freshwaters of the developing countries is expected to rise shortly.

10.4.6 Antiepileptics

Carbamazepine is the most common anti-epileptic drug studied worldwide. Generally, the quantities of carbamazepine detected in freshwaters are minimal (Table 10.1) and the levels reported in African waters are comparable with those reported in European countries (Germany and Portugal) and the United States of America (Madikizela et al., 2017b). For example, Choi et al. (2008) observed that carbamazepine levels of 6–36 ng L^{-1} in the Han River (Korea) were comparable with those reported in rivers of Ontario (Canada) (Choi et al., 2008). The reported low levels of this pharmaceutical in water could be a result of its phototransformation when exposed to natural UV light (Daneshvar et al., 2010). Its metabolites (10,11-dihydroxy-carbamazepine and 10-hydroxy-carbamazepine) have been detected in surface water from the developed countries (Ferrer and Thurman, 2012). In Spain (Ebro river basin), the concentration of 10,11-epoxy-carbamazepine was approximately 10 times higher than carbamazepine (López-serna et al., 2012). This is an indication that carbamazepine should be monitored in the environment simultaneously with its metabolites. This pharmaceutical was found to be most abundant among the 15 environmental pollutants investigated in Hartbeespoort Dam groundwater (South Africa) (Rimayi et al., 2018). Gabapentin and Dilantin are other anti-epileptic drugs found present in freshwaters of developing countries notably Nigeria and Korea with their levels not exceeding 100 ng L^{-1} (Table 10.1).

10.4.7 Steroid hormones

Steroid hormones are noticeable water pollutants in Africa (Fekadu et al., 2019; Madikizela et al., 2017b, 2020). In the context of the developing countries, steroid hormones have been found present in freshwaters of South Africa, Ghana, Egypt, Nigeria, Brazil, South Korea, and China (Fig. 10.2). Two steroid hormones (estriol and 17β-estradiol) were listed in the top 10 pharmaceuticals with the highest concentrations ever reported in the African aquatic environment (Fekadu et al., 2019). In a comparison study, Fekadu et al. (2019) observed that the highest concentrations reported in Africa were about 3140 times and 20,000 times higher than in Europe for 17β-estradiol and estriol, respectively (Fekadu et al., 2019). The general trend in Brazil was that steroid hormones are the most investigated pharmaceuticals in water with relatively higher concentrations detected when compared to other compounds (Quadra et al., 2017). However, this was not the case in the surface waters of a central urban region of São Paulo State of Southeast Brazil where 17β-estradiol and estriol were the least detected with concentration levels of up to 14.8 ng L^{-1} (Campanha et al., 2015). In a different Brazilian study, the concentrations of steroid hormones in the Atibaia River Basin varied from 2.2 to 39 ng L^{-1} (Sodré et al., 2010). Surface and drinking water from Brazil were also found to be contaminated with estriol, estrone, progesterone, 17β-estradiol, and 17α-ethinylestradiol with concentrations reaching 90, 28, 26, 137, and 194 ng L^{-1}, respectively (Torres et al., 2015). In South Korean surface water, two steroid hormones, estrone, and androstenedione were detected with a concentration of 3.6 and 2.6 ng L^{-1}, respectively (Kim et al., 2007). Other steroid hormones investigated in the same South Korean study and not detected were estriol, 17α-ethynylestradiol, 17β-estradiol, and testosterone. Steroid hormones are also common in freshwaters of China (Peng et al., 2008; Zhao et al., 2009).

10.4.8 Other pharmaceuticals

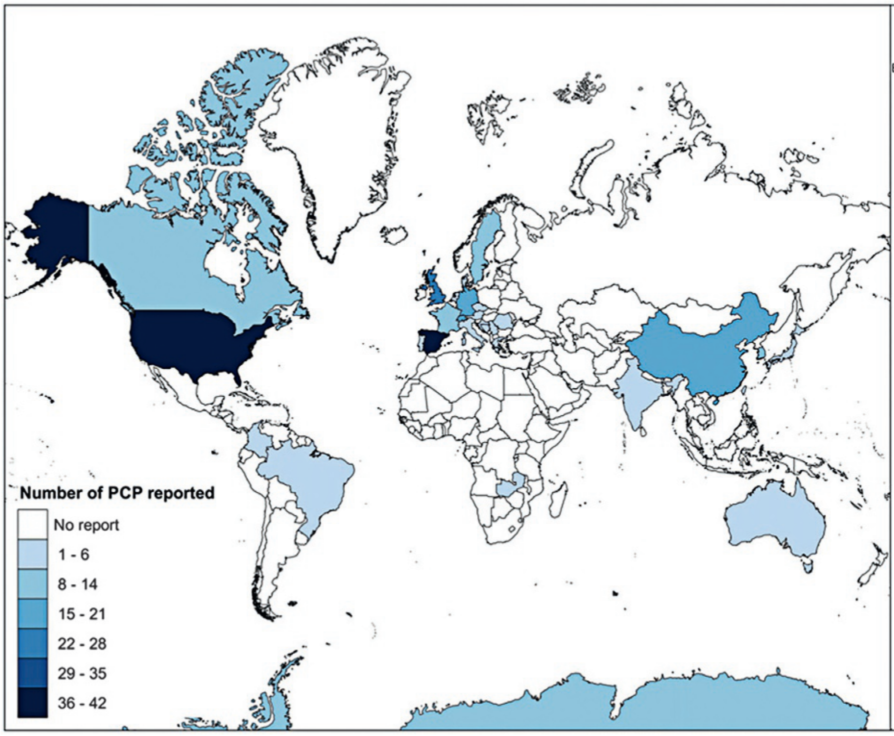
In addition to the major classes of pharmaceuticals already discussed in this document, other drugs are occasionally detected in freshwaters from developing countries. The examples are amitriptyline (antidepressant), hydrocortisone (glucocorticoids), diazepam (benzodiazepines), rimantadine (antiviral), sulfadoxine (antimalarial) detected in Kenyan rivers (Bagnis et al., 2020; K'oreje et al., 2016). Notably, an antimalarial (sulfadoxine) was found present in the Kenyan rivers while another antimalarial, mefloquine has been detected with concentrations of up to 58 ng L^{-1} in Lagos State surface water (Nigeria) was observed (Ebele et al., 2020). As noted in our previous research (Madikizela et al., 2017b), an interest to monitor antimalarial drugs in African waters could be due to high malaria infections in the continent. A study conducted in the Lagos State of Nigeria showed the occurrence of various pharmaceuticals in surface water and groundwater that is not commonly reported in freshwaters of developing countries (Ebele et al., 2020). These pharmaceuticals with concentrations reaching 1220, 42, 618, and 3330 ng L^{-1} are oxazepam, diazepam (both benzodiazepines), clotrimazole (antifungal), and valsartan (angiotensin receptor blocker) respectively. In Malaysia, the concentration of chlorothiazide used as antihypertensive found in surface water reached 103 ng L^{-1} (Al-odaini et al., 2013). Other drugs detected in Malaysian surface waters are furosemide (diuretic), salbutamol (bronchodilator), perindopril (angiotensin-converting enzyme inhibitor), salicylic acid (keratolytic agent), dexamethasone (corticosteroid), and glibenclamide (sulfonylurea) at 177, 2, 6, 115, 9, and 3 ng L^{-1}, respectively (Al-odaini et al., 2013;

Praveena et al., 2018). Salicylic acid had a maximum concentration of 2098 ng L^{-1} in Pearl River Delta, China (Peng et al., 2008). In Liao River (China), the maximum concentration for the same drug was 295 ng L^{-1} (Wang et al., 2010). Salicylic acid should be monitored alongside aspirin (acetylsalicylic acid) which is commonly detected in environmental waters as these two drugs are related. Previous research suggests that approximately 10% of aspirin is excreted as part of the urine in the form of salicylic acid (Gumbi et al., 2017). Furthermore, aspirin in the environment degrades is easily converted into salicylic acid (Gumbi et al., 2017). The concentrations of pentoxifylline (hemorheologic agent) and iopromide (non-ionic X-ray contrast) in Korean surface waters reached 2 and 361 ng L^{-1} respectively (Kim et al., 2007). Iopromide was also found present in the Han River (Korea) with its concentration reaching 1800 ng L^{-1} (Yoon et al., 2010). Follow-up investigations are required to determine the extent, fate, and effects of these drugs in freshwater. This should be also done in developed countries since the environmental occurrence of these pharmaceuticals is not well known worldwide.

In few instances, pharmaceuticals belonging to the groups of antidiabetics, muscle relaxants, and antipsychotics have been found present in freshwaters of the developing countries. As shown in Table 10.1, an antipsychotic drug, sulpiride has been found in tap water and urban rivers in China with the highest concentration of 200 ng L^{-1}. Antidiabetics have been detected in Nigeria and Malaysia (Table 10.1).

10.5 Occurrence of personal care products in freshwater

Global reviews on the occurrence of PCPs in aquatic environments have been presented (Brausch and Rand, 2011; Montes-grajales et al., 2017). In this context, a book devoted to the occurrence of PCPs in the aquatic environment has been published (Diaz-cruz and Barcelo, 2015). The contents of the book include the chapters that focused on the presence of PCPs in waters from Europe, the USA, and China, with the inclusion of the environmental risk assessment. The chapter focusing on PCPs in the aquatic environment of China is an indication that China is leading other developing countries on the environmental monitoring of these compounds. Furthermore, Liu and Wong (2013) published a review article mainly focusing on the environmental contamination in China due to the occurrence of PPCPs (Liu and Wong, 2013). In the Global context, some review articles have focused on the occurrence of both pharmaceuticals and PCPs in water bodies (Balakrishna et al., 2017; Bu et al., 2013; Cizmas et al., 2015; Ebele et al., 2017; Sui et al., 2015). The current section is devoted to the monitored PCPs in freshwaters of the developing countries, despite the limited



Place	No. PCPs	PCP reported
Antarctic	8	4MBC, BP-1, BP-3, BPB, MPB, MTCS, PPB, TCS
Australia	1	TCS
Austria	5	AHTN, HHCB, NP, NP1EO, OP
Bosnia-Herzegovina	7	AHTN, ATII, DEET, HHCB, HHCB-Lactone, MX, NP
Brasil	2	AHTN, HHCB
Canada	11	ADBI, AHMI, AHTN, ATII, DPMI, HHCB, MK, MX, NP, TCC, TCS
China	19	2-NP, 4-NP, ADBI, AHMI, AHTN, ATII, BPB, DEET, DPMI, EPB, HHCB, MK, MPB, MX, OP, OPP, PPB, TCC, TCS
Colombia	2	AHTN, HHCB
Croatia	7	AHTN, ATII, DEET, HHCB, HHCB-Lactone, MX, NP
Czech Republic	1	TCS
Denmark	4	AHTN,DPMI,HHCB,TCS
France	9	ADBI, AHMI, AHTN, ATII, DPMI, HHCB, MA, MK, MX
Germany	20	2-amino-MK, 2-amino-MX, 4-amino-MX, 4MBC, 4-NP, ADBI, AHMI, AHTN, ATII, BP-3, EHMC, HHCB, HHCB-lactone, Lilial, MK, MNT, MX, OC, OP, OTNE
Greece	2	NP, TCS
India	5	EPB, MPB, PPB, TCC, TCS
Italy	3	BP-3, EHMC, OC
Japan	3	DEET, NP, TCS
Netherlands	2	AHTN, HHCB
Portugal	5	ADBI, AHTN, ATII, DPMI, HHCB
Romania	3	AHTN, HHCB, TCS
Serbia	7	AHTN, ATII, DEET, HHCB, HHCB-Lactone, MX, NP
Singapore	1	DEET
South Korea	11	AHMI, AHTN, BP, BP3, ADBI, DEET, HHCB, MK, MX, TCC, TCS
Spain	42	2-EHMC, 4MBC, ADBI, AHMI, AHTN, AMB, ATII, BS, BHT, BP-3, Celvetolide, Civetone, CPD, DEET, DPMI, EHMC, Eugenol, Helvetolide, HHCB, HHCB-Lactone,LAS C10, LAS C11, LAS C12, LAS C13, Lilial, Limonene, Linalool, MA, MJD, MK, MM, Muscone, Musk MC4, Musk NN, MX, NP, OC, PDL, Romandolide, TBCr, TCC, TCS
Sweden	10	ADBI, AHMI, AHTN, ATII, BP, DPMI, HHCB, MK, MX, NP
Switzerland	18	4MBC, AMA, AMM, ADBI, AHMI, AHTN, ATII, DPMI, HHCB, HHCB-lactone, MA, MK, MM, MT, MX, OC, OMC, OT
Taiwan	6	AHMI, AHTN, BP-3, BP4, DPMI, HHCB
UK	22	3,4,5,6-tetrabromo-o-cresol , ADBI, AHMI, AHTN, ATII, BP, BP-1, BP-2, BP-3, BP-4, BPB, CP, EPB, HHCB, MK, MPB, MX, OP, p-benzylphenol, PCPMX, PPB, TCS
USA	36	2-amino-MK, 2-amino-MX, 4-amino-MX, 4-NP, ACN, ADBI, AETT, AHMI, AHTN, ATII, BHT, BP, BP-3, CMP, CP, DEET, DPMI, HHCB, HHCB-lactone, Limonene, MA, MK, MM, MT, MX, MNT, MPB, MTCS, NP, OP, OPP, OTNE, PCMX, PPB, TCC, TCS
Zambia	2	DEET, TCS

FIG. 10.3 Countries with reports on monitoring PCPs in water (Montes-grajales et al., 2017). Literature search conducted in 2016.

TABLE 10.2 Maximum concentrations of personal care products found in freshwaters of the developing countries.

Compound	Concentration ($ng\,L^{-1}$)	Location	Reference
Triclosan	900	Mbokodweni River, South Africa	Madikizela et al., 2014)
	30	Groundwater, Zambia	Sorensen et al. (2015)
	281	Monjolinho River, Brazil	Campanha et al. (2015)
	789	Upper Tibagi River basin, Brazil	Reichert et al. (2020)
	9650	Gomti River, India	Nag et al. (2018)
Triclocarban	17	Dongting Lake, China	Wu et al. (2014)
Methyl paraben	1,192,390	Lobo reservoir, Brazil	Pompei et al. (2019)
	265	Upper Tibagi River basin, Brazil	Reichert et al. (2020)
Ethyl paraben	145	Upper Tibagi River basin, Brazil	Reichert et al. (2020)
Propyl paraben	487	Upper Tibagi River basin, Brazil	Reichert et al. (2020)
Butyl paraben	133	Upper Tibagi River basin, Brazil	Reichert et al. (2020)
2-Hydroxy-4-methoxybenzophenone	2100	Lobo reservoir, Brazil	Pompei et al. (2019)
Caffeine	786	Yangtze River, China	Wu et al. (2014)
	4200	Beiyun River, China	Dai et al. (2015a)
	1080	Surface water, Nigeria	Ebele et al. (2020)
N,*N*-diethyl-meta-toluamide (DEET)	1350	Surface water, Nigeria	Ebele et al. (2020)
	1800	Groundwater, Zambia	Sorensen et al. (2015)
	546	Beiyun River, China	Dai et al. (2015a)
	36	Tone River basin, Japan	Nakada et al. (2007)

availability of published data (Fig. 10.3). The literature search conducted in 2016 indicated the extensive availability of analytical data in Europe, North America, and China while there was a poor representation from the rest of the world (Fig. 10.3) (Montes-grajales et al., 2017). Bu et al. (2013) observed the monitoring of three categories of PCPs (musk fragrances, disinfectants, and preservatives) in surface waters of China (Bu et al., 2013). Their levels in the water were comparable with those detected in developed countries such as the USA and Germany; while they were much lower than the concentrations found in Korea, Baltimore, and Maryland (Bu et al., 2013).

Table 10.2 gives a list of some PCPs and their respective concentrations that have been monitored in developing countries. There is some progress in the monitoring data observed since the publication of the information in Fig. 10.2. In the present study, more reports are found from African countries (South Africa, Zambia, and Nigeria) (Ebele et al., 2020; Madikizela et al., 2014; Sorensen et al., 2015). In China where intensive monitoring of freshwater contaminants occurs, caffeine was observed as the predominant compound among the 15 PCPs monitored in the Beiyun River with its concentration reaching 4200 $ng\,L^{-1}$ (Dai et al., 2015a). The concentration of the same compound was 1080 $ng\,L^{-1}$ in surface water from Nigeria (Ebele et al., 2020). Monitoring of triclosan (an antibacterial agent) has been reported in few cases with its concentration reaching 900 $ng\,L^{-1}$ in a South African river (Madikizela et al., 2014), while the concentration range of 1100–9650 $ng\,L^{-1}$ was reported in the Gomti River, India (Nag et al., 2018). A series of preservatives were found in the Brazilian river basin (Reichert et al., 2020), but the highest concentration of 1,192,390 $ng\,L^{-1}$ was recorded for methylparaben in the Lobo reservoir, Brazil (Pompei et al., 2019). Preservatives were also detected in the surface waters of Japan (Kimura et al., 2014). An insect repellent, DEET, is also a noticeable PCP in freshwaters of developing countries. The concentration range reported for UV filters in rivers of Korea is 62.9–412 $ng\,L^{-1}$ (Ekpeghere et al., 2016).

Based on the presented information, it is noticeable that in the developing countries there is more scientific data on the occurrence of PCPs in freshwaters that are published from the African and Asian countries as well as in Brazil. Without reviewing the literature that is already published in the form of review articles or book chapters, it can be concluded that researchers from the developing countries are concerned with the environmental occurrence of PCPs that belong to different groups including antibacterial agents (Madikizela et al., 2014), UV filters (Ekpeghere et al., 2016), preservatives (Pompei et al., 2019) and insect repellent in the form of DEET (Nakada et al., 2007).

10.6 Health effects and environmental concerns

Environmental effects of PPCPs in freshwater systems are important to estimate their impact and to protect the environment from exposure risks. Herein, the health risks and environmental concerns related to unintentional consumption of PPCPs due to their presence in freshwater are summarized. In this context, the presence of antibiotics in freshwater resources and the fate of antibiotic-resistant bacteria in freshwater is still an emerging area of research (Li et al., 2019). Antibiotics in the environment can alter the normal bacterial compositions in stable ecosystems (Archer et al., 2017). Also, chronic levels of antihypertensives and β-blockers in aquatic systems whose mechanism of action is primarily to act as a vasodilator and lowering blood pressure may lead to low blood circulation in aquatic animals (Gu et al., 2019). Anesthetics and sedatives such as methaqualone which are frequently detected in urban freshwaters can also have a chronic sedative effect on aquatic animals. However, some anesthetics are noted to cause an opposite effect and have been found to increase brain activity in zebrafish, a phenomenon termed paradoxical excitation (Mccarroll et al., 2019). These effects can increase their risk of survival in aquatic ecosystems.

Antidiabetic drugs may affect a range of biochemical processes in aquatic animals especially the widely used metformin which has been shown to cause higher hepatic glycogen levels in brown trout larvae when the larvae were exposed to $1\,\mu g\,L^{-1}$ (environmentally relevant concentration) compared to controls (Eur et al., 2018). Antiepileptic drugs act by altering electrical activities in the neurons, for example by blocking gated sodium and calcium channels or enhancement of gamma-aminobutyric acid (GABA)-mediated inhibitory neurotransmission. There is concern over the chronic presence of antiepileptic drugs in freshwater resources which can lead to adverse effects on the neurological functions of aquatic animals with carbamazepine known to cause neurotoxicity, oxidative stress, and diminished predator evasive behavior in exposed Daphnia magma (Nkoom et al., 2019). Antiviral drugs are widely found in Kenyan and South African surface water resources (K'oreje et al., 2018; Wood et al., 2017), and there have been concerns about the wide range of ARVDs detected amidst the scant information about their environmental effects (Ncube et al., 2018).

The zebrafish embryos exposed to triclosan at concentrations ranging from 0.1 to $0.9\,mg\,L^{-1}$ developed spine malformations, pericardial edema, stunted growth, and exposed eggs experienced delayed hatching (Oliveira and Domingues, 2009). All these effects could adversely affect fish survival in the aquatic environment. Ethinyl estradiol is one of the most ubiquitous estrogenic compounds in effluent-dominated waters worldwide (Bhandari et al., 2015). It has been found to induce phenotypic plasticity, cause reproductive impairment, reduce fertilization rates in fish and affect embryonic survival of Japanese rice fish (Bhandari et al., 2015). Antipsychotic and antidepressant medications such as venlafaxine and amitriptyline caused oxidative stress, reduced hatching time, and stunted growth in embryos of exposed zebrafish (Yang et al., 2014).

Parabens are some of the most common preservatives used as biocides in the cosmetics, pharmaceutical, and food industries (Nowak et al., 2018). They consist of alkyl or aryl homologs of p-hydroxybenzoic acid (PHBA) and are endocrine disruptors (Bazin et al., 2010). The risk of parabens from freshwater resources on humans is likely low compared to parabens in food as they have been extensively detected in many foodstuffs, at very high concentrations up to $109\,ng\,g^{-1}$ in vegetables (Nowak et al., 2018). Parabens have been shown to bind to endocrine receptor cells, causing weak estrogenic activity (Okubo et al., 2001).

10.7 Regulations

Among the few countries which have set regulations for assessing the environmental risk of human pharmaceuticals, the USA, EU, and Canada have established frameworks and instruments for assessing the environmental impact of PPCPs in the environment (Lee and Choi, 2019; Letsinger and Kay, 2019). Their legislation differs in some ways between the countries, with the US and EU assessing the pharmaceutical products and Canada assessing the active pharmaceutical ingredients (Lee and Choi, 2019). The European Medical Agency has made it mandatory to perform an environmental risk assessment on new pharmaceuticals before seeking registration and authorization to market a drug (Bound and Voulvoulis, 2004). PCP regulations in the EU fall under Directive 98/8/EC, with set conditions for approval and authorization of biocides. The directive specifically prohibits the approval of biocides which may cause adverse health impacts on nontarget organisms, unacceptable resistance to micro-organisms, adverse effects on human and animal reproduction, cause pain and suffering to invertebrates exposed directly and indirectly, and are toxic to humans and animals (Patryn et al., 2011). Under the Canadian Environmental Protection Act of 1999, Directive 2001/83/EC mandates the submission of an environmental risk assessment before marketing authorization can be granted for human pharmaceuticals (Lee and Choi, 2019). The Veterinary International Cooperation on Harmonization program has set guidelines for evaluating the environmental safety of veterinary pharmaceuticals before marketing authorization can be granted (Lee and Choi, 2019).

The European Medical Agency has noted that active pharmaceutical ingredients may enter the environment during manufacture, use, and disposal, therefore the Agency has mandated that their impact should be given due consideration and assessed on a case-by-case basis (Agency, 2018). Annex II of Commission Regulation (EC) No. 1085/2003 mandates that an environmental risk assessment must also be performed if there is a significant increase in the use of the active pharmaceutical ingredients which is linked to an increase in environmental exposure. The European Medical Agency has made exemptions for vitamins, amino acids, proteins, peptides, lipids, carbohydrates, electrolytes, herbal medicinal products, and vaccines as they have been deemed a low risk to the environment (Lee and Choi, 2019). The EC regulations however require that a justification be submitted instead, motivating why an environmental risk assessment should not be submitted. For risk assessment, Organization for Economic Co-operation and Development guideline 308 for testing aerobic and anaerobic transformation of organic chemicals in aquatic sediment systems is the requisite test for generating data for the environmental risk assessment (Agency, 2018). In the USA, the National Environmental Policy Act regulates the manufacture, use, and distribution of human and veterinary drugs. The US Food and Drug Administration is the regulatory authority that requires an environmental risk assessment before the approval of drugs. Currently, none of the developing countries have developed or implemented guidelines or legislation to regulate or assess PPCPs in freshwater resources.

10.8 Conclusions

In this chapter, the occurrence of PPCPs in freshwaters of the developing countries is noted. In some instances, the concentrations of these water pollutants in developing countries exceed the levels found in well-developed countries with efficient health care facilities that could assist in alleviating any health risks and concerns. The environmental monitoring assessments in developing countries focus mostly on the urban areas, however, PPCPs in rural communities are reported haphazardly. The common practice in urban areas is the discharge of PPCPs into the sewer systems. The disposal of unused or expired medications as garbage in municipal refuse or flushing down the toilets is also common. Therefore, it is highly recommended that authorities should establish a framework for customers to return unused or expired medicines for proper disposal. It is also recommended that authorities set target minimum PPCP levels for WWTP effluent. A notable, significant amount of environmental monitoring studies focusing on pollution of freshwaters in developing countries are reported in the upper-middle-income countries such as those belonging to the BRICS. This falls under the section on fate and occurrence of emerging pollutants within aquatic ecosystems with other chapters e.g., Ajayi et al. (2022), Cristale (2022), Vizioli et al. (2022), Galhardi et al. (2022), Hashemi and Kaykhaii (2022), Mashile et al. (2022), Montagner et al. (2022), Moodley et al. (2022), Ntshani and Tavengwa (2022), Sanganyando and Kajau (2022), and Yardy et al. (2022).

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C H A P T E R

11

Innovative liquid phase extraction based analytical extraction techniques of antibiotics

Gershom M. Ntshani and Nikita T. Tavengwa

11.1 Introduction

The life expectancy for human beings before the discovery of antibiotics was very short, with an estimation of 47 years. Diseases like smallpox, cholera, tuberculosis, diphtheria, pneumonia, and fever were rampant (Adedeji, 2016). Infections caused by a cut or burn were fatal. The discovery of penicillin during World War II was one of the most profound discoveries in the world (Gaynes, 2017). Penicillin is one of the naturally produced antibiotics which is produced by or derived from fungus as defense against microbes (Jiang et al., 2020). Recently, a lot of efforts have been made in laboratories to modify naturally produced antibiotics to produce semisynthetic antibiotics such as doxycycline, metacycline, minocycline, and other antibiotics that have unique structures or properties from naturally produced antibiotics called synthetic antibiotics (Chopra and Roberts, 2001). The uses of antibiotics have been expanded to agriculture for the treatment of diseases, prevention of incoming infections, and improvement of animal production. During the midst of World War II, food supply was very crucial both for the citizens and the men and women on the forefront. For the protection of livestock against diseases, different antibiotics were trialed against infectious diseases, and it was found that subtherapeutic antibiotics could not just improve animal health, but the animal could also gain body weight (Kirchhelle, 2018). This was an important discovery because antibiotics in animal feed can act as a growth promoter and was a very good substituent for the expensive vitamin B_{12} supplement. Until now, different antibiotics have been used in different agricultural practices and their estimated consumption is higher compared to human consumption (Manyi-Loh et al., 2018).

There is no doubt that antibiotics have been a very useful tool for protection against deadly infections and to improve the higher production of food in agriculture, but if care is not taken, they could also be deadly. For years, researchers have observed that antibiotics are not completely digested after they are consumed and their residues are being released in active form into the environment (Youngquist et al., 2016; Yin et al., 2019). A high antibiotic content has been detected in agricultural manure and wastewater treatment plants (Van Epps and Blaney, 2016; Pham-Duc et al., 2020; Rodriguez-Mozaz et al., 2020). The use of irrigation in agricultural farmlands has resulted in residues of antibiotics in fruits and vegetables (Pan and Chu, 2017). More concerning is their release and detection in freshwater sources such as lakes/reservoirs and rivers. This water is normally used by people for drinking and domestic uses in rural areas. Indirectly, people in urban areas are even more exposed because the wastewater treatment plants meant to remove emerging contaminants such as antibiotics are not 100% efficient as they are not originally designed to do so.

The ingestion of food and drinking of water contaminated with antibiotic residues is associated with severe health consequences including carcinogenic effects, and in a serious situation the results can be fatal (Bilal et al., 2020; Kraemer et al., 2019). The presence of antibiotics in the environment is also another challenge. This is because the main function of antibiotics is to kill or inhibit the growth or metabolic activities of microorganisms (Kovalakova et al., 2020). While the environment has teemed with different kinds of microorganisms, some of these are essential for environmental regulation such as biodegradation and convention of the greenhouse compounds (Ngqwala and Muchesa, 2020). Antibiotic resistance bacteria and antibiotic resistance genes caused by selective pressure due to the presence of antibiotic residues in the environment are also one of the global concerns (Saxena et al., 2021). Antibiotic resistance genes can simply be transferred to other microbes without any physical contact among organisms through horizontal

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gene transfer (Ben et al., 2019; Danner et al., 2019). This results in a large pool of dangerous untreatable microbes in the environment, which will be devastating both economically and socially (Friedman et al., 2016).

Previously, analysis of organic compounds (Kim et al., 2020) and metal ions (Liu et al., 2020) have been a routine to protect the environment from hazardous chemicals and to ensure the quality of food and water security (Domínguez et al., 2020). Antibiotics were seldom analyzed probably because the instruments that were used back then were incapable of detecting them. The recently developed analytical instruments or methods such as enzyme-linked immunosorbent assay (Wang et al., 2019), capillary electrophoresis (He et al., 2019), gas chromatography, and liquid chromatography coupled to tandem mass spectroscopy or high-resolution mass spectroscopy (Zhao et al., 2020; Li et al., 2020a,b; Uddin et al., 2020) with the capability to detect and quantify analytes in parts per trillion had made it possible for analysis of trace antibiotic analytes. Trace analyses are very important not just for awareness but to open doors for researchers to determine their effect on human health and other living organisms (Rodriguez-Mozaz et al., 2020). These include the effect of the long-term exposure and the induction of selective pressure for bacterial resistance (Luo et al., 2020). Recently, it has been proposed that analytical techniques should adhere to the concept of green analytical chemistry (Billiard et al., 2020). The principle states that, if possible, samples should be directly analyzed (Armenta et al., 2018). However, due to the complex nature of environmental samples, it is not simple to directly analyze samples. Environmental samples constitute a wide range of compounds including organic compounds, organometallic compounds, and metal ions (Zhang et al., 2019). Thus, these contaminants can cause false positives or false negatives during analysis (Van den Meersche et al., 2016). Isolation of analytes is a very important step before analysis (Dugheri et al., 2020). To comply with green chemistry, miniaturized extraction techniques have been proven environmentally friendly, selective, sensitive, and accurate (Soares da Silva Burato et al., 2020). Liquid phase micro-extraction (LPME) is one of the some of the most widely used miniaturized extraction techniques (Vakh et al., 2021; Ma and Row, 2021; Shahi et al., 2021). Compared to miniaturized-SPME techniques (see Kaykhaii and Hashemi, 2022, Chapter 4), miniaturized LPME solvents are easy to prepare, the solvents are cheap and widely available, and they are compatible with the chromatographic instruments. In contrast, SPE sorbents are associated with poor elution of analytes, and mostly their preparations are lengthy while most of them are not reusable (Farajzadeh et al., 2020).

This chapter aims to discuss the use of LPME techniques in antibiotics as emerging contaminants of freshwater, focusing on the advantages and disadvantages of the LPME techniques. The use of new extractive solvents to minimize the environmental burden of antibiotic residues in freshwater will also be explored through recent miniaturize extraction techniques. Lastly, future trends are discussed looking into improving the extraction process in terms of reducing coat, time, labor, and hazardous chemicals.

11.2 Liquid phase extraction

Liquid phase extraction is an extraction technique that is used to isolate or extract the desired analytes from a sample matrix through partitioning between two immiscible solvents, i.e., water and an organic solvent such as dichloromethane (Smink et al., 2020; Kebede et al., 2021, Chapter 5). This technique has been used for the extraction of a wide spectrum of antibiotics in different environmental samples. Antibiotics are classified as polar organic compounds, and they have more affinity to polar organic solvents, i.e., dichloromethane, chloroform, methanol, and acetonitrile (Zhang et al., 2019). The conventional liquid-liquid extraction (LLE) technique requires 100% extraction efficiency, and this can be done through a series of repetitions until the ideal recovery is reached. This is because the extraction solvents have poor selectivity toward the desired analytes. The use of the conventional LLE technique has also been criticized based on its failure to comply with the principles of green analytical chemistry (Dugheri et al., 2020; Dmitrienko et al., 2020). These shortfalls include high organic solvent consumption, high waste discharge, tedious and inability to be automated. A lot of effort has therefore been made over the past few years to improve the extraction process (Fig. 11.1).

Recently, LLE techniques have evolved from a 500 mL separatory funnel (Peng et al., 2020) to a 10 mL centrifuge tube/test tube and thus reducing the amount of extraction solvent and sample solution to about 1–5 mL and 10 mL, respectively (Fig. 11.1) The volume of extraction solvent and the sample have been further reduced through the introduction of innovative extraction techniques called miniaturized liquid phase extraction techniques. Miniaturized LLME has been introduced to reduce some of the disadvantages encountered in the conventional LLE technique by using a low volume of organic solvent (in microliter) to improve the extraction efficiency, accuracy and to increase the enrichment factor. The enrichment factor is improved because when analytes are being extracted into a low volume of organic solvent, their concentration will be enhanced. The use of low extraction volume does not only comply with the green extraction technique but to be able to preconcentrate the desired analytes. In this case, analytes that are present in trace levels can be preconcentrated into small volumes of organic solvents to increase their concentration so that they will be detected with instruments with slightly higher detection limits.

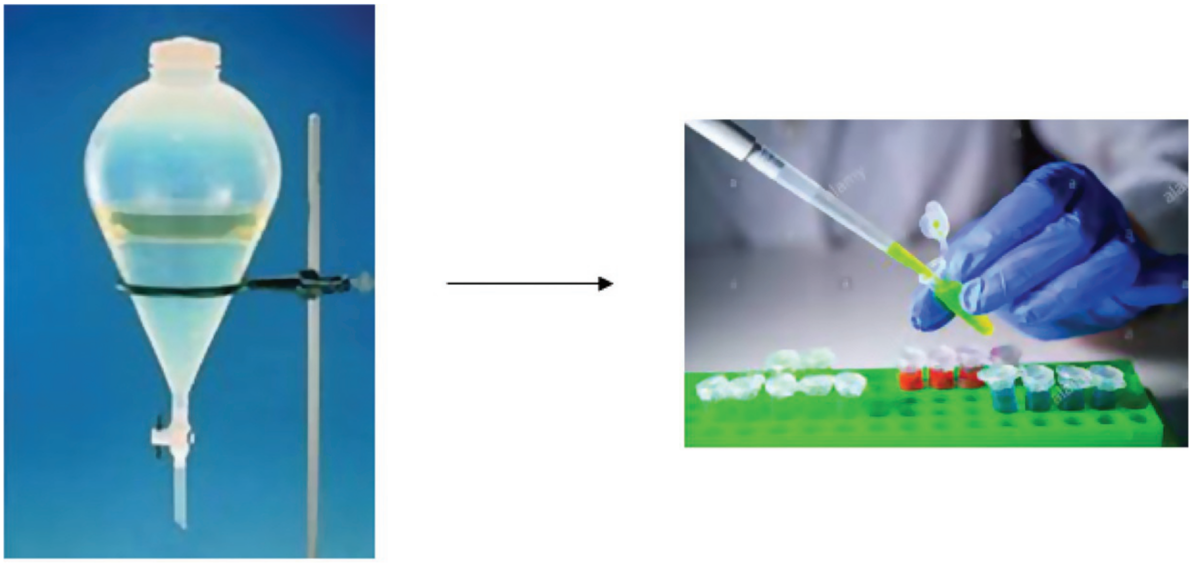

FIG. 11.1 Transformation of the extraction from classical to modern extraction technique.

The organic solvent can be separated through alteration of temperature, sample pH, or ionic strength. The most used phase separation technique is the change of ionic strength (Farajzadeh et al., 2018). This has been made possible through the extraction technique called homogeneous salt assisted LLE or H-SA-LLE (Khatibi et al., 2020; Moreno-González et al., 2021). One of the requirements is that the type of salt added into the solution should have a partial solubility with the organic solvent, e.g., sodium chloride, sodium acetate, and ammonium acetate (Ahmed et al., 2020). The mechanism around this process is that, as salt molecules dissociate in water, some of the salt ions are attracted to the water molecules resulting in less interaction between water molecules and organic molecules, the process is called the salting out effect (Li et al., 2020a,b). The addition of salt is also beneficial to the extraction process because it increases the ionic strength in the aqueous phase which facilitates the partitioning of analytes into the organic phase. But there is a precaution that needs to be considered when adding salt into the mixture because too much ionic strength can increase viscosity of the extraction solvent, which in turn reduce the analytes partitioning or extraction efficiency (Khatibi et al., 2020; Rashidipour et al., 2019). H-SA-LLE have been recently applied for the extraction of antibiotics in milk (Mohebi et al., 2020), urine (Fikarova et al., 2021), honey (Thompson et al., 2019), and water (Chandrakar et al., 2020; Mokhtar et al., 2019) due to its high enrichment factor, percentage recovery and low limits of detection (Moreno-González and García-Campaña, 2017). However, due to the poor selectivity of the used polar extractive solvents mentioned above, this technique is coupled with other clean-up techniques such as DLLME (Mohebi et al., 2020) or SPE (Fikarova et al., 2021). The use of acetonitrile of methanol is beneficial for DLLME because this solvent is in turn used as the dispersive solvent (Mohebi et al., 2020).

Over the past few years, different innovative miniaturized extraction techniques have been studied for the extraction of antibiotics in different environmental, biological, and food samples. The first miniaturized LLME called single drop micro-extraction (SDME) was introduced by Jeannot and Cantwell (1996) for the extraction of 4-methylacetophenone using 8 μL of *n*-octane as an extractive solvent. In this technique, a small droplet of an extractive solvent is held above the sample solution (headspace-SDME) or directly immersed in the sample solution (direct immerse-SDME) using a micro-syringe for extraction of analytes. However, its application for the extraction of antibiotics has recently dropped due to some limitations such as instability of the droplet and limited choice of the extractive solvents (Khatibi et al., 2020). To overcome such drawbacks, new techniques with the capability to store the extractive solvent in a porous hollow fiber membrane in the technique called hollow fiber liquid phase micro-extraction (HF-LPME) have been introduced. The recommendations are that solvents must be immiscible with the aqueous phase and should have a higher affinity with the desired analytes. HF-LPME is a miniaturized liquid phase micro-extraction technique that applies porous hollow fiber membrane for isolation of desired analytes. In this extraction technique, an organic solvent and sometimes an ion-pair reagent, usually 1-octanol and aliquat-336, is applied on the surface of the HF membrane to allow analytes to be extracted in the organic surface layer and then to the aqueous phase inside the membrane with an assistant of agitation. The use of ion-pair reagent is one of the techniques used through HF-LPME and other techniques include pH gradient and electro-membrane extraction. The detailed procedures of miniaturized-LLME techniques are illustrated in Fig. 11.2.

LLME

Add sample aliquot in 5 mL tube.

Add about 200 µL extractive solvent.

Vortex the sample for few minutes.

Centrifuge the mixture for few minutes.

Take the organic layer into the autosampler vial for analysis.

DLLME

Add sample aliquot in 5 mL tube.

Vigorously add the mixture of about 500 µL dispersive solvent and 200 µL extractive solvent.

Agitate the sample for few minutes.

Centrifuge the mixture for few minutes.

Remove the organic layer into the autosampler vial for analysis.

SDLPME

Directly immerse or suspend the droplet carried on the syringe into a vial containing the donor solution.

Agitate the sample using a magnetic stirrer.

Put the droplet into the autosampler vial for analysis.

HF-LPME

Immerse the HF into the orgic solvent to fill its pores.

Load the extractive solvent into the lumen.

Immerse the fiber into the vial containing sample solution describe below and the stir bar.

Agitate for an hour while HF is in the solution.

Withdraw the extractive solvent with a micro-syringe and inject it into HPLC.

FIG. 11.2 Miniaturized liquid phase extraction techniques.

The interesting fact about miniaturized-LLME techniques is their flexibility to be automated, quick, inexpensive, selective, and the use of environmentally friendly extractive solvents (Madikizela et al., 2020). Other innovative miniaturized extraction techniques are LLME and dispersive liquid-liquid micro-extraction (DLLME) and their procedure have been well outlined in Fig. 11.1. These extraction techniques share the same concept of minimizing the extractive solvent and complying with the principles of green analytical chemistry. Another benefit associated with these techniques includes their ease of operation which does not require any intricate steps. LLME of antibiotics requires the optimum organic solvent, normally methanol and acetonitrile as in SALLE described above, and the optimum condition such as pH and ionic strength adjusted and the optimum vortex and centrifuging time. The difference between DLLME and LLME is that DLLME uses a dispersive solvent to facilitate the movement of analytes into the extractive solvent but the procedures are similar with few additional steps in DLLME (see Fig. 11.2).

11.3 Extractive solvents

The extraction techniques mentioned above are regularly performed with the use of hazardous chemicals that are normally derived from petroleum and natural gases and other hazardous reagents. Using water as an extractive or eluting solvent would be ideal since water is the best environmentally friendly solvent which is cheap in terms of production, transportation, and disposal (Castro-Puyana et al., 2017). But water is not a solvent of choice when extracting antibiotics in normal conditions. However, the properties of water can be tuned by increasing the temperature and pressure until it is at the state called the subcritical point (Esmaeelian et al., 2020). At this state, water behaves like polar solvents, such as methanol, and can be used to extract analytes through the technique called subcritical water extraction. Wang et al. (2008) have extracted three tetracyclines in animal feed with the method percentage recovery of 82.1% and 90.0%. Besides the high recovery of this method on extracting tetracyclines, subcritical water extraction is not suitable for the extraction of other antibiotics. These disadvantages arise from using high temperatures which might degrade some of the thermolabile antibiotics. At these conditions, water can also be more soluble in such a way it loses its selectivity in complex matrices. Recently, a large focus is on the use of biodegradable and environmentally friendly solvents for extraction and elution of antibiotics and other contaminants.

11.3.1 Supermolecular solvents

Supermolecular solvents (SUPRASs) are nanostructured liquids produced in colloidal solutions of amphiphilic compounds by spontaneous, sequential phenomena of self-assembly and coacervation (González-Rubio et al., 2020). SUPRASs are insoluble in water which makes them ideal for LLME with high extraction efficiency. Another unique feature is that when they are added to the solution, they self-assemble or aggregate into micelle or vesicles (Fig. 11.3) depending on the type of solution they are added (Torres-Valenzuela et al., 2019). Their density is usually less than that of the water, and after the extraction is completed, they can be withdrawn on top of the sample solution.

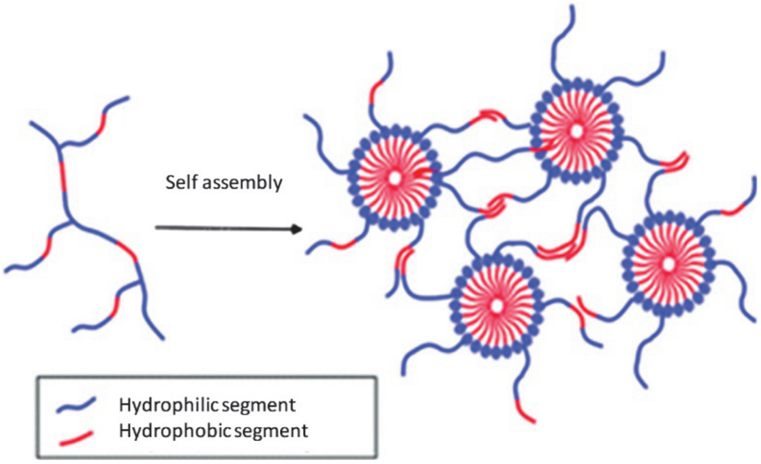

FIG. 11.3 Self-assembly of SUPRAS solvent.

The analytes can be extracted without the use of organic solvents, acids, and heating (Seebunrueng et al., 2017). The mechanism which leads to better extraction of antibiotics is through hydrophilic and electrostatic interaction with the solvent (Gissawong et al., 2019; Selahle and Nomngongo, 2019) have used the mixture of decanoic acid and tricaprylmethylammonium chloride as supermolecular solvent base LLME for the extraction of three fluoroquinolones in wastewater before HPLC-DAD. The method had LOD and LOQ of 0.06–0.14 $\mu g\,L^{-1}$ and 0.22–0.47 $\mu\,L^{-1}$, respectively. Gissawong et al. (2019) have used a mixture of didodecyldimethylammonium bromide and dodecyltrimethylammonium bromide based LLME for extraction of tetracyclines in milk and honey samples. The method had a high enrichment factor of 48–198 and a low limit of detection.

The disadvantage of the technique is that its effects on biological samples may be poor. These arise due to the presence of hydrophobic parts in compounds which might interact with hydrophobic compounds such as lipids that might increase the matrix effect. While evaporation through the microwave could be effective but it could have some effect on some thermal sensitive antibiotics. In most cases for biological molecules, the method is coupled with other extraction techniques such as DSPE and still, the method has been proven to be environmentally compliant (González-Rubio et al., 2020).

11.3.2 Ionic liquids

Ionic liquids are classified as organic salts that constitute anionic and polyatomic inorganic anion (de los Ríos et al., 2013). These salts are characterized by being liquid below 100°C, negligible vapor pressure, good thermal stabilities, high ionic conductivity, and simple functionality (Vafaeezadeh and Alinezhad, 2016). These properties are ideal for ionic liquids to be used as a substituent of volatile solvents and other hazardous chemicals. Ionic liquids have also been coupled with adsorption particles that are used in miniaturized-SPME techniques to improve the extraction performance. da Silva and Lanças (2018) have developed a reproducible, simple, and fully automated online SPE-LC-ESI-TOF-MS for extraction and detection of sulfonamides in bovine milk samples using silica-based ionic liquid. 1-Butyl-3-methylimidazolium hexafluorophosphate as ionic liquid proved to be very effective for isolation of the desired analytes with lower LOD of 5–7.5 $\mu g\,mL^{-1}$ and high percentage recovery of 74%–93%. Lu et al. (2020) have also incorporated 1-aminopropyl-3-methylimidazolium chloride bis(trifluoromethane)sulfonamide lithium salt ($[H_2Nmim]$ $[NTf_2]$) as an ionic liquid and Zr molecular (UiO-66-Br) organic framework to form $[H_2Nmim]$ $[NTf_2]$ @UiO-66-Br based DSPE for extraction of sulfonamides in water samples. The key interaction of the desired analytes and the nanocomposite, as demonstrated by the author was through electrostatic interaction, pi-pi interaction, and hydrogen bonding interaction. The method is a fast, sensitive, efficient, and economical method for the detection of SAs with 270 enrichment factors and 90.5%–101.9% recovery.

The use of ionic liquids has recently dropped because most of them are toxic. However, their application in antibiotics is found to be more effective through miniaturize-LLME. Wei et al. (2018) have effectively developed a simple LLME for extraction of five sulfonamides in blood samples using 1-hexyl-3-methylImidazolium chloride($[C_6MIM]$ Cl), K_2HPO_4 ionic liquid as an extractive solvent. The solvent proved to be effective with an LOD range of 2.45–4.13 $\mu g\,mL^{-1}$ lower than MRL for sulfonamides and higher percentage recovery of 85.5% and 110.9%. Chatzimitakos et al. (2018) have applied magnetic ionic liquid-based DLLME for the extraction of sulfonamides and triazines in aqueous samples. The use of magnetic ionic liquid facilitated the extraction process and limited the extraction time. Clearly, more research is needed for the synthesis of ionic liquids that are compatible with the environment.

11.3.3 Deep eutectic solvents

Deep eutectic solvents are eutectic mixtures that are composed of two or more components whose melting points are lower compared to those of their components (Lee et al., 2020). They are liquid at room temperature and can be used as an extractive solvent. These solvents have been used as an alternative for ionic liquids to replace disadvantages associated with them (Liang et al., 2016). DESs are considered subclasses of ionic liquid which consist of hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA). These solvents share some common properties with ionic liquids, such as being liquid below 100°C, negligible vapor pressure, good thermal stabilities, and high ionic conductivity. There are different types of DES, and normally those that are used for antibiotics extraction are composed of a mixture of organic acid (as HBD) and the hydrogen bond acceptor (HBA) (Saei et al., 2020). The most common HBA used for sample extraction techniques is choline chloride. Saini and Panesar (2020) have synthesized DES using the combination of choline chloride as HBA and pivalic acid as HBD for extraction of penicillin G, oxytetracycline, and tilmicosin in hamburger and cow liver through dispersive liquid-liquid microextraction and the method was very selective and have higher percentage recovery. However, choline chloride DES are normally water-miscible and to break their miscibility a demulsifier such as a tetrahydrofuran or acetonitrile is added (Lee et al., 2020). A technique called solidification of floating organic droplets such as the one used by Saei et al. (2020) can be used to separate the DES from an aqueous sample. Other DES that is immiscible in water called hydrophobic DES has also been used for antibiotics extraction. Sereshti et al. (2020a,b) have synthesized the hydrophobic DES using octanoic acid as HBD and thymol as HBA for extraction of oxytetracycline, tetracycline, and doxycycline in milk through DLLME. The method proved to be very effective with high percentage recoveries. Mohebi et al. (2020) have synthesized DES (the combination of phosphocholine chloride, dichloroacetic acid, and dodecanoic acid in a 1:1:1 ratio) before extraction of antibiotics in milk samples using the combination of salt assisted LLE and DLLME. The method solvent was also immiscible in water and has successfully extracted the antibiotics with 65%–81% recoveries and 2.0–2.8 $\mu g\,L^{-1}$ and 6.5–9.3 $\mu g\,L^{-1}$ LOD and LOQ, respectively.

11.3.4 Other solvents

Supercritical fluid can be defined as a fluid that is at a state higher than critical temperature and pressure. Of interest is the fact that these fluids can be tailored by varying the temperature and pressure into selective and extractive solvents (Pourmortazavi et al., 2014). Carbon dioxide supercritical fluid is the widely used solvent for the extraction of various analytes as it has a low critical state (Table 11.1).

11.4 Conclusion and future work

The presence of antibiotics in the environment is associated with a high negative impact on health and food and water security. Major action needs to be taken before it is too late. It is apparent from the literature that much attention on the presence of antibiotics is focused on developed countries and urban areas. Poor wastewater treatment plants, lack of sanitation, and high prevalence of diseases in developing countries are the major sources of antibiotic exposure (see Tavengwa and Dalu, 2022, Chapter 1; Tavengwa et al., 2022, Chapter 20). Because antibiotics are ubiquitous, their continuous exposure can affect everyone. Thus, more attention is needed in all environmental compartments, especially freshwater sources.

The rise in pharmaceutical companies and the demand for new antibiotics increase the number of antibiotics that can be found in freshwater systems. This is a problem since an analysis of every antibiotic in the environment is time-consuming, expensive, and sometimes their standards are scarce. To solve such shortcomings, it is highly recommended to introduce innovative analytical methods with capabilities to extract and analyze different classes of antibiotics simultaneously through the method called multiclass analysis. A multiclass analysis is still an emerging concept in the field of analytical chemistry, and it has received much attention due to its advantages such as time-saving and the ability to analyze a wide range of antibiotics in a single run. Thus, much effort is needed for this technique. The recent invention of chromatographic analytical instruments coupled to quadrupole time of flight mass spectroscopy (QToF/MS) has been a success in the field of analytical chemistry. The advantages arising from its capability to perform a quick analysis and the ability to detect the mass of an analyte with the highest possible precision and accuracy.

TABLE 11.1 Solvent extraction of antibiotics from different water sources.

Method	Solvent	Matrix	Analytes	LOD and LOQ	Recoveries	RSD (intra and inter) (%)	Reference
In situ hDES-SA-LLME-MS/MS	Thymol:heptanoic acid as DES	Surface water	Fluoroquinolones	3.0 ng mL^{-1} and 9.0 ng mL^{-1}	84.4–113.63	$\leq$7.78 and $\leq$7.14	Li et al. (2020a,b)
pH-induced deep eutectic solvents based - HLLME-HPLC	Thymol:hexanoic acid as DES	Environmental water	Levofloxacin and ciprofloxacin	0.018–0.027 μg mL^{-1} and 0.06–0.09 μg mL^{-1}	94.52–110.8	$\leq$4.21	Ma and Row (2021)
SUPRAS based LLME-HPLC-PDA	Decanoic acid and tricaprylymethylammonium chloride	Wastewater effluent and influent	Ciprofloxacin, danofloxacin, and enrofloxacin	0.06–0.14 μg L^{-1} and 0.22–0.47 μg L^{-1}	153–241 (PF)	3.4–4 and 4.1–5.0	Selahle and Nomngongo (2019)
Magnetic ionic liquid-based-DLLME-LC-MS/MS	[P66614+][Dy(III)(hfacac) 4−]	Lake water and effluent from a municipal WWTPs	Triazines and sulfonamides	0.034–0.091 μg L^{-1}	89–101	5.2–8.1	Chatzimitakos et al. (2018)
Temperature-Induced Ionic Liquids - DLLME-HPLC-UV	[Bmim]PF6	Environmental water	4-Epitetracycline, 4-epichlortetracycline, doxycycline, chlortetracycline oxytetracycline, tetracycline, 4-epianhydrotetracycline, and anhydrotetracycline	0.031–0.079 μg L^{-1} and 0.10–0.26 μg L^{-1}	55.1–94.5	–	Hou et al. (2011)
DLLME based on deep eutectic solvents doped with β-cyclodextrin-LC-UV	Thymol:octanoic acid (extractant) and choline chloride:ethylene glycol (disperser)	Well water, rainforest water, coastal sea water, Gardening water and mineral water	Oxytetracycline, tetracycline, and doxycycline	1.37–4.38 μg L^{-1} 1.37–4.38 and 4.58–14.60 μg L^{-1}	74–113	2.9–4.6	Sereshti et al. (2021)
Magnetic nanoparticles assisted DLLME-UV-Vis	Methanol (desorbing solvent) and decanoic acid (extractor)	Tap water and lake water	Chloramphenicol	16.5 and 50.0 μg L^{-1}	91–92.7	0.45–6.29	Saad et al. (2020)

The ability of high-resolution mass spectrometry to identify the wide range of analytes that are found in a sample with high precision in a single can be used to analyze the presence of unknown hazardous antibiotics residues in the environment with the method called nontargeted analysis (Getzinger and Ferguson, 2020).

One can say that the miniaturization of LLME has more advantages over the conventional extraction techniques. Extraction of analytes no longer requires a high quantity of samples, reagents, and solvents. This achievement is very important to protect the environment against exposure to hazardous chemicals. It is also advisable to continue improving these extraction techniques until they are completely environmentally friendly. Such achievement can be successful through innovation and much effort in research. As discussed above, more effort has been made to perform analysis using green solvents which replace petrochemicals in miniaturized LLME techniques. Synthesis of adsorption particles that are reusable is another subject of interest in miniaturized SPME technique.

The uses of automation such as robots, flow techniques, and microfluidic devices through analytical chemistry have been very useful in reducing some labor-intensive work during sample pretreatment and reducing the analysis time (Soares da Silva Burato et al., 2020). These innovations together with the use of powerful analytical instruments and environmentally friendly solvents are very effective through the detection of ultra-trace analytes that are reproducible. The use of environmentally friendly analysis should be the responsibility of every analytical chemist, and for decades, a lot of effort has been made to achieve such goals. Agrochemical solvents, sorbents, and reagents have been proven to be effective for the extraction of analytes and much research needs to be conducted using these solvents (see Sanganyado, 2022, Chapter 19).

This chapter falls under the section on fate and occurrence of emerging pollutants within aquatic ecosystems with other chapters, e.g., Ajayi et al. (2022), Cristale (2022), Vizioli et al. (2022), Galhardi et al. (2022), Hashemi and Kaykhaii (2022), Madikizela et al. (2022), Mashile et al. (2022), Montagner et al. (2022), Moodley et al. (2022), Sanganyando and Kajau (2022), and Yardy et al. (2022) that aims to make an understanding of the different emerging pollutants within the aquatic environment.

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CHAPTER

12

Pesticides in aquatic matrices in developing countries: What do we know so far?

Cassiana C. Montagner, Jéssyca Ferreira de Medeiros, Eder de Vilhena Araújo, B.C. Vizioli, and Nívea C.G. Munin

12.1 Introduction

Plant cultivation generates a biological imbalance in the environment by removing competitive plants, using strains selectively obtained, allocating a planting area for one crop, fertilization, irrigation, pruning, and pest control (Bellaver et al., 2002).

A pesticide can be a chemical, physical or biological agent that interfere with the regular biological activity of living beings considered harmful to crops, changing the target flora or fauna's composition to guarantee crop protection. The diversity of pesticide use is due to the various modes of action, which can act against plants (herbicides), insects (insecticides), fungi (fungicides), mites (acaricides), soil microorganisms (nematicides), avicides (birds), among others (Kim et al., 2017). Also, every year, new active ingredients have developed to obtain a selective and effective mode of action against target organisms while presenting lower toxicity to non-target organisms (e.g., pollinators, domestic and wild animals, and humans), thus ensuring the protection of the environment as a whole (Carvalho, 2017; Lushchak et al., 2018; Singh et al., 2020).

Pesticide use is of fundamental importance to sustain and protect the agricultural model globally, mainly to achieve high productivity indices and support the food supply of an increasingly growing population (Singh et al., 2020). However, the preservation of environmental quality remains one of the main challenges because of the large number of released pesticides.

Environmental protection is also related to the water quality criteria and the regulations applied in each country. Unfortunately, environmental protection mostly depends on public policies specific to each country. The contaminant selection for water regulation is not a trivial task (UNESCO, 2017). It is necessary to consider the amount of substance used, its potential hazard to the non-target species, its physical-chemical characteristics, its occurrence in the aquatic environment, and the availability of proper analytical methods (see Tavengwa and Dalu, 2022, Chapter 1). All previous factors must be addressed to manage pesticide environmental contamination, and it requires investment in Science, Technology, and Innovation. However, more often than not, such investments are not the main priority in developing countries. As a result, there are scarce data about pesticides in freshwaters and drinking waters in countries from Africa, Asia (i.e., India), Latin America, and the Caribbean (UNESCO, 2017).

This chapter presents a comprehensive discussion of pesticide dynamics in the environment after application. Also, it provides a review of pesticide occurrence in surface waters in developing countries. An example of the risk assessment was provided to highlight such an important tool that may be used to assure aquatic life protection in freshwater bodies. Finally, some emerging countries' regulations will be summarized, highlighting different approaches to address environmental protection.

12.2 Sources, transport, and fate in the environment

Pesticides can be classified by several criteria: chemical classes, functional groups, mode of action, and toxicity (Kaur et al., 2019). Another pesticide classification is according to the type of target pest and chemical classes, such

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as insecticides (organochlorines, organophosphates, carbamate esters, pyrethroids, and botanicals insecticides), fungicides (hexachlorobenzene, organomercurials, pentachlorophenol, phthalimides, and dithiocarbamate), herbicides (chlorophenoxy compounds, bipyridyl derivatives), among others (Cooper and Dobson, 2007; Kim et al., 2017; van de Merwe et al., 2018).

Apart from the wide variety of available compounds and their extensive use, several factors may influence the dynamics in the environment, such as toxicity, persistency, and physical-chemical properties that determine their ability to percolate the soil, adsorb in organic matter, solubilize in water, and bioaccumulate in organisms. Pesticides can interfere with basic ecosystem processes, such as soil breathing, nutrient cycling, adverse effects, and enhanced mortality of non-target organisms (IBAMA, 2018). Thus, it is important to understand the risk caused by residual concentrations of such contaminants present in the environment that may result in chronic effects after long-term exposure.

12.2.1 Sources in the environment

Agriculture activity is responsible for the majority of pesticide use worldwide. Therefore, it is the primary source in the environment. However, pesticide use in urban settings is growing steadily and is regarded as a relevant source of contamination, especially when freshwater systems receive pluvial urban runoff (Md Meftaul et al., 2020; Tiryaki and Temus, 2010).

12.2.1.1 Agriculture use

The use of pesticides for agricultural purposes is considered the main source of contamination of surface waters (Climent et al., 2018). Many developing countries have similar climatic conditions, such as the tropical climate and the higher temperatures, which, when combined with adequate humidity conditions, favor the infection of plants by microorganisms and the growth of a wide variety of weed, demanding an excessive use of pesticides in the cultivated area to control and guarantee crop production efficiency (Barratt et al., 2018). However, the indiscriminate use associated with cheaper and non-selective pesticides (usually banned in developed countries due to the toxic potential to the environment) and the lack of efficient regulation aggravate the environmental contamination scenario, mainly in regions of family farming or small crops (Mahmood et al., 2016; Ramakrishnan et al., 2019).

Contamination of surface and groundwater may come from different sources, such as direct application of pesticides in crops through aerial spraying (da Cunha et al., 2017), spraying with the aid of tractors (Tona et al., 2018), direct application in the foliage of plants (Md Meftaul et al., 2020), and incorporation of the pesticides into the soil (Shao and Zhang, 2017). In a conventional pesticide application in crops, about 45% of them reach the target area (crop), 30% reach outside the target area due to incorrect application, 15% are absorbed by the soil and 10% are lost through leaching, volatilization, and runoff (Gravilescu, 2005). Incorrect residual disposal after pesticide application is another path to contaminate freshwaters (Damalas and Eleftherohorinos, 2011) and may cause harmful effects to the biota inhabiting the immediate area (Etchegoyen et al., 2017; Pérez-Lucas et al., 2019).

12.2.1.2 Urban use

In urban centers, it is possible to find various environments such as houses, buildings, patios, gardens, public parks, and recreation areas threatened continuously by pests, weeds, or microbial (Wittmer et al., 2010). In most cases, pesticide application in urban environments is limited to specific targets (Md Meftaul et al., 2020). These applications help control pests in public and domestic settings.

In some developing countries, insecticides are widely used to control vectors, such as malaria, yellow fever, or dengue, with high priority for public health (Jayaraj et al., 2016; Olisah et al., 2019; van de Merwe et al., 2018). In India, the insecticide dichloro-diphenyl-trichloroethane (DDT) has been restricted since 1985 for agricultural applications, yet it is still possible to find it commercialized in various parts of the country to control the malaria vector mosquito (Yadav et al., 2015; Zhang et al., 2011). In a study by Gakuba et al. (2018), the identification of DDT in surface water samples in South African rivers was also reported. In South Africa, DDT has wide application in both agriculture and control of malaria vectors.

Urban pesticide residues contaminate the application site and several external sites (Tiryaki and Temus, 2010). In urban settings, pesticide dissipation and mobility behave differently, mainly due to the impermeable concrete surfaces, facilitating transport over great distances. Thus, pesticides are carried through washing yards, sidewalks, streets, and torrential rains, contaminating mainly surface waters by runoff (Jiang et al., 2010; van de Merwe et al., 2018). The scenario can be different in cities where the runoff is directed to the sewage system. In this case, residual concentrations may be lower due to the removal in the wastewater treatment plants. In addition, in certain regions where surface water receives runoff from urban and agricultural areas, the urban contribution of pesticides is likely to be a small percentage of total pesticide input due to the much greater use of pesticides in agriculture (Aktar et al., 2009; Tauchnitz et al., 2020).

Finally, it is important to consider the use of surface water for public supply. In general, conventional drinking water treatment plants are not planned to remove trace levels of pesticides. Consequently, it may be possible to find pesticide residues in drinking water originated from impaired sources. Fig. 12.1 represents the use, transport, and fate of pesticides in the environment (Costanzini et al., 2018; Langenbach et al., 2017).

12.2.2 Pesticide transport in surface waters

Once the pesticide is in an aquatic matrix, there are three possible pathways: (i) remain in the aquatic system; (ii) be transported by processes that can happen with phase change (air, water, or soil) such as volatilization, dissolution, adsorption or precipitation, or without phase change, by gravity or diffusion, and (iii) be transformed into other chemical species through chemical or biological processes, such as biodegradation (aerobic or anaerobic), bioaccumulation, and oxidation-reduction, acid-base, hydration, hydrolysis, complexation and photolysis reactions (Costanzini et al., 2018; Langenbach et al., 2017; Vryzas, 2018).

Pesticides have adverse impacts on the environment due to their contamination at the application site and other places through diffusive routes (Børgensen et al., 2015). To understand the fate of pesticides and subsequently apply risk assessment strategies, it is essential to have a thorough knowledge of the various ways and mechanisms by which pesticides arrive at the external site (Vryzas, 2018). The main pesticide transport processes are atmospheric and aquatic: spray drift, volatilization, and atmospheric transport followed by re-deposition, and drainage, leaching, and surface and ground runoff (Alletto et al., 2010; Costanzini et al., 2018; Langenbach et al., 2017). Surface waters can also receive undesirable amounts of pesticides due to improper cleaning of spray equipment or inappropriate applications in residential areas (Knauer, 2016).

Pesticide mobility in natural soil is strongly influenced by their physicochemical properties, such as water solubility, vapor pressure, K_{oc} (sediment-water coefficient normalized for organic carbon), half-life, K_{ow} (octanol-water partition coefficient), and K_d (sediment-water coefficient), as well as the soil properties, including organic matter content, moisture, texture, structure, soil pH and infiltration capacity (Takeshita et al., 2019; Tiryaki and Temus, 2010). Other environmental factors such as climate, temperature, relative humidity, and precipitation can also affect the transport to different environmental compartments (Børgensen et al., 2015; Takeshita et al., 2019; Tiryaki and Temus, 2010). For example, pesticide mobility can be assessed using the partition coefficients log K_d, log K_{oc} and log K_{ow}

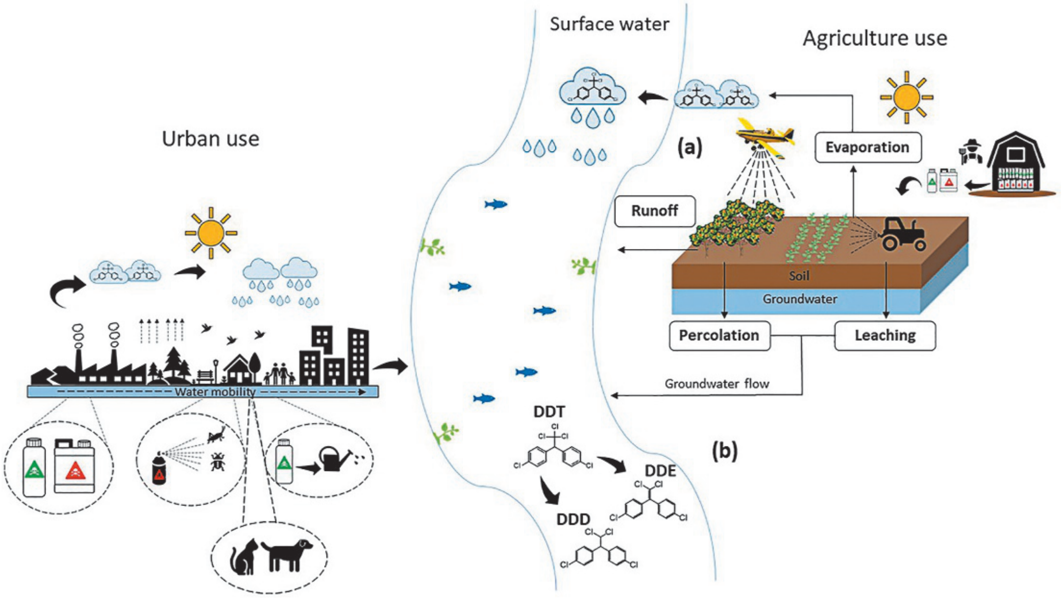


FIG. 12.1 Source, transport, and the fate of the pesticides in the environment. (A) Represents the main processes for the mobility of pesticides into surface waters: spraying, volatilization, re-deposition, or moved to water through leaching or percolation. (B) Transformation of pesticides in aquatic surfaces and coexistence of compounds with their metabolites, which may cause accumulation in aquatic organisms.

(Ogbeide et al., 2018). Such studies suggest that understanding the mobility of these compounds through the partition coefficients in field studies can help assess the effects of pesticides on biota and humans and is essential for modeling transport and designing corrective measures against pollution (Aldana et al., 2011; Arias-Estévez et al., 2008).

12.2.3 Transformation products of the pesticides in aquatic matrices

Transformation products are metabolites or degradation products of the precursor analyte. Once in an aquatic environment, a pesticide molecule can be partially or degraded by chemical or biological mechanisms, remain unchanged, deposit in the sediment of rivers and lakes, bioaccumulate in aquatic organisms, or return to the atmosphere by volatilization (Climent et al., 2018). Although there is a gap in data for pesticide transformation pathways, fate, behavior, and occurrence in the environment (Ulrich et al., 2018), recent research shows concerns about the possible environmental impacts of transformation products in surface waters (Chau et al., 2018; Lundqvist et al., 2019; Mahai et al., 2019).

For most pesticides, knowledge of the occurrence and behavior of transformation products is incomplete or nonexistent for a few reasons: (a) reference material for transformation products is often not available, (b) analytical methods are not available, (c) several transformations products are unknown because the analyte registration data is not readily accessible or not available at all, and (d) many transformation products are transient species and may exist only for seconds or minutes; thus only transformation products with relatively long half-lives in aquatic environments (usually longer than days) can be isolated and detected (Aktar et al., 2009; Damalas and Eleftherohorinos, 2011; Kiefer et al., 2019).

Some pesticide transformation products may be more stable in surface waters than their original compound or have similar stability (Székács et al., 2015). For example, Sibali et al. (2009) identified the concomitant presence of the pesticide DDT and its metabolites dichlorodiphenyldichloroethylene (DDE) and dichlorodiphenyldichloroethane (DDD) in the Jukskei River in South Africa, suggesting the stability of the pesticide and its metabolites in the environment. Thus, the probability of finding a given transformation product in surface waters depends on the matrix and the physicochemical properties of the transformation product (Lushchak et al., 2018).

Several transformation products may co-exist with their parental compounds (Caldas et al., 2018). However, there is a significant lack of knowledge about their simultaneous occurrence the possible synergistic, additive, or antagonistic effects they may pose (Hernández et al., 2017; Mansouri et al., 2017). In this regard, Cui et al. (2011) investigated the toxicity of bronopol and its secondary metabolites 2-bromo-2-nitroethanol (BNE) and bromonitromethane (BNM). Both metabolites showed higher stability, persistence in surface waters, and toxicity than their parental molecule. Thus, it is possible to highlight the importance of including transformation products in pesticide analysis in surface waters.

12.3 Pesticide occurrence in developing countries

The presence of pesticides in freshwaters is mainly due to agricultural activities. After application, pesticides can enter surface waters during spraying, runoff, erosion, and leaching (Malyan et al., 2019). In the International Union of Pure and Applied Chemistry (IUPAC) database, there are over 1590 compounds described as pesticides, including approved and banned substances (International Union of Pure and Applied Chemistry – IUPAC, 2020). A review on pesticide occurrence in freshwaters from developing countries from Latin America and the Caribbean, Africa, and Asia (i.e., India), is shown in Table 12.1.

A comprehensive literature review was performed, in which the displayed data were retrieved from the online databases of Web of Science, Scopus, and PubMed. All data was collected until April 2020. The following words were searched topic terms within the year limitation from 1900 to 2020: “pesticide,” “freshwater,” “surface water,” “groundwater,” and “country of search.” A total of 79 scientific articles were selected according to the described criteria. Pesticide occurrence data in freshwaters were gathered from 18 countries (Fig. 12.2); 8 from Latin America (Brazil, Argentina, Chile, Colombia, Costa Rica, El Salvador, Ecuador, and Mexico), 1 from the Caribbean (Barbados), 8 from Africa (South Africa, Morroco, Tunisia, Gana, Ethiopia, Kenya, Tanzania, and Togo), and 1 from Asia (India).

In Latin America, the Caribbean, Africa, and Asia (i.e., India), different classes of pesticides were found in freshwater, such as fungicides, herbicides, insecticides, acaricides, nematicides, avicides, among others. Together, 124 different pesticides were detected in freshwater samples, the majority belonging to the classes of carbamates,

TABLE 12.1 Pesticide occurrence in freshwater in developing countries.

Country	Source	Year of sampling	Sample preparation	Instrumental technique	Pesticides	Range of concentration (μg L^{-1})	References
Brazil	Tibagi River	2015	SPE	LC–MS/MS	Carbendazim; Imidacloprid; Imazethapyr; Ametryn; Atrazine; Imazaquin; Tebuthiuron; Diuron; Propiconazole; Tebuconazole	0.01–12.59	Almeida et al. (2019)
Brazil	Paraná 3 hydrographic Basin	2017	DLLME	GC–MS	Atrazine; Deethylatrazine	0.23–2.89	Della-Flora et al. (2019)
Brazil	Japaratuba River	2015–2016	Aqueous two-phase system	LC–TOF	Diuron; 3,4-dichlorophenylurea; 3,4-dichloroaniline	0.075–1.9	Buarque et al. (2019)
Brazil	São Francisco River Basin	–	HF-LPME	GC–MS	Atrazine; Propazine; γ-HCH; Diazinone; δ-HCH; Alachlor; Pirimiphos-methyl; Procymidone; Fenthion; Napropamide; Hexaconazole; p,p′-DDE; Dieldrin; Oxyfluorfen; Kresoxim-methyl.; p,p′-DDD; Triazophos; Carfentrazone	0.37–10.72	Valenzuela et al. (2019)
Brazil	Patos-Mirim lagoon	2011–2014	SPE	LC–MS/MS	Atrazine; Azoxystrobin; Bentazone; Carbofuran; Cyproconazole; Clomazone; Diuron; Epoxiconazole; Imazapic; Imazethapyr; Irgarol; Propanil; Quinclorac; Tebuconazole; Trifloxystrobin	0.008–1.0	Caldas et al. (2018)
Brazil	Dourados River Brilhante River	2016	SPE	LC–MS/MS	Imidacloprid; Carbendazim; Atrazine	0.007–0.171	Sposito et al. (2018)
Brazil	Lontra River Sarandizinho River Rio Santa Cruz River Siemens River	2015–2016	SPE	LC–MS/MS	Atrazine; Epoxiconazole; Fipronil; Iprodione; Malathion; Penoxsulam; Simazine; Tebuconazole	0.005–1.0	Vieira et al. (2017)
Brazil	Casca River São Lourenço River Lajes Stream Lucas River Verde River Itambiquara River Cedro River	2007–2008	SPE	GC–MS	Atrazine; Deethylatrazine; Chlorpyrifos; α-Endosulfan; β-Endosulfan; Endosulfan sulfate; Flutriafol; Malathion; Metolachlor	0.02–57.1	Nogueira et al. (2012)
Brazil	Poxim-Mirim River Poxim River	2009–2010	LLE	GC–ECD	Diuron; Ametryn	0.03–0.9	Britto et al. (2012)
Brazil	Mogi Guaçu River	2003–2004	LLE	LC–MS/MS	Ametryn	0.048–0.054	Jacomini et al. (2011)
Brazil	Camanducaia River	2015–2016	SPE DI	GC–MS/MS UHPLC–MS/MS	Atrazine	0.3–1.4	Barizon et al. (2020)

Continued

TABLE 12.1 Pesticide occurrence in freshwater in developing countries—cont'd

Country	Source	Year of sampling	Sample preparation	Instrumental technique	Pesticides	Range of concentration (μg L^{-1})	References
Brazil	Formoso River	–	SPE	UHPLC–MS/MS	Propoxur	0.025	Guarda et al. (2020)
Brazil	13 Rivers in the State of São Paulo	2013	SPE	LC–MS/MS	Difenoconazole; Epoxiconazole; Tebuconazole; Atrazine; Azoxystrobin; Pyraclostrobin; Picoxystrobin; Trifloxystrobin; Carbendazim	0.003–0.293	Montagner et al. (2014)
Brazil	Jaguaribe River	–	SPME SPE	GC–MS HPLC–DAD	Atrazine; Azoxystrobin; Chlorpyrifos; Difenoconazole; Parathion-methyl; Propiconazole; Triazophos	0.11–17.30	Milhome et al. (2015)
Brazil	Surface water in Morro Redondo	2010–2011	SPE	LC–MS/MS	Bentazone; Clomazone; Diuron; Irgarol; Tebuconazole	0.008–0.128	Caldas et al. (2013)
Brazil	São Lourenço River	2010–2011	SPE	HPLC–DAD	Acetamipride; Carbendazim; Carbofuran; Epoxiconazole; Piraclostrobim; Tiaclopride	0.15–35.25	Ribeiro et al. (2013)
Brazil	São Lourenço River	2009–2010	SPE	GC–MS	Deisopropylatrazine; Atrazine; Metolachlor; Flutriafol; β-Endosulfan; Endosulfan sulfate	0.04–0.82	Casara et al. (2012)
Brazil	21 surface water points in the state of Rio Grande do Sul	2007–2008	SPE	LC–MS/MS	Clomazone; Quinclorac; Penoxsulam; Imazethapyr; Imazapic; Carbofuran; 3-hydroxycarbofuran; Fipronil; Tebuconazole	0.007–0.737	da Silva et al. (2009)
Brazil	River in Primavera do Leste	1998–1999	SPE	GC–NPD	Simazine	0.046–0.047	Dores et al. (2008)
Brazil	Batalha River Vargem Limpa River	–	LLE	GC–MS	α-HCH; β-HCH; γ-HCH; δ-HCH; Aldrin; α-Endosulfan; o,p′-DDT; p,p′-DDD; β-Endosulfan; p,p′-DDT; Endosulfan sulfate; Methoxychlor; Mirex	0.01–0.137	Rissato et al. (2006)
Brazil	São Gonçalo Channel	2006–2007	SPE	HPLC–DAD LC–MS/MS	Clomazone	5.4–23.0	Primel et al. (2010)
Brazil	Vacacaí-Mirim River Vacacaí River	2003–2004 2007–2008	SPE	HPLC–DAD GC–ECD	Clomazone; Propanil; Bentazone; 2,4-D; Imazethapyr; Carbofuran; Fipronil	0.05–26.2	Marchesan et al. (2010)
Brazil	Vacacaí-Mirim River Vacacaí River	2000–2003	SPE	HPLC–UV	Clomazone; Propanil; Quinclorac	0.41–7.72	Marchesan et al. (2007)
Brazil	Ribeira de Iguape River Basin	2002–2004	SPE	HPLC–UV-vis	Aldicarb; Simazine; Carbofuran; Atrazine; Trifluralin	0.01–2.15	Marques et al. (2007)
Argentina	Pampeano aquifer	2000–2015	LLE	GC–ECD	α-Endosulfan; β-Endosulfan; Endosulfan sulfate; β-HCH; γ-HCH; δ-HCH; Heptachlor; Heptachlor epoxide	0.00003–0.01992	Grondona et al. (2019)
Argentina	Pampean and Patagonian lakes	2015	Extraction with a phosphate solution	UHLC–MS/MS	Glyphosate; AMPA	0.77–4.52	Berman et al. (2018)

Argentina	Colastiné-Corralito stream	2011–2012	SPE	UHPLC–MS/MS	Atrazine; Endosulfan	0.015–0.86	Regaldo et al. (2018)
Argentina	Quequén Grande River Basin	2012–2013	Extraction with a phosphate solution	UHPLC–MS/MS	AMPA	0.5	Lupi et al. (2015)
Argentina	Four sub-Basins	2011	SPE	UHPLC–MS/MS	Atrazine; Piperonyl butoxide; Imazapic; Metsulfuron; Dimethoate; Carbofuran; Diethyltoluamide; Epoxiconazole; Tebuconazole	0.00025–0.0014	De Gerónimo et al. (2014)
Argentina	Suquía River Basin	2010–2011	SPE SPME	GC–MS	Atrazine; α-Endosulfan; β-Endosulfan; Endosulfan sulfate; α-Cypermethrin; Chlorpyrifos; Acetochlor	0.0001–0.434	Bonansea et al. (2013)
Argentina	Xanaes River	2010	SPE	GC–ECD	β-HCH; Chlorpyrifos; p,p′-DDE; α-Endosulfan; Endosulfan sulfate; Heptachlor	0.00003–0.0043	Schreiber et al. (2013)
Argentina	El Crespo watershed	2014–2015	LLE SPE	UHPLC–MS/MS	Glyphosate; AMPA; Atrazine; 2-Hydroxyatrazine; 2,4-D; Metolachlor; Acetochlor; Metsulfuron-methyl; Fluorochloridone; Imidacloprid; Chlorpyrifos; Tebuconazole; Epoxiconazole; Metalaxyl	0.003–2.9	Pérez et al. (2017)
Argentina	Quequén Grande River	2007–2008	LLE	GC–ECD	α-Endosulfan; β-Endosulfan; Endosulfan sulfate	0.00003–0.00115	Gonzalez et al. (2012)
Argentina	Neuquen River	1995–1998	LLE	GC–NPD GC–FPD	Azinphos methyl	0.223–7.664	Loewy et al. (2006)
Argentina	Reconquista River	1994–1996	LLE	GC–ECD	p,p′-DDE; α-Endosulfan; β-Endosulfan; Endosulfan sulfate; β-HCH; γ-HCH; Heptachlor; Heptachlor epoxide	0.1–4.9	Rovedatti et al. (2001)
Argentina	Groundwater in the Northern Patagonic Region	1995–1997	LLE	GC–NPD GC–ECD	Dimethoate; Methidathion; Azinphos methyl; Fosmet; Cypermethrin; Carbaryl; Propoxur; Carbofuran; Benomyl; Carbendazim	0.08–223	Loewy et al. (1999)
Argentina	Arroyo Ramallo Stream Areco River Arrecifes River	2004	Extraction with a phosphate solution	HPLC–UV-vis	Glyphosate	100–660	Peruzzo et al. (2008)
Argentina	Reconquista River Luján River Antonio River Paraná de las Palmas	1996	LLE	GC–FID GC–ECD	γ-HCH; Heptachlor; trans-Chlordane; α-Chlordane; DDE	0.00056–0.00244	Cataldo et al. (2001)

Continued

TABLE 12.1 Pesticide occurrence in freshwater in developing countries—cont'd

Country	Source	Year of sampling	Sample preparation	Instrumental technique	Pesticides	Range of concentration (μg L^{-1})	References
Chile	Cachapoal River Basin	2015–2016	SPE	LC–MS GC–MS	Diuron; Atrazine; Deisopropylhydroxyatrazine; Deisopropylatrazine; Deethylatrazine; Flutriafol; Pyrimethanil; Tebuconazole; Azoxystrobin; Acephate; Imidacloprid; Diazinon; Pyrimidinol; Chlorpyrifos; Chlorpyrifos-oxon	0.005–4.887	Climent et al. (2019)
Chile	Cachapoal River Basin	2016	SPE	GC–MS	Terbuthylazine; Simazine; Atrazine; Deisopropylatrazine; Deethylatrazine; Desethylterbuthylazine; Pyrimethanil; Cyprodinil; Diazinon; Chlorpyrifos	0.098–21.897	Climent et al. (2018)
Chile	Petrohue River Cochamo River Puelo River	2013	SPE	GC–ECD	α-HCH; β-HCH; γ-HCH; p,p′-DDT; p,p′-DDE; p,p′-DDD; α-Endosulfan; β-Endosulfan; Endosulfan sulfate	0.0002–0.053	Placencia and Contreras (2018)
Chile	Ñuble River	2013–2015	SPE	GC–ECD	α-HCH; β-HCH; γ-HCH; δ-HCH; Heptachlor; Aldrin; Heptachlor epoxide; α-Endosulfan; p,p′-DDE; Dieldrin; Endrin; β-Endosulfan; p,p′-DDD; o,p′-DDT; Endrin aldehyde; Endosulfan sulfate; p,p′-DDT; Methoxychlor	0.00012–0.026	Grimalt et al. (2017)
Chile	Traiguén River Basin	2001–2003	SPE	HPLC–DAD	Simazine; 2,4-D; Picloram; Carbendazim	0.7–9.7	Palma et al. (2004)
Colombia	Cauca River	2010–2011	SPE	HPLC–UV-vis	Atrazine; Simazine	0.050–0.481	Villamizar and Brown (2016)
Colombia	Tota Lake Basin	2009	LLE	GC–ECD GC–NPD	Difenoconazole; Tebuconazole	0.33–4.8	Mojica and Guerrero (2013)
Costa Rica	La Mula Micro-catchment	2007–2012	SPE LLE	HPLC–DAD GC–ECD	Bentazone; Carbendazim; Dimethoate; Diuron; α-Endosulfan; β-Endosulfan; Epoxiconazole; Propanil; Terbutryn; Triazophos	0.025–61.2	Carazo-Rojas et al. (2018)
Costa Rica	Suerte River Basin	1993–1997	LLE	GC–NPD GC–ECD	Cadusafos; Carbofuran; Ethoprophos; Thiabendazole; Propiconazole; Imazalil	0.05–6.2	Castillo et al. (2000)
Ecuador	Guayas river Basin	2016	SPE	GC–ECD LC–MS/MS	Butachlor; Cadusafos; Chlorpyrifos; Fenpropimorph; Malathion; Oxadiazon; Pendimethalin; Pyraclostrobin; Spiroxamine; Tebuconazole; Triadimenol	0.02–2.00	Deknock et al. (2019)
El Salvador	Jiquilisco Bay	2008	LLE	GC–ECD	p,p′-DDE; Dieldrin	0.085–0.182	Nomen et al. (2012)
Mexico	Aquifer in Yucatan	2012–2014	SPE	GC–ECD	p,p′-DDT; p,p′-DDD; p,p′-DDE; α-HCH; β-HCH; δ-HCH; γ-HCH	0.01–37.4	Giácoman-Vallejos et al. (2018)

Mexico	Aquifer of the Ring of Cenotes in Yacatan	2010–2011	SPE	GC–ECD	α-Endosulfan; β-Endosulfan; Dieldrin; p,p′-DDE; p,p′-DDD; Endrin; Endrin aldehyde; Endosulfan sulfate; p,p′-DDT; Heptachlor; α-HCH; β-HCH; γ-HCH; δ-HCH	45–13,617	Rodríguez et al. (2015)
Mexico	Ohuira Bay	1995–1996	LLE	GC–ECD	Aldrin; γ-HCH; δ-HCH; DDE; p,p′-DDT; Dieldrin; α-Endosulfan; Heptachlor epoxide; Heptachlor	0.010–3.75	Osuna-Flores and Riva (2002)
Mexico	Groundwater in Yaqui Valley	–	Online SPE	HPLC–DAD	Methiocarb; 3-Hydroxycarbofuran	5.4–18	De Llasera and Bernal-González (2001)
Barbados	Belle Catchments Hampton Catchments Western Catchments Barbados Catchments	1991–1992	LLE	GC–NPD	Atrazine; Deethylatrazine	0.2–0.93	Wood et al. (2002)
South Africa	Swartkops River Sundays River	2017–2018	SPE	GC–ECD	α-HCH; β-HCH; γ-HCH; δ-HCH; Heptachlor; Heptachlor epoxide; Methoxychlor; Aldrin; Dieldrin; Endrin; Endrin aldehyde; Endrin ketone; α-Endosulfan; β-Endosulfan; Endosulfan sulfate; p,p′-DDE; p,p′-DDD; p,p′-DDT	0.0006–0.0863	Olisah et al. (2019)
South Africa	uMngeni River	2013	LLE	GC–MS	HCB; γ-HCH; Heptachlor; Aldrin; o,p′-DDE; p,p′-DDE; o,p′-DDD; p,p′-DDD; o,p′-DDT; Dieldrin; Endrin; Mirex	0.01–3.48	Gakuba et al. (2018)
South Africa	Buffalo River	2015–2016	LLE	GC–ECD	α-HCH; β-HCH; δ-HCH; γ-HCH; Aldrin; Heptachlor Epoxide; α-Endosulfan; p,p′-DDE; Dieldrin; Endrin; p,p′-DDD; β-Endosulfan; p,p′-DDT; Endrin Aldehyde; Endosulfan Sulfate; Methoxychlor	0.021–4.403	Yahaya et al. (2017)
Morocco	Drader–Soueir–Skhar Aquifer Loukkos Aquifer R′mel Aquifer	2004	SPE	GC–MS	α-Endosulfan; β-Endosulfan; Endosulfan sulfate; Endosulfan ether; Endosulfan lactone	0.005–0.247	El Bakouri et al. (2008)
Tunisia	Bizerte Lagoon	2015–2016	LLE	LC–MS/MS	Acetochlor; Alachlor; Chlortoluron; 3,4-dichlorophenylurea; Desethylterbuthylazine; Deisopropylatrazine; Isoproturon; Simazine; Azoxystrobin; Epoxiconazole; Tebuconazole	0.0002–0.4316	Mhadhbi et al. (2019)
Tunisia	Bizerte Lagoon	2013	LLE	GC–ECD	HCB; Heptachlor; γ-HCH; Aldrin; Dieldrin; Endrin; p,p′-DD; p,p′-DDE; p,p′-DDT	0.00002–0.00783	Necibi et al. (2015)
Ghana	Ankobra Basin	2016	LLE	GC–ECD	β-HCH; p,p′-DDE; p,p′-DDT; p,p′-DDD; Dieldrin; Endrin; Methoxychlor; Methamidophos; Parathion-ethyl; Allethrin; Fenpropathrin; L-Cyhalothrin; Permethrin; Cyfluthrin; Cypermethrin; Deltamethrin; Chlorpyrifos; Ethoprophos; Pirimiphos-methyl; Malathion; Fenitrothion	0.025–2.0	Affum et al. (2018)

Continued

TABLE 12.1 Pesticide occurrence in freshwater in developing countries—cont'd

Country	Source	Year of sampling	Sample preparation	Instrumental technique	Pesticides	Range of concentration (μg L^{-1})	References
Ethiopia	Stream in Addis Ababa	–	SLE LLE	LC–MS/MS	2,4-D; diazinon; fenpropimorph	0.0002–164	Mekonen et al. (2016)
Kenya	Nairobi River	2009	LLE	GC–ECD	α-HCH; β-HCH; γ-HCH; δ-HCH; Heptachlor; Heptachlor epoxide; Aldrin; Dieldrin; Endrin; Endrin aldehyde; α-Endosulfan; β-Endosulfan; Endosulfan sulfate; p,p′-DDE; p,p′-DDD; p,p′-DDT; Methoxychlor	0.0001–0.0397	Ndunda et al. (2018)
Tanzania	Lake Victoria	2016	LLE	GC–ECD	α-HCH; β-HCH; γ-HCH; p,p′-DDT; p,p′-DDE; p,p′-DDD; α-Endosulfan; HCB	0.13–0.76	Wenaty et al. (2019)
Tanzania	Pangani river Basin	2009–2010	LLE	GC–ECD	p,p′-DDT; p,p′-DDE; α-HCH; β-HCH; γ-HCH; α-Endosulfan; γ-Chlordane	0.00016–0.00446	Hellar-Kihampa et al. (2013)
Togo	Zio River	2012	LLE	GC–ECD	Heptachlor epoxide; o,p′-DDD; p,p′-DDD; p,p′-DDE; α-Endosulfan; β-Endosulfan; Endosulfan sulfate	0.001–0.116	Mawussi et al. (2014)
India	Gangetic river Basin	2014–2016	SPE	GC–MS	Alachlor; Atrazine; Chlorpyrifos; p,p′-DDT; γ-HCH; Malaoxon; Malathion; Parathion-methyl; 2,4-D	0.01–9033	Duttagupta et al. (2020)
India	Tapi River	2013–2014	LLE	GC–FID	α-Endosulfan; β-Endosulfan; Chlorpyrifos; Parathion-methyl; p,p′-DDT	0.17–37.56	Hashmi et al. (2020)
India	Thamirabarani River	–	QuEChERS	GC–MS	α-HCH; β-HCH; γ-HCH; δ-HCH; Heptachlor; Heptachlor epoxide; α-Endosulfan; β-Endosulfan; Endosulfan sulfate; p,p′ DDE; p,p′-DDD; p,p′-DDT; Dieldrin; Aldrin; Endrin; Endrin aldhyde; Methoxychlor; α-Cypermethrin; β-Cypermethrin; γ-Cypermethrin	0.001–34.44	Arisekar et al. (2019)
India	Hooghly River Basin	2014–2016	LLE	GC–MS/MS	α-HCH; β-HCH; γ-HCH; δ-HCH; o,p′-DDE; p,p′-DDE; o,p′-DDD; p,p′-DDD; o,p′-DDT; p,p′-DDT; α-Endosulfan; β-Endosulfan; Parathion-methyl; Monocrotophos; Phorate; Butachlor	0.041–2.940	Mondal et al. (2018)
India	Hooghly River Brahmaputra River	2012	LLE	GC–MS	α-HCH; β-HCH; γ-HCH; δ-HCH; o,p′-DDT; p,p′-DDE; p,p′-DDT; p,p′-DDD; Heptachlor; Aldrin; Dieldrin; α-Endosulfan; β-Endosulfan	0.002–0.245	Chakraborty et al. (2016)
India	Vasai Creek	2009–2011	LLE	GC–ECD GC–NPD	α-HCH; γ-HCH; o,p′-DDD; o,p′-DDT; p,p′-DDT; α-Endosulfan; β-Endosulfan; Endosulfan sulfate; Aldrin; Dieldrin; Endrin; Chlorpyrifos; Ethion	0.0085–0.2025	Singare (2016)

India	Sacco River	2012–2013	SPE	GC–MS	β-HCH; ε-HCH	0.010–0.066	Fuscoletti et al. (2015)
India	Brahmaputra River Ganga River	–	LLE	GC–ECD	α-HCH; β-HCH; γ-HCH; δ-HCH; Heptachlor; Aldrin; α-Endosulfan; β-Endosulfan; Dieldrin; p,p′-DDE; p,p′-DDD; o,p′-DDT; p,p′-DDT	0.0001–0.114	Chakraborty et al. (2014)
India	Tamiraparani River Basin	2008–2009	LLE	GC–MS	Heptachlor; cis-Chlordane; Dieldrin; Mirex	0.0001–0.0799	Kumarasamy et al. (2012)
India	Gomti River	2004–2005	LLE	GC–ECD	Aldrin; α-Chlordane; γ-Chlordane; Dieldrin; o,p′-DDT; p,p′-DDT; p,p′-DDE; p,p′-DDD; Endrin; α-Endosulfan; β-Endosulfan; endosulfan sulfate; HCB; α-HCH; β-HCH; γ-HCH; δ-HCH; Heptachlor epoxide-A; Heptachlor epoxide-B	0.004–0.301	Malik et al. (2009)
India	Ganges River	2003	LLE	GC–ECD	α-HCH; γ-HCH; Dieldrin; Malathion	0.000145–0.01624	Sankararamakrishnan et al. (2005)
India	Indo-Gangetic alluvial	2003	LLE	GC–ECD	Aldrin; o,p′-DDT; p,p′-DDT; p,p′-DDE; p,p′-DDD; Dieldrin; Endrin; α-Endosulfan; β-Endosulfan; α-HCH; β-HCH; γ-HCH; δ-HCH	0.01–3.72	Singh et al. (2007)
India	Gangetic Plains Aquifer	2003	LLE	GC–ECD	Aldrin; α-Chlordane; β-Chlordane; o,p′-DDT; p,p′-DDT; p,p′-DDE; p,p′-DDD; Dieldrin; Endrin; α-Endosulfan; β-Endosulfan; α-HCH; β-HCH; γ-HCH; δ-HCH; Heptachlor; Heptachlor epoxide-A; Heptachlor epoxide-B; Methoxychlor	0.0025–1.3552	Singh et al. (2005)

DI, direct injection; *DLLME*, dispersive liquid-liquid microextraction; *GC–ECD*, gas chromatography with electron capture detection; *GC–FID*, gas chromatography with flame ionization detection; *GC–FPD*, gas chromatography with flame photometric detection; *GC–MS/MS*, gas chromatography-tandem mass spectrometry; *GC–MS*, gas chromatography-mass spectrometry; *GC–NPD*, gas chromatography with nitrogen–phosphorus detection; *HF–LPME*, hollow-fiber liquid-phase microextraction; *HPLC–DAD*, high-performance liquid chromatography with photodiode array detection; *HPLC–UV*, high-performance liquid chromatography with ultraviolet detection; *HPLC–UV-vis*, high-performance liquid chromatography with ultraviolet-visible detection; *LC–MS/MS*, liquid chromatography-tandem mass spectrometry; *LC–MS*, liquid chromatography mass spectrometry; *LC–TOF*, liquid chromatography time-of-flight; *LLE*, liquid-liquid extraction; *QuEChERS*, Quick, Easy, Cheap, Effective, Rugged, and Safe; *SPE*, solid-phase extraction; *SPME*, solid-phase microextraction; *UHPLC–MS/MS*, ultra-high performance liquid chromatography-tandem mass spectrometry.

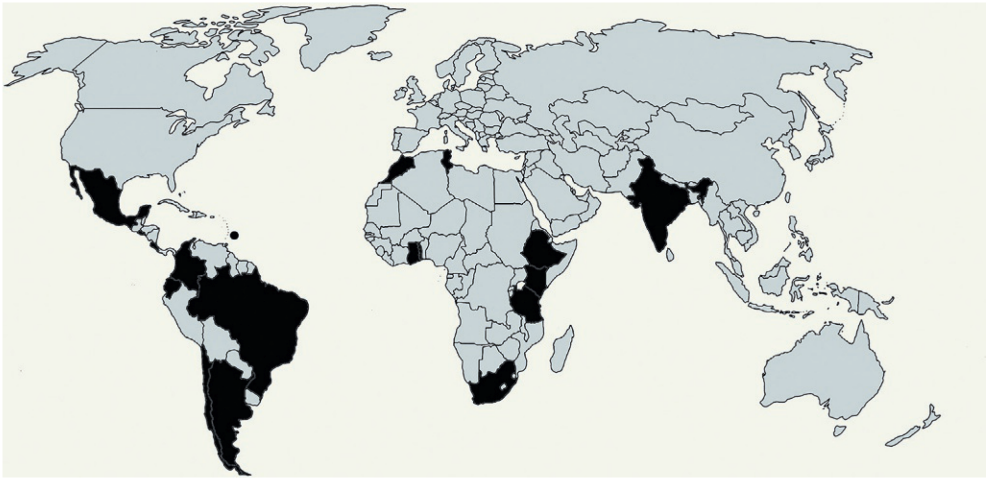
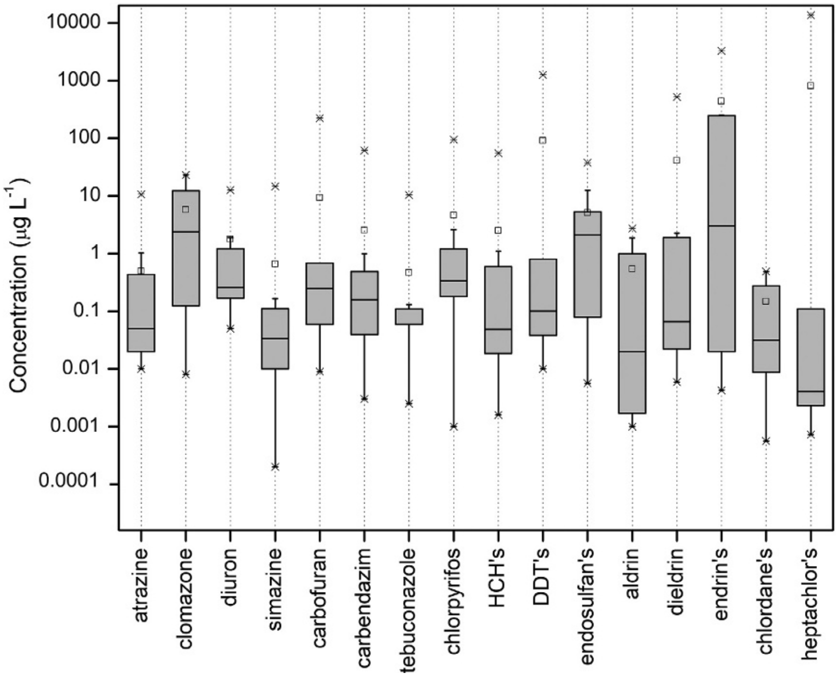


FIG. 12.2 Developing countries included in pesticide occurrence data research (marked in *black*).

organochlorines, organophosphates, pyrethroids, triazines, and triazoles. In Latin America, the most detected pesticides in freshwaters were carbendazim, atrazine, diuron, clomazone, carbofuran, tebuconazole, malathion, simazine, chlorpyrifos, hexachlorocyclohexane (HCH), and DDT. In India and African countries, most pesticides found in water sources belonged to the class of organochlorines, such as HCH, DDT, and its metabolites dichlorodiphenyldichloroethylene (DDE) and dichlorodiphenyldichloroethane (DDD), aldrin, dieldrin, and endrin (Table 12.1).

Pesticides are generally present in freshwaters in the range of ng to $\mu g\,L^{-1}$. Fig. 12.3 shows the concentrations of the most frequently detected pesticides described in Table 12.1. Yet, significantly high concentrations of pesticides have been found in developing countries. Recent research on the Gangetic River in India (Duttagupta et al., 2020) showed concerning levels of chlorpyrifos (21–94 $\mu g\,L^{-1}$), malathion (162–9330 $\mu g\,L^{-1}$), and its degradation product malaoxon (360–4520 $\mu g\,L^{-1}$). Also, in India, endosulfan was found in the rivers Thamirabarani (Arisekar et al., 2019) and Tapi (Hashmi et al., 2020), in concentrations of 34.44 and 37.56 $\mu g\,L^{-1}$, respectively. In Ethiopia (Mekonen et al., 2016), 127 $\mu g\,L^{-1}$ of 2,4-D and 164 $\mu g\,L^{-1}$ of fenpropimorph were detected in a stream in Addis Ababa. In Mexico, α-HCH (37.4 $\mu g\,L^{-1}$) was found in an aquifer in Yacantan (Giácoman-Vallejos et al., 2018), whereas several organochlorine

FIG. 12.3 Concentrations of the most frequently detected pesticides are described in Table 12.1. The DDT's = p,p′-DDT; o,p′-DDT; p,p′-DDD; o,p′-DDD; p,p′-DDE and o,p′-DDE; HCH's = α-HCH; β-HCH; γ-HCH; δ-HCH and ε-HCH; Endrin's = endrin; endrin aldehyde and endrin ketone; Chlordane's = cis-Chlordane and trans-Chlordane; Heptachlor's = heptachlor epoxido A; heptachlor epoxido B and heptachlor epoxide.



pesticides were quantified in the Ring of Cenotes aquifer (Rodríguez et al., 2015), including heptachlor ($13.617\,\mathrm{mg\,L^{-1}}$), δ-HCH ($10.864\,\mathrm{mg\,L^{-1}}$), α-HCH ($6.538\,\mathrm{mg\,L^{-1}}$), γ-HCH ($3.265\,\mathrm{mg\,L^{-1}}$), and endrin ($3.265\,\mathrm{mg\,L^{-1}}$). In Argentina, $600\,\mu\mathrm{g\,L^{-1}}$ of glyphosate was quantified in the Pergamino-Arrecifes system (Peruzzo et al., 2008), while carbofuran ($223\,\mu\mathrm{g\,L^{-1}}$), carbendazim ($156\,\mu\mathrm{g\,L^{-1}}$), propoxur ($71\,\mu\mathrm{g\,L^{-1}}$), and azinphos-methyl ($79.3\,\mu\mathrm{g\,L^{-1}}$) were found in groundwater samples from the Northern Patagonian Region (Loewy et al., 1999). In Brazil, $35\,\mu\mathrm{g\,L^{-1}}$ of carbofuran were found in the São Lourenço river (Ribeiro et al., 2013) and $26.2\,\mu\mathrm{g\,L^{-1}}$ of fipronil in the Vacacaí river (Marchesan et al., 2010). In the Cachapoal River basin, Chile (Climent et al., 2018), desethylterbuthylazine, a transformation product from atrazine, was quantified in a concentration of $21.897\,\mu\mathrm{g\,L^{-1}}$. In La Mula micro-catchment, Costa Rica, $61.2\,\mu\mathrm{g\,L^{-1}}$ of dimethoate, $22.8\,\mu\mathrm{g\,L^{-1}}$ of diuron, and $30.6\,\mu\mathrm{g\,L^{-1}}$ of propanyl were found (Carazo-Rojas et al., 2018).

Due to the risks to the environment and effects on human health and wildlife, organochlorine pesticides have been banned or restricted in several countries since the Stockholm Convention (de Souza et al., 2020). Consequently, other classes of pesticides, such as organophosphates, have been considered an alternative, mainly due to their low cost and unselective mode of action (Abubakar et al., 2019). However, organochlorine pesticides are still widely used to increase agricultural productivity and control vector-borne diseases, especially in developing countries (Pokhrel et al., 2018; Shunthirasingham et al., 2010). Several organochlorine pesticides that had been banned in Kenya since 1986 have been identified in surface waters (Olaka, 2020).

In Brazil, Argentina, and Chile, organochlorine pesticides have been either banned or restricted, while DDT, endosulfan, and HCHs were banned in India. Nevertheless, as noted in Table 12.1, these compounds are still found in such countries' water bodies. The presence of these pesticides in the environment may be related to their persistence and illegal use (Girones et al., 2020; Grimalt et al., 2017; Joseph et al., 2020; Magalhães et al., 2017). In African countries and Mexico, organochlorine pesticides are still widely used in agriculture, livestock, and to control disease vectors, such as dengue and malaria (Rodríguez et al., 2018; Taiwo, 2019).

The literature review showcased that most studies used solid-phase extraction (SPE) and liquid-liquid extraction (LLE) for sample preparation and liquid (LC) or gas chromatography (GC) coupled with mass spectrometry (MS) to identify and quantify pesticides in water. However, GC with electron capture detection (ECD) was widely used to determine organochlorine pesticides. With the advancement of analytical methodologies, most works published after 2010 used GC-MS or LC-MS/MS to determine pesticides in water due to their analytical suitability in trace analysis, promoting high detectability, selectivity, and accuracy (Hurtado-Sánchez et al., 2013; Montagner et al., 2017).

12.4 Risk assessment for the protection of aquatic life

Risk assessment is a dynamic and changeable process and there are several ways to perform a risk assessment based on the Water Quality Criteria (WQC). Herein, an example to measure the potential risk to aquatic life using the methodology and pesticides described by Albuquerque et al. (2016) is provided to illustrate the scenario for developing countries shown in Table 12.1. The Risk Quotient (RQ) (Eq. 12.1) was calculated as the quotient between each observed concentration (C_{obs}) and the selected WQC (Isidori et al., 2005). Values greater than 1 indicate risk. The WQC values used in Fig. 12.4 were obtained from Albuquerque et al. (2016).

$$RQ = \frac{C_{obs}}{WQC} \tag{12.1}$$

Fig. 12.4 shows that most concentrations determined for pesticides in developing countries present a risk to aquatic life according to the methodology applied. Thus, environmental pesticide contamination should be carefully addressed and further explored.

12.5 Regulatory challenges in Africa, Asia, Latin America, and the Caribbean

This topic intends to address a few pesticide regulations for surface waters in countries from Latin America, the Caribbean, Africa, and Asia, highlighting the differences in legislation development.

Worldwide jurisdictions are committed to developing standard values for different environmental compartments (soil, air, drinking water, surface water, groundwater, and food). According to Li and Jennings (2017), there are currently more than 19,400 soil regulatory guidance values and 5400 drinking water maximum concentration levels (MCLs) adopted by 54 and 102 nations, respectively. Yet, the authors found that several standard values were not derived conservatively enough to avoid human health risks posed by pesticides in a few countries.

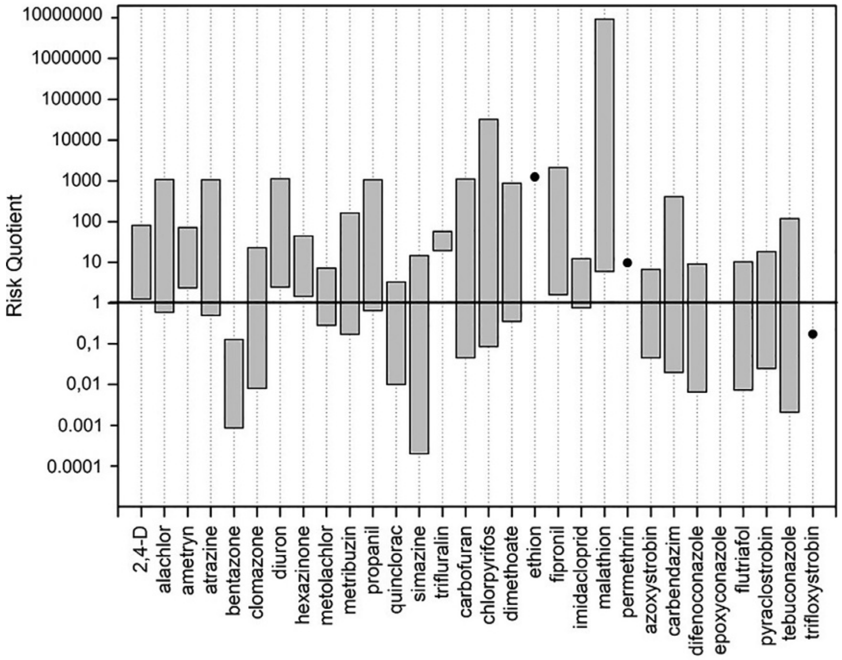


FIG. 12.4 Risk quotient (RQ) values for pesticides in freshwaters from developing countries are presented in Table 12.1. Bars represent concentration ranges and dots represent a single concentration level. RQ values greater than 1 indicate risk.

Developing countries lag in pesticide legislation (Sanganyado, 2022, Chapter 19). Thus, little to no health and safety legislation is currently enforced in many of them. The little information available is scattered through official documents and secondary sources such as annual reports, research articles, and government statements.

The available data on pesticide occurrence in surface waters provide subsidies for registration, authorization/restriction processes, and regulation development based on maximum concentration levels allowed in drinking/surface water. Thus, developing countries should promote the development of a robust and complete monitoring network of emerging substances, such as the NORMAN network for emerging substances in Europe (NORMAN, 2020).

In this respect, Brazil accounts for 37% of scientific publications concerning pesticides in surface waters amongst Latin and Central American countries, followed by Argentina and Mexico, with 24% and 17%, respectively. In Africa, South Africa (23.4%) and Egypt (16.8%) stand out. The Caribbean countries Barbados and Puerto Rico have 41% of publications together. In India, there were near 800 papers on this subject. Thus, the following sections provide a summary of current legislation in a few selected developing countries.

12.5.1 Brazil

In Brazil, pesticide registration requires the concerned substance to be evaluated and approved under three instances; the Ministry of Agriculture, regarding agronomic efficiency; the National Health Surveillance Agency (ANVISA), regarding the impact on human health; and the Brazilian Institute for the Environment and Renewable Natural Resources (IBAMA), regarding effects on the environment, according to Federal Decree nº 4,074/2002 (Brazil, 2002).

In recent years, several bureaucratic measures have been adopted to accelerate pesticide registration in Brazil. Until 2020, the Phytosanitary Pesticide System (AGROFIT) had near 2370 registered products, of which approximately 50% were generic products. It is also noteworthy that using agricultural biopesticides as a biological control strategy for pests grows substantially (Brazil, 2020; Fontes and Valadares-Inglis, 2020; Brazil, 2019a). Figs. 12.5 and 12.6 show products registered annually in Brazil and their classifications, respectively.

According to the first survey of Grain Harvest 2020/21 released by the National Supply Company (CONAB), Brazil is a prominent country in soybean, corn, rice, and cotton production. Brazil has yearly maintained an increase in cultivated area and food production, setting yet another production record (National Supply Company – CONAB, 2020).

Brazil has regulations for pesticide residues in food, soil, drinking water, surface water, and groundwater. The Regulations of the National Council of the Environment (CONAMA) Nº 430/2011 (Brazil, 2011) and Nº 357/2005 (Brazil, 2005) are complementary to each other and provide waterbody classification with respective environmental

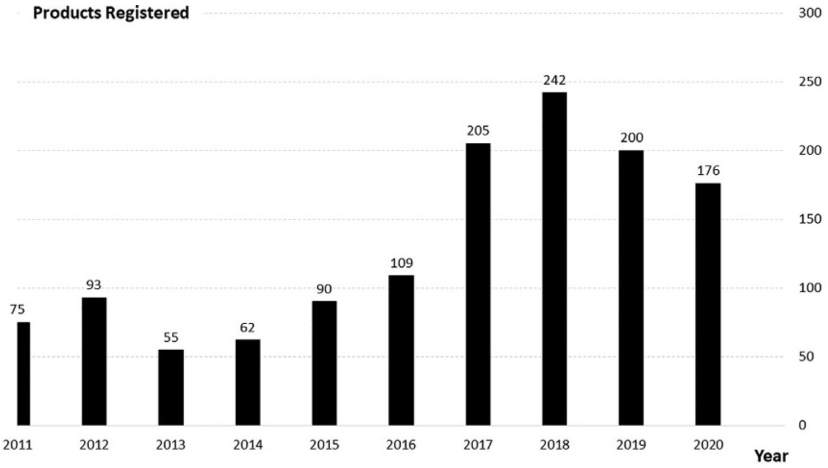


FIG. 12.5 Pesticide products are registered annually in Brazil (Brazil, 2020).

guidelines, as well as standardization of effluent discharge. However, only 28 pesticides are regulated for surface water bodies ranked Class 1 (aquatic bodies intended for human consumption and/or aquatic life preservation), whereas no pesticides are regulated for effluent discharge.

Of the 28 compounds legislated for surface water, approximately 50% are currently prohibited in the country. For instance, in 2009, a sanction of Law No. 11936 banned the manufacture, import, export, stock maintenance, marketing, and use of pesticide DDT throughout the national territory (Brazil, 2009). The last evaluations of banned pesticide active ingredients in Brazil were endosulfan and trichlorfon (2010), methamidophos (2011), parathion methyl and phorate (2015), prochloraz (2016), carbofuran (2017), and paraquat (2020), whereas lactofen (2016) and 2,4-D (2019) were classified as restricted use (Brazil, 2019b).

12.5.2 Argentina

Argentina has a robust legal framework for the conservation and sustainable use of the environment, including aquatic ecosystems (Argentina, 2003). However, the country globally ranks eighth in cultivated areas, with soybean accounting for the highest share of pesticide use (Argentina, 2019; World Bank, 2016).

The country is one of the world's largest transgenic soy producers, in which the grain is broadly used in cattle farming and biofuel production. However, Argentina has been at the stage of social and political conflicts about pesticide use in transgenic agriculture, leading to significant changes in pesticide regulation (Rauchecker, 2019).

The National Service for Agro-Food Health and Quality (SENASA) had 2038 registered substances until 2020 (Argentina, 2020). Plant protection products are registered in the National Register of Plant Therapeutics under the provisions of Decree No. 3,489/58 and Decree No. 5,769/59. In addition, plant product registration must be following the Manual of Procedures, Criteria, and Scopes for the Registration of Phytosanitary Products in the Argentine Republic, approved by Resolution SAGPYA No. 350/99 (SENASA, 2020).

General Environmental Law No. 25,675 and Environmental Water Management Regime (Law No. 25,688) (Argentina, 2003) define that the national authority should determine the acceptable maximum pollution limits for water according to the different uses. The Civil and Commercial Code of the Nation Law 26,994 of 2014 defines environmental waters of public, private, collective domain, and damages (Argentina, 2014). Due to the structural changes in pesticide legislation, the Freshwater Quality Guide to Protect Aquatic Life (GNCA, 2003) of the Argentine Subdepartment of Water Resources is commonly used for guidance, which presents short communications for each substance.

12.5.3 Chile

In 2020, 336 pesticides were granted authorization by the *Servicio Agrícola y Ganadero* (SAG) in Chile, including eight organochlorines. Pesticides paraquat and methyl bromide became of restrictive use, while five others were banned for use in December 2020 (Chile, 2020a). The drinking water quality standard in Chile (NCh 409/1 of 1984) establishes the maximum individual limit for twelve pesticides, with concentrations ranging from 0.01 (hexachlorobenzene) to 100 (2,4-D) $\mu g\,L^{-1}$. The Decree DS 143/2008 establishes eleven pesticides' primary standards in continental surface waters,

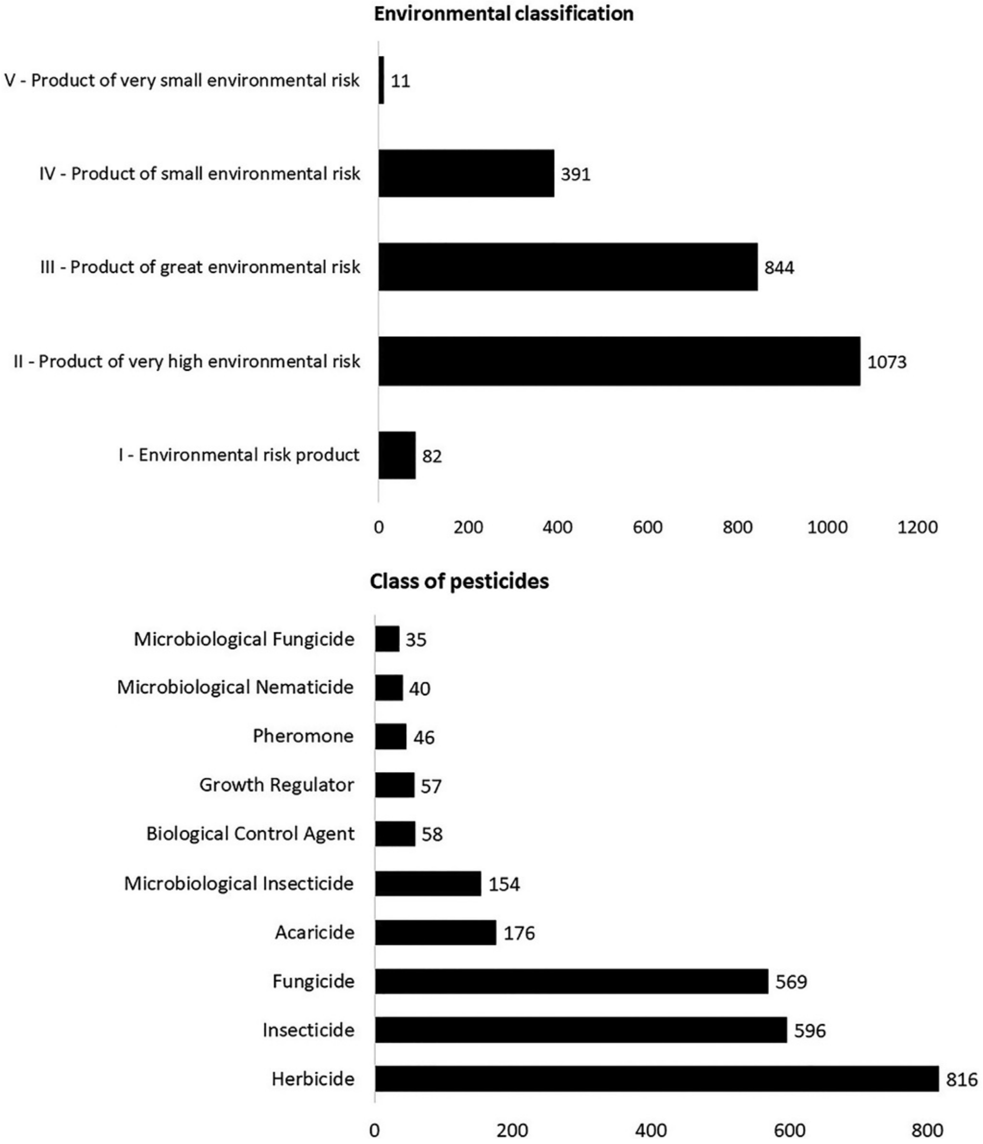


FIG. 12.6 Class of pesticide products registered annually in Brazil (*left*) and pesticide environmental classification (*right*). *Adapted from Brazil, 2020. Ministry of Agriculture, Pesticide and Phytosanitary System—AGROFIT. Pesticide Registration. <http://indicadores.agricultura.gov.br/agrofit/index.htm> (accessed 18.09.20).*

sampling frequency, and the methodology for evaluation of aquatic bodies quality. In addition, Chile is negotiating formalized agreements with both Bolivia and Argentina to manage shared resources and water storage projects (Chile, 2020a, 2020b).

12.5.4 Mexico

Mexico is the third-largest market of agrochemicals in North America, with a growing market at a compound annual growth rate (CAGR) of 5.2% during 2017–2022, in which insecticides and herbicides account for more than 36% of such market (Mordor, 2020). The country held one of the first places in DDT use until it was banned in 2000. Despite Mexico's active participation in several international pesticide agreements, recent studies indicated the use of pesticides such as paraquat, endosulfan, lindane, methyl bromide, parathion, and malathion banned in other industrialized countries (Sharma et al., 2019).

Three government agencies are involved in pesticide registration in Mexico: Federal Commission for the Protection of Health Risks (COFEPRIS); Secretary of Environment and Natural Resources (SEMARNAT); and Secretariat for

Agriculture and Rural Development (SADER). In 2017, there were 11.57 thousand tons of produced pesticides. In addition, in May 2019, the list of applications for sanitary records of pesticides and plant nutrients of the Health Department (COFEPRIS) recorded 88 additional substances. However, over 110 active ingredients banned in other countries are still allowed in Mexico, mainly because such pesticides have indefinite use permits in the country, and there is a lack of an updated legal framework that regulates their use (Castillo, 2019).

The Official Mexican Standard NOM-127-SSA1-1994, "Environmental health, water for use and human consumption–Permissible limits of quality and treatment to which water must be submitted for potabilization," establishes MCL values for eight pesticides ranging from $0.03\,\mu g\,L^{-1}$ (aldrin, dieldrin, heptachlor, and heptachlor epoxy) to $30\,\mu g\,L^{-1}$ (2,4-D). In 2018, the National Human Rights Commission (CNDH-ONU) issued the 82/2018 recommendation that suggests the adoption of regulatory, administrative, and public policy actions to regulate the management of hazardous pesticides properly, recognizing that the lack of control in pesticide usage constitutes rights violation of food, clean water, a healthy environment, and health (Castillo, 2019).

12.5.5 Puerto Rico

In 2019, the Puerto Rico Water Quality Standards Regulation was promulgated following Law No. 416-2004. Such regulation nullifies any previous provision, resolution, agreement, or restriction of Puerto Rico's Government on the same subject that may be conflictual. The purpose of this regulation is to: (1) designate water use according to water quality; (2) promulgate water quality standards required to sustain the designated use; (3) identify other rules and regulations applicable to sources of pollution that may affect the quality of the waters subject to this regulation; and (4) establish other measures necessary for achieving and maintaining the quality of the waters of Puerto Rico.

Puerto Rico's legislation is considered one of the most complete among the group of countries estuded, presenting maximum values allowed for thirty-one volatile, semi-volatile, and persistent organic substances in surface, ground, estuarine and coastal waters. Persistent (organochlorides, sulfurs, and organophosphates) and non-persistent pesticide residues shall not exceed 1/100th and 1/10th of the 96-h LC_{50} value obtained according to the designated toxicity test, respectively (Puerto Rico, 2019).

Although not a major part of the nation's Gross Domestic Product (GDP), agriculture in Puerto Rico has various crops grown, including rice, sugar cane, coffee, corn, plantains, vegetables, and melons. According to the 2018 Puerto Rico Census of Agriculture, 80% of the farm business is family-owned, whereas less than 20% is corporate-owned. In addition, approximately 50% of the farm business is primarily destined for agricultural activities (Puerto Rico, 2020).

12.5.6 Africa and Asia

The African continent contributes with 2%–4% of the global market share of pesticides, accounting for its lowest pesticide usage rate. Conversely, India is among the top ten pesticide consumers globally (Sharma et al., 2019).

Pesticide registration in Western Africa (comprising 16 nations; Niger, Nigerian, Congo, Benin, among others) is a multi-national process called *Comité Sahélien des Pesticides* (CSP). In Niger, due to the limited capacity of CSP, 44% of pesticide dealers are unlicensed. Therefore, the distribution and sale of pesticides in West Africa are not effectively regulated, analytical facilities are lacking to support any monitoring of environmental residues, and there is no routine assessment of pesticide contamination of surface waters (Jepson et al., 2014).

South African food crops dominate the agricultural market in the region. Maize is the most important food crop, followed by wheat and barley. The Department of Agriculture, Forestry, and Fisheries (DAFF) of the Environment Affairs Department of Republic South Africa regulate the manufacture, distribution, sales, and use of pesticides. Also, the regulation aims to ensure the protection of the health and safety of people, animals, crops, the environment, and trade (according to with Fertilizers, Farm Feeds, Agricultural Remedies and Stock Remedies Act, Act No. 36 of 1947). The South African agriculture sector is estimated to register a compound annual growth rate of 4.5% during the forecast period 2020–2025 (South Africa, 2020).

The National Water Act of 1998 (Act No. 36 of 1998) aims to ensure that South Africa's water resources are protected, used, developed, conserved, managed, and controlled sustainably and equitably for all persons' benefit. The Act provides that the National Government, acting through the Ministry of Water Affairs and Forestry, is the public trustee of the nation's water resources and must regulate the use, flow, and control of all water in the country. The Decree South African for National Standard Drinking water is SANS 241:2015, but it does not establish maximum levels for any pesticide (Mudzunga, 2015).

In South Africa and India, agriculture plays a significant role, just like in China, the Philippines, Germany, the United Kingdom, Canada, the United States, Mexico, Costa Rica, Brazil, New Zealand, and Australia (Li and Jennings, 2017). In 2016, India was the country with the highest percentage of arable land globally, with almost 53% of territory destined for agriculture. In contrast, the USA ranked second with only 16.8% (World Bank, 2016). According to projections, the Indian market will grow at an annual compound rate of 8.3% between 2018 and 2023. Based on the product type, the market has been segmented as synthetic pesticides and biopesticides. Synthetic pesticides currently dominate the Indian market (Wood, 2018).

The present network of monitoring Indian National Aquatic Resources comprises 870 stations on rivers, lentic water bodies, and subsurface waters. Water samples are analyzed for 28 parameters consisting of physicochemical and bacteriological parameters for ambient water. In addition, 15 pesticides (alpha BHC, beta BHC, gamma BHC, OP DDT, PP DDT, alpha endosulfan, beta endosulfan, dieldrin, aldrin, carbaryl, 2-4 D, malathion, methyl parathion, anilophos, and ahoropyriphos) are analyzed in selected samples (Bhardwaj, 2005).

However, in May 2020, the Pesticide Action Network (PAN) India has welcomed the draft order issued by the Centre banning 27 pesticides already banned in several other countries. The network has also requested the Ministry of Agriculture to review the remaining pesticides registered in India with the same criteria, issuing stringent regulatory measures, including the possible ban of more hazardous pesticides (Telegana, 2020).

12.6 Conclusions and final considerations

Pesticide use and application bring plenty of benefits, such as enhancing food production, securing food produce during harvest and storage, and controlling urban diseases transmitted by pests. However, it also brings environmental and human health hazards associated with chronic exposure (see Sanganyado, 2022, Chapter 19; Tavengwa et al., 2022, Chapter 20). Current issues involving pesticides in the environment are not evenly addressed in the world. Environmental pesticide contamination may vary drastically among different regions globally because of cultural, social, and economic factors and climatic and ecological characteristics that affect the countries differently.

While pesticide legislation has been extensively addressed in several developed countries, in most developing countries, the increase in agricultural production leads to a substantial rise in novel active ingredients, yet regulatory agencies of environmental protection struggle to keep pace.

Overall, there is a dearth of studies related to pesticides in freshwaters in developing countries. However, human health and aquatic life protection are strictly related to the integrative approach between science, technology, and public policies. Fortunately, there are encouraging trends towards strategies for the rational use of pesticides and risk minimization. For instance, there is a demand for integrated approaches involving chemistry, toxicology, and epidemiology to comprehend and monitor adverse outcomes of pesticide exposure and plan preventive strategies. In addition, there is a need to implement legislation and standards to regulate the manufacturing, distribution, handling, and application of pesticides. Finally, the establishment of maximum residue levels for water bodies shall be prioritized, ensuring strict adherence. This chapter is interconnected under the section on fate and occurrence of emerging pollutants within aquatic ecosystems with other chapters, e.g., Ajayi et al. (2022), Cristale (2022), Vizioli et al. (2022), Galhardi et al. (2022), Hashemi and Kaykhaii (2022), Madikizela et al. (2022), Mashile et al. (2022), Montagner et al. (2022), Moodley et al. (2022), Ntshani and Tavengwa (2022), Sanganyando and Kajau (2022), and Yardy et al. (2022).

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CHAPTER

13

Antiretrovirals (ARVs) in the environment

Isaac Kudu, Vishalan Pillay, and Brenda Moodley

13.1 Introduction

13.1.1 General overview

Numerous types of diseases have affected the world, such as smallpox, Ebola, and various types of coronaviruses, but none have reached the magnitude of human immunodeficiency virus/acquired immunodeficiency syndrome (HIV/AIDS). It is transmitted through contact with infected body fluids: blood, preseminal fluid, semen, vaginal fluid, and breast milk. Infection with HIV leads to the weakening of the human body by destroying the cells within the immune system (Di Giamberardino and Iacoviello, 2020). The first stage of the infection of the disease is known as HIV and as it progresses, it becomes AIDS. Increasing HIV infection rates increase demand for antiretroviral (ARV) drugs, which automatically leads to a greater output of ARV drugs into wastewater systems. Due to a lack of suitable technologies to remove ARVs from wastewater treatment systems, they eventually make their way into the environment with continued input leading to an accumulation of these drugs in the environment.

This disease is more prevalent in Africa (Fig. 13.1) and in South Africa alone, 13.1% of the population is estimated to be living with HIV (Statistics South Africa, 2018). Of those infected in South Africa, 62% receive ARV treatment (UNAIDS, 2018).

The first ARVs administered in 1987 contained only zidovudine, while current patients infected with HIV may be treated from a selection of 30 ARVs (Mlunguza et al., 2020). A commonly used ARV in South Africa since 1998 is efavirenz, which is also ranked third among the most used ARVs in the treatment of HIV-1 mutant strains in the world (Robson et al., 2017). As the first line of treatment, nevirapine is generally used to treat mothers infected with HIV-1, thus preventing mother-to-child transmission of the virus (Wood et al., 2016). ARVs may also be administered to infected adolescents, adults, and pregnant women as a combination of efavirenz, emtricitabine or lamivudine, and tenofovir (Schoeman et al., 2017). These drugs eventually make their way into the environment via wastewater treatment plants (WWTP), which are not able to remove the complex pharmaceutical compounds that are not completely metabolized by the human body (Robson et al., 2017). In a study conducted by Prasse et al. (2010), it was stated that the current wastewater treatment process was inadequate for the removal of nevirapine, which was detected in surface water. Furthermore, illicit drugs have now been found to contain ARVs as part of their composition, which also eventually make their way into WWTPs and adds to the concentrations of ARVs in WWTPs (Khine et al., 2015; Grelotti et al., 2018).

The United Nations general assembly expected 15 million people to have access to ARV treatment by 2015 (Hirnschall et al., 2013). This global target was set in 2011, with an estimated 9.7 million people have received treatment by the end of 2012 (Hirnschall et al., 2013). This remarkable target assisted many infected individuals but added more pharmaceutical emerging contaminants to the environment. With the increased demand for the use of ARVs, trace concentrations have been quantified in the South African aquatic environment (Robson et al., 2017). ARVs are classified as emerging pollutants, which means that ARVs may potentially have detrimental effects on an environment's ecosystem. Furthermore, it is not regularly monitored, and therefore limited knowledge is available as to its environmental toxicity (Rimayi et al., 2018). The high usage of ARVs could result in an estimated 159,000 kg entering the South African aquatic environment (Swanepoel et al., 2015). Currently, there are only health guidelines for the use of ARVs for the treatment of HIV/AIDS but no environmental guidelines exist for ARVs present in environmental matrices. Most of the research conducted has been a comparison to previous work to justify the inclusion of ARVs as emerging pollutants.

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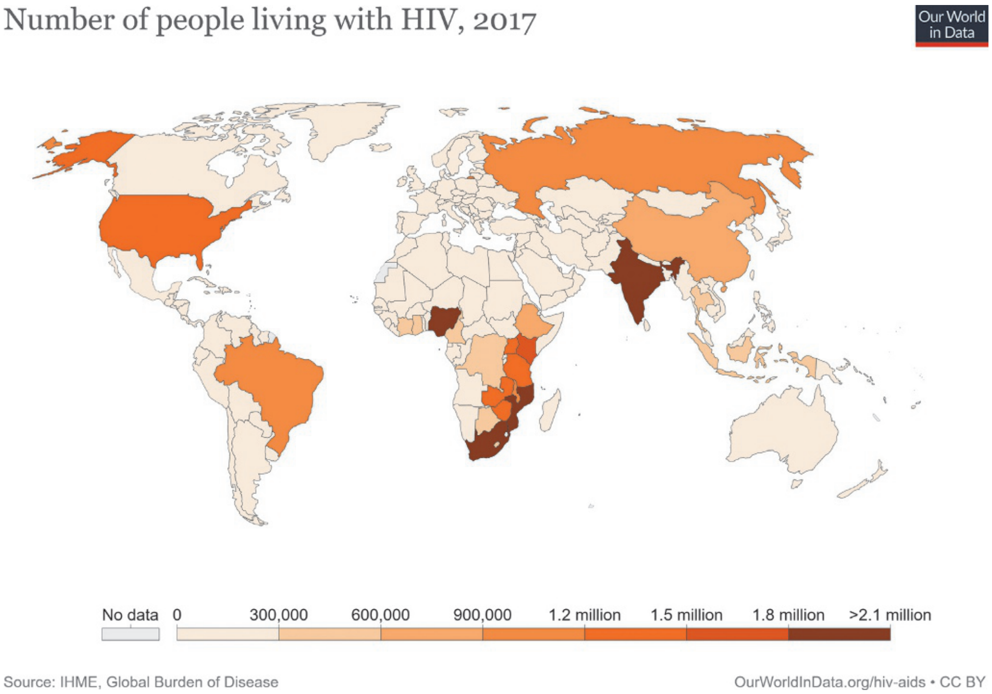

FIG. 13.1 Global map showing the number of people living with HIV (Our World in Data, n.d.).

Common extraction techniques used in these studies for the isolation of these drugs from various sample matrices include solid-phase extraction (SPE) and sonication, with either gas chromatography (GC) or liquid chromatography (LC) used for quantifying the ARVs (Abafe et al., 2018; Aminot et al., 2015; Hu et al., 2010; Ibáñez et al., 2017; Kairigo et al., 2020; K'oreje et al., 2016, 2018; Mlunguza et al., 2020; Ngumba et al., 2016a,b; Peng et al., 2014; Prasse et al., 2010; Rimayi et al., 2018; Schoeman et al., 2015; Swanepoel et al., 2015; Wood et al., 2015; Wooding et al., 2017). A variety of SPE cartridges have been used such as Oasis HLB (Abafe et al., 2018; Ngumba et al., 2016a,b, 2020), Isolute ENV+ (Prasse et al., 2010), Waters Oasis MCX (Aminot et al., 2015, 2016), as well as Strata SDB-L, StrataX, StrataWAX, and StrataWCX (Ibáñez et al., 2017; Mosekiemang et al., 2019), but Oasis HLB has proved to be the most commonly used SPE for these studies. Apart from SPE, other extraction techniques used are microwave extraction, sonication, and QuEChERs method. Liquid chromatography is the preferred technique as it eliminates the need for derivatization since most pharmaceuticals are not volatile and have high polarity. ARVs are generally found in complex matrices hence Schoeman et al. (2017) used the more sensitive technique of gas chromatography with a mass spectrometer (MS) as the detector, which is selective for these types of compounds. For LC analysis, MS/MS is commonly used as the detector (Abafe et al., 2018; Aminot et al., 2015, 2016) but various other detectors have also been utilized such as, triple quadrupole (QqQ) (Mosekiemang et al., 2019), magnetic sector HRMS (K'oreje et al., 2016), Orbitrap MS (K'oreje et al., 2018), and quadrupole time-of-flight (QTOF) (Mlunguza et al., 2020; Wood et al., 2016). More recent studies have used a Quattro micro tandem MS (Kairigo et al., 2020). These all show that sophisticated analytical instrumentation is required for suitable analysis of ARVs, which may be a contributing factor in the limited studies available. Furthermore, some studies on the African continent were only possible with collaborations with European partners where the actual analysis took place. This somewhat explains the reason for the fairly low number of investigations by researchers on the African continent due to the limited availability of suitable instrumentation.

This review aims to collate information relating to ARVs as an emerging pollutant in the aquatic environment. This includes a review of research conducted in Africa and Europe. Africa was chosen since the continent has a large proportion of the population living with HIV prompting research into the occurrence of ARVs in this continent's environment. Europe was chosen as a continent to compare against which has carried out some studies in this field of research. There also exist more collaborations between African researchers and their European counterparts rather than with North American researchers. Little to no studies have been carried out in other southern hemisphere continents and therefore it was felt that a comparison with studies on the European continent would provide interesting and comparable results. The research on each continent is based on different sample matrices such as wastewater/freshwater, sediment, and biota. The source, persistence, transport, and toxicity of ARVs are evaluated for each continent and the different sample matrices. Future research possibilities are provided to assist researchers and environmentalists in dealing with ARVs as an emerging pollutant.

13.2 Environmental fate, behavior, and risk of antiretrovirals

13.2.1 Sources

Antiretroviral (ARV) drugs enter the environment via both point and nonpoint sources. The point sources include effluent from municipal wastewater treatment plants (WWTPs), discharge from health facilities and pharmaceutical production plants, and leachate from landfill sites that receive expired or unused drugs (Bottoni et al., 2010; Nannou et al., 2019; Peng et al., 2014). Nonpoint sources include surface runoff from farms treated with sewage sludge, open dumpsites in rural areas, and informal settlements that lack adequate solid waste removal services. The absence of proper sanitary facilities may also lead to the direct disposal of raw sewage to surface water systems as well as land (Kairigo et al., 2020; Ngumba et al., 2016a). The amount of ARVs entering the environment in a geographical region or country is influenced by the following factors; (i) HIV infection prevalence rate, (ii) pharmacokinetic behavior of ARVs, (iii) municipal wastewater treatment, and (iv) environmental factors that influence their occurrence.

13.2.1.1 HIV infections prevalence rate

The HIV infection prevalence rate in a region or country and the subsequent existence of an antiretroviral therapy (ART) program has a direct correlation with the quantities of ARVs that make their way into the environment (Ncube et al., 2018; Swanepoel et al., 2015). For example, the levels of efavirenz, lamivudine, and nevirapine detected in WWTP effluents and surface water reported from Kenya (K'oreje et al., 2016; Ngumba et al., 2016a) and South Africa (Abafe et al., 2018; Rimayi et al., 2018; Schoeman et al., 2017) were significantly higher than levels from studies in Finland (Ngumba et al., 2016b), Germany (Funke et al., 2016; Prasse et al., 2010), and France (Aminot et al., 2015). This trend is consistent with the fact that Kenya and South Africa account for close to 24% (9 million) of persons living with HIV out of an estimated 38 million persons globally. Furthermore, about 70% of these infected persons are estimated to be covered under an ART program (The World Health Organization, 2020).

13.2.1.2 Pharmacokinetic behavior of ARVs

The amount of ARVs that are released into the environment is dependent on the proportion of the orally administered drug that is absorbed (bioavailable), metabolized, and excreted from the body. The majority of ARVs in use are not completely absorbed from the gastrointestinal tract (Harlass, 1996; Ngumba et al., 2020). Consequently, the bioavailability of ARVs in the bloodstream is low and large fractions of the drug are excreted unchanged (bioactive) or only partially transformed (Ncube et al., 2018; Ray et al., 2016). From Table 13.1, abacavir, emtricitabine, lamivudine, stavudine, and nevirapine have a bioavailability of above 80% while tenofovir and darunavir, on the other hand, have bioavailability values of 25% and 37%, respectively.

13.2.1.3 Municipal and industrial wastewater treatment

Municipal wastewater treatment facilities play a critical role in determining the number of ARVs that enter surface water systems (Abafe et al., 2018; Schoeman et al., 2017). Though conventional WWTPs have not been designed for the effective removal of ARVs from sewage, significant removal of abacavir, indinavir, lamivudine, zidovudine, efavirenz, and stavudine from influent have been reported in WWTPs in South Africa (Abafe et al., 2018; Schoeman et al., 2017), Kenya (K'oreje et al., 2018), and Germany (Prasse et al., 2010). The ARV residues either are degraded during the wastewater treatment process or are enriched in the sludge by adsorption to the biosolid phase in the treatment plant (Schoeman et al., 2017). WWTPs however, can also contribute to the accumulation of ARVs in the treated effluent. Schoeman et al. (2017) recorded elevated levels of nevirapine in effluent samples over a 4-week monitoring period of a WWTP in the Gauteng province of South Africa. K'oreje et al. (2016) and Prasse et al. (2010) have also reported similar observations for WWTPs in Kenya and Germany. The de-conjugation of hydroxylated metabolites of nevirapine in the WWTPs coupled with the fact that nevirapine binds poorly to biosolids have been put forward as the possible explanation for the observed trend (K'oreje et al., 2016; Schoeman et al., 2017).

TABLE 13.1 A compilation of formulation, daily dose, and bioavailability of ARV drugs.

Drug	Formulation (mg/tablet)	Dosage (tablets/ day)	Total (mg/ day)	Bioavailability (%)	Excretion (%) In urine	Excretion (%) In feces	Metabolites
Abacavir	300	2	600	83	1.2	16	5′-Carboxylic acid metabolite and 5′-glucuronide metabolite
Emtricitabine	200	1	200	93	86	–	Emtricitabine 3′-sulfoxide (M-III), emtricitabine 3′-sulfoxide (M-IV), emtricitabine *O*-glucuronide (M-II), 5-fluorocytosine
Lamivudine	300	1	300	86	70	–	Lamivudine sulfoxide
Zidovudine	300	1	300	65	29	–	3′-Azido-3′-deoxy-5′-*O*-beta-D-glucopyranuronosylthymidine (GZDV), 3′-aminothymidine, 3′-amino-3′-deoxythymidine glucuronide, 5′ glucuronylzidovudine
Tenofovir	300	1	300	25	70	–	Tenofovir monophosphate, tenofovir biphosphate
Stavudine	40	1	40	68–104	N/A	–	Stavudine triphosphate
Nevirapine	200	1 × 2	400	>90	<3	–	*n*-Hydroxynevirapine,
Darunavir	800	1	800	37	13.9	79.5	Oxidative metabolites of darunavir

Modified from Ncube, S., Madikizela, L.M., Chimuka, L., Nindi, M.M., 2018. Environmental fate and ecotoxicological effects of antiretrovirals: a current global status and future perspectives. Water Res. 145, 231–247 with modifications and https://go.drugbank.com/drugs.

13.2.2 Persistence

Like all pharmaceutical compounds, the persistence of ARVs in the environment is controlled by the chemical properties (such as p*K*a and *K*ow) of the compounds, the surrounding environmental/climatic factors, and the physicochemical properties of environmental matrices (Michael et al., 2013). An indicator of the persistence of ARVs and their metabolites in the environment is the ease with which they are degraded via abiotic and biotic processes (Prasse et al., 2015). Abiotic degradation of ARVs in water is controlled by temperature (dry or wet climatic conditions), pH, and turbidity (Aminot et al., 2016). In a study to understand the effect of chlorination on nevirapine, Wood et al. (2016) reported that in high pH (basic) medium nevirapine was degraded more rapidly than in low pH (acidic) medium. This observation is one of the plausible explanations for why nevirapine tends to be persistent in WWTP effluents. In the sewage treatment process, chlorine is added as a disinfectant. For optimum disinfection to be achieved a low pH condition is maintained. Consequently, the low pH environment in the aqueous phase of WWTPs results in reduced degradation of nevirapine hence its persistence in the effluent (Wood et al., 2016). For WWTPs that use biological processes, the pH of the process needs to be maintained between 6.5 and 7 for optimum functioning of the bio-organisms. At this pH, nevirapine is expected to be only slightly dissociated and may lead to minimal degradation. If the pH increases, degradation should increase. However, most WWTPs have a slightly acidic to neutral pH, which accounts for the persistence of nevirapine in WWTPs. However, more studies are needed to further confirm this.

The biotic degradation of ARVs in water and soil is mediated by microorganisms attached to suspended solids in water and on soil particles. In water, the number of suspended solids, temperature, pH, and oxygen demand (OD) influence the breakdown process while soil texture, moisture content, organic matter as well as pH are the controlling factors of ARVs degradation in soil (Al-Rajab et al., 2010; Aminot et al., 2018). Al-Rajab et al. (2010) evaluated the persistence of tenofovir in sand, loam, and clay loam soil; the authors reported that tenofovir showed more persistence in the clay loam soil than the loam and sand soil. In assessing the impact of the various factors on tenofovir degradation in loam soil, it was observed that the mineralization of tenofovir occurred faster at warm temperatures (20–45°C) and in saturated soil moisture conditions. The addition of biosolids to the soil increased the rate of mineralization further (Al-Rajab et al., 2010).

13.2.3 Transport

Aside from the direct release of ARVs to surface water systems from WWTP effluents and discharge from health facilities, there are other potential routes by which ARVs are dispersed in various compartments of the environment.

One such route is runoff water from farms treated with sewage sludge or reclaimed wastewater, open dumpsites, and land contaminated with untreated sewage. The use of sewage sludge as fertilizers on farms present a potential pathway by which ARVs can enter the human diet given that the uptake of pharmaceuticals by plants from water and soil is well documented in the literature (Azanu et al., 2016; Ben Mordechay et al., 2018; Hu et al., 2010; Wu et al., 2010). No data has been published as yet on the uptake of ARVs by food crops but emtricitabine, tenofovir disoproxil, and efavirenz have been detected in water hyacinth from the Hartebeespoort dam and uMngeni river in South Africa (Mlunguza et al., 2020).

An issue with developing countries is the lack of adequate or limited sanitation, such as sewage treatment plants, which leads to human excrement being disposed of onto the ground or into rivers leading to contamination of groundwater sources as the fecal matter seeps into the ground (Fekadu et al., 2019). Evidence of ARVs migrating into groundwater sources has been reported in Kenya, the United States of America, and South Africa (Fisher et al., 2016; K'oreje et al., 2016; Rimayi et al., 2018). Nevirapine concentration in the range of 1.2–1.6 $\mu g\,L^{-1}$ was detected in two out of the three shallow wells sampled in the Kisumu region of Kenya (K'oreje et al., 2016). In the Gauteng province of South Africa, Rimayi et al. (2018) reported concentrations of nevirapine and efavirenz in all groundwater samples from the Hartbeespoort dam catchment area. Sampling was done over the summer, autumn, winter, and spring seasons. Nevirapine concentrations for summer, autumn, winter, and spring were 8, 10, 13, and 13 $ng\,L^{-1}$, respectively. Efavirenz concentrations on the other hand were lower with 3, 5, 2, and 3 $ng\,L^{-1}$ recorded for summer, autumn, winter, and spring, respectively (Rimayi et al., 2018). The detection of ARVs in groundwater poses a risk of chronic exposure for communities that depend on groundwater as their source of drinking water. The risk of exposure is further heightened by the fact that groundwater is normally not treated before consumption.

13.2.4 Ecotoxicological effects

Therapeutic use of ARVs produces a range of short term and long-term toxic effects in humans (Table 13.2). Short-term effects include; gastrointestinal toxicities, skin rash, hypersensitivity reaction, central nervous system toxicity, anemia, jaundice, and scleral icterus. Long-term toxic effects are cardiovascular disease, hepatotoxicity, renal disease, lipodystrophy, distal sensory peripheral neuropathy, (DSPN) and bone loss (Hawkins, 2010).

Like all other active pharmaceutical agents, concentrations of ARVs detected in effluent and surface water are largely low ($ng\,L^{-1}$ to $\mu g\,L^{-1}$ range) and not likely to produce acute toxic effects in nontarget organisms and humans. Despite this fact, scientists have raised concerns about the possibility of chronic toxic effects occurring from long-term

TABLE 13.2 Short term and long-term toxic effects in humans from therapeutic use of ARVs.

Period	Type of health effect	Responsible ARV drug
Short-term	Gastrointestinal toxicities (nausea, diarrhea)	Zidovudine
	Skin rash	Zidovudine, emitricitabine, nevirapine
	Hypersensitivity reaction (paraesthesia, fever, rash, headache)	Abacavir, nevirapine
	Nervous system toxicity	Efavirenz
	Anemia	Zidovudine
	Jaundice and scleral icterus	Indinavir
Long-term	Cardiovascular disease	Indinavir, abacavir, stavudine
	Hepatotoxicity	Nevirapine, efavirenz, abacavir, abacavir
	Renal disease	Tenofovir, emtricitabine
	Lipoatrophy (loss of fat tissue)	Efavirenz, stavudine
	Distal sensory peripheral neuropathy (DSPN)	Stavudine
	Bone loss	Tenofovir
	Nephrolithiasis (kidney stones)	Indinavir

Modified from Hawkins, T., 2010. Understanding and managing the adverse effects of antiretroviral therapy. Antivir. Res. 85, 201–209 and Ncube, S., Madikizela, L.M., Chimuka, L., Nindi, M.M., 2018. Environmental fate and ecotoxicological effects of antiretrovirals: a current global status and future perspectives. Water Res. 145, 231–247 with modifications.

exposure to low levels of ARVs (Ncube et al., 2018; Wood et al., 2015). However, there is very limited data on the ecotoxicological effects of ARVs on nontarget organisms given that the study of the adverse impacts of ARVs in the environment is an emerging area of environmental research. Robson et al. (2017) carried out an acute exposure study to assess the potential effects of efavirenz on the health of *Oreochromis mossambicus* (tilapia fish). After exposing the test group to 20.6 ng L^{-1} of efavirenz for 96 hours, elevated levels of fish liver indices were observed in the test group indicating liver damage and a general decline in fish health (Robson et al., 2017).

Silva et al. (2019) assessed the toxicity of tenofovir disoproxil fumarate (a prodrug of tenofovir) to different trophic level organisms. The authors used *Microcystis novacekii* (cyanobacteria), *Artemia salina* (microcrustacean), and *Aliivibrio fischeri* (saprophytic bacterium) representing primary producer, primary consumer, and decomposer species, respectively as model organisms. Inhibition concentration (IC_{50}) was used as the endpoint for the exposure study. *A. fischeri* exhibited the highest sensitivity with inhibition of luminescence after 15 minutes of exposure to a concentration of 14.83 mg L^{-1}. *M. novacekii* was the least sensitive organism tolerating a concentration level as high as 161 mg L^{-1} over 96 hours (Silva et al., 2019).

To overcome the challenge of limited experimental ecotoxicity data, environmental risk assessment for ARVs is a useful tool that can be employed to fill the knowledge gap. Calculating the risk quotient (RQ) is a simple, inexpensive, and quick approach to assess the potential risk of a chemical contaminant to an organism (Ncube et al., 2018; Wan Mohtar et al., 2019). RQ is computed as a ratio of the measured environmental concentration (MEC) of a target chemical to the predicted no-effect concentration (PNEC) of the chemical concerning the organism of interest. The risk level is categorized as low, medium, or high based on the value obtained (Table 13.3).

Ngumba et al. (2016a) employed the RQ method to assess the potential risk of lamivudine, nevirapine, and zidovudine to algae, daphnia, and fish in a river system. Algae was found to be most at risk of nevirapine and zidovudine. Nevirapine was a high risk to all three organisms while zidovudine was a low risk to daphnia and had no risk to fish. RQ values of lamivudine were below 0.01 indicating no risk to the organisms under consideration (Ngumba et al., 2016a).

Similar information on the respective metabolites of ARVs is not available and shows there is a knowledge gap that requires further investigations. However, analysis of the presence of selected ARV metabolites has been published and their results are included in various sections in this chapter.

13.3 Environmental occurrence of antiretroviral drugs in Africa and Europe

13.3.1 Wastewater/fresh water and groundwater

Africa is considered one of the most infected continents concerning HIV and AIDs, with the leading nations involved in ARV treatment programs mostly located on the African continent. As a result, most consumption of ARVs is in Africa and hence a larger proportion of the research on ARV environmental contamination is expected to be centered around Africa. However, research on ARVs in the African and European continent environments are scarce with currently only 20 studies (13 in South Africa, 6 in Kenya, and 1 study in Zambia) in Africa versus 16 studies in Europe published in the literature. In a study conducted in South Africa, Mlunguza et al. (2020) both identified and quantified emtricitabine, tenofovir disoproxil, and efavirenz in wastewater. Water samples were collected from the wastewater treatment plants (WWTPs) in Durban and surface water from the Hartbeespoort dam located in Johannesburg. Table 13.4 shows the average concentration of tenofovir disoproxil was 0.11 μg L^{-1} from the Hartbeespoort dam samples, which fell in the same range detected from the Durban WWTPs of between 0.10 and 0.25 μg L^{-1}. Emtricitabine ranged from 0.11–3.10 μg L^{-1} and efavirenz ranged from 1.02 to 37.3 μg L^{-1} in the Durban wastewater treatment plants (Mlunguza et al., 2020). These ARVs were also detected in the Hartbeespoort dam but could not be quantified.

TABLE 13.3 Risk quotient (RQ) values and their corresponding risk levels.

RQ value	Risk level
$RQ < 0.1$	Low
$1 > RQ \geq 0.1$	Medium risk
$RQ \geq 1$	High risk

TABLE 13.4 Average ARV concentration determined in water samples collected from various locations on the African continent.

Compound	Concentration ($\mu g\,L^{-1}$)	Location
Darunavir	43	DEWATS WWTP[a]
Efavirenz	34	DEWATS WWTP[a]
	1.02–37.3	Durban WWTP[b]
	0.70	Hartbeespoort Dam[c]
	17.4 (influent) and 7.1 (effluent)	Gauteng WWTP[d]
	24 (influent) and 33 (effluent)	Northern works WWTP[a]
	34	Phoenix WWTP[a]
	15.4	Western Cape WWTP[e]
Emtricitabine	0.11–3.10	Durban WWTP[b]
	0.36	Hartbeespoort Dam[c]
	172	Western Cape WWTP[e]
Lamivudine	167	Kenya[f]
Nevirapine	6	Kenya[f]
Tenofovir disoproxil	0.10–0.25	Durban WWTP[b]
	0.11	Hartbeespoort Dam[b]
	4.23	Western Cape WWTP[e]
Zidovudine	53	DEWATS WWTP[a]
	17	Kenya[f]

[a] *Abafe et al. (2018).*
[b] *Mlunguza et al. (2020).*
[c] *Wooding et al. (2017).*
[d] *Schoeman et al. (2015).*
[e] *Mosekiemang et al. (2019).*
[f] *K'oreje et al. (2016).*

ARV research is being increasingly conducted in the aquatic environment on other continents, as the number of individuals infected with HIV/AIDs increases globally. Table 13.5 shows the concentrations for the different ARVs detected in various locations in Europe. The river Jalle de Blanquefort in Bordeaux, France, which is affected by the effluent flowing out from the Cantinolle WWTP was shown to have significant concentrations of several ARVs. The ARVs with the highest concentrations were ritonavir, 116.1 $ng\,L^{-1}$, and zidovudine, 189 $ng\,L^{-1}$ (Aminot et al., 2015). Analysis of ARVs in Frankfurt, Germany revealed that zidovudine was present in a Hessian Reid region rivers and streams at a concentration of 625 $ng\,L^{-1}$, and 310 $ng\,L^{-1}$ at a WWTP influent (Prasse et al., 2010).

There were also high concentrations of zidovudine (53 $\mu g\,L^{-1}$), darunavir (43 $\mu g\,L^{-1}$), and efavirenz (34 $\mu g\,L^{-1}$) determined at the South African DEWATS WWTP, while efavirenz was also detected at the Northern and Phoenix WWTPs, at 24 $\mu g\,L^{-1}$ and 34 $\mu g\,L^{-1}$, respectively (Abafe et al., 2018). There has been efficient removal of zidovudine from the DEWATS, Northern, and Phoenix WWTPs, with the latter two also showing complete removal of abacavir and saquinavir (Abafe et al., 2018). Previous research conducted on the Hartbeespoort dam by Rimayi et al. (2018) found only efavirenz, while Wood et al. (2015) detected tenofovir disoproxil and emtricitabine in addition to also detecting efavirenz. The highest concentration reported for emtricitabine and efavirenz by Wooding et al. (2017) was 0.36 and 0.70 $\mu g\,L^{-1}$, respectively in South African surface water. Mlunguza et al. (2020) determined the most abundant ARV was efavirenz, a trend also seen in WWTPs located in Kenya (K'oreje et al., 2018). There have been numerous studies conducted on the presence of efavirenz in the aquatic environment of South Africa, where Abafe et al. (2018) found concentrations of 24 $\mu g\,L^{-1}$ and 33 $\mu g\,L^{-1}$ in the influent and effluent of the Northern works WWTP (Durban), respectively. Schoeman et al. (2015) also reported efavirenz concentrations in the influent, 17.4 $\mu g\,L^{-1}$ and the effluent, 7.1 $\mu g\,L^{-1}$ in a Gauteng WWTP. In a study conducted in the Western Cape, Mosekiemang et al. (2019) reported a high concentration of 15.4 $\mu g\,L^{-1}$ efavirenz in the WWTP influent.

TABLE 13.5 ARV concentration in water samples collected from various locations on the European continent.

Compound	Concentration ($ng\,L^{-1}$)	Location
Abacavir	34.4	Jalle de Blanquefort River, France[a]
	1.4	Hessian Reid, Germany[b]
	21	WWTP Germany[c]
	4.2	Garonne River, France[d]
	2.3	Garonne River, France[e]
Darunavir	3.4 (tap) and 169 (river)	Poland[f]
Emtricitabine	980	WWTP Germany[c]
Indinavir	1.5	Jalle de Blanquefort River, France[a]
Lamivudine	27.75	Jalle de Blanquefort River, France[a]
	210 (influent)	WWTP1 Germany[b]
	720 (influent)	WWTP2 Germany[b]
	46 (influent) and 21 (effluent)	Jyväskylä WWTP, Finland[g]
	12	Lake Päijanne, Finland[g]
	2.6	Garonne River, France[e]
Nevirapine	6.2	Jalle de Blanquefort River, France[a]
	34.7	Hessian Reid, Germany[b]
	4.8 (influent) and 7.2 (effluent)	WWTP1 Germany[b]
	21.8 (influent) and 32.1 (effluent)	WWTP2 Germany[b]
	16 (influent) and 9 (effluent)	Jyväskylä WWTP, Finland[g]
	0.5	Garonne River, France[e]
Ritonavir	116.1	Jalle de Blanquefort River, France[a]
	1.1	Garonne River, France[d]
	90	WWTP, Lausanne, Switzerland[h]
	0.5	Garonne River, France[e]
Saquinavir	0.2	Jalle de Blanquefort River, France[a]
Stavudine	7.2	Hessian Reid, Germany[b]
Zidovudine	189	Jalle de Blanquefort River, France[a]
	625	Hessian Reid, Germany[b]
	310 (influent) and 98.2 (effluent)	WWTP1 Germany[b]
	380 (influent) and 564 (effluent)	WWTP2 Germany[b]
	30	WWTP Germany[c]
	54 (influent) and 29.5 (effluent)	Jyväskylä WWTP, Finland[g]

[a] *Aminot et al. (2015).*
[b] *Prasse et al. (2010).*
[c] *Funke et al. (2016).*
[d] *Aminot et al. (2016).*
[e] *Aminot et al. (2018).*
[f] *Giebułtowicz et al. (2018).*
[g] *Ngumba et al. (2016b).*
[h] *Margot et al. (2013).*

Although emtricitabine and tenofovir disoproxil are not frequently monitored in South African surface water, Mosekiemang et al. (2019) determined high concentrations of emtricitabine in the Western Cape WWTP, 172 μg L^{-1} and 4.23 μg L^{-1} in the influent and effluent, respectively. In a 2018 study conducted in the KwaZulu-Natal province, 13 ARVs were assessed: abacavir, atazanavir, darunavir, efavirenz, indinavir, lamivudine, lopinavir, maraviroc, nevirapine, raltegravir, ritonavir, saquinavir, and zidovudine at the Phoenix WWTP, DEWATS WWTP, and Northern WWTP situated in Durban. In the cities of Nairobi and Kisumu in Kenya, a high concentration of lamivudine (167 μg L^{-1}), as well as zidovudine (17 μg L^{-1}) and nevirapine (6 μg L^{-1}) were collectively determined at the Dandora WWTP which leads to the River Ngong', and the Nyalenda and Kisat WWTPs leading to the Auji and Kisat rivers, respectively (K'oreje et al., 2016). High concentrations of lamivudine (720 ng L^{-1}) were also found in the influent of a WWTP (Prasse et al., 2010). Analysis conducted by Funke et al. (2016) on a range of WWTPs and rivers across Germany, revealed high concentrations of emtricitabine, 980 ng L^{-1}, as well as the presence of abacavir, zidovudine, and lamivudine.

The following ARVs abacavir, indinavir, lamivudine, nevirapine, ritonavir, saquinavir, and zidovudine were quantified at various locations on the Garonne River estuary in France; however, these concentrations were considerably lower compared to other areas of Europe (Aminot et al., 2016). Margot et al. (2013) detected ritonavir, 90 ng L^{-1}, from wastewater samples collected at the largest municipal WWTP of the Lake Geneva watershed, which consists of a major hospital and clinics. ARV research in Finland involved samples from the influent and effluent of the Jyväskylä WWTP and Lake Päijanne. The only ARV detected in the lake was lamivudine, 12 ng L^{-1}, while the WWTP samples contained zidovudine, lamivudine, and nevirapine, with concentrations of 46 ng L^{-1} (influent) and 21 ng L^{-1} (effluent), 54 ng L^{-1} (influent), and 29.5 ng L^{-1} (effluent), 16 ng L^{-1} (influent) and 9 ng L^{-1} (effluent), respectively (Ngumba et al., 2016a,b). Giebułtowicz et al. (2018) collected water samples in Poland from the Vistula River and tap water from the Medical University of Warsaw, which contained 3.4 ng L^{-1} and 169 ng L^{-1} in the tap and river water samples, respectively. In another study conducted on the Garonne River estuary, Aminot et al. (2018) determined 2.3 ng L^{-1} abacavir, 2.6 ng L^{-1} lamivudine, 0.5 ng L^{-1} nevirapine, and 0.5 ng L^{-1} ritonavir in the river water samples collected adjacent to Bègles city.

Studies on groundwater have found that ARVs have also found their way into these water sources. Rimayi et al. (2018) and K'oreje et al. (2016) found high concentrations of nevirapine and efavirenz in groundwater in the Hartbeespoort Dam (3–13 ng L^{-1}) and high concentrations of nevirapine in shallow wells in Nairobi and Kisumu city in Kenya (1.2–1.6 μg L^{-1}) (Rimayi et al., 2018; K'oreje et al., 2016). Analysis of 21 groundwater samples from boreholes and shallow wells in the Chunga region in Zambia found only nevirapine at a concentration of 410 ng L^{-1} (Ngumba et al., 2020). Even though lamivudine and zidovudine were present in significant concentrations in surface water, they were not easily detected in groundwater as they tend to partition to sediment.

13.3.2 Sediment

Studies on the presence of ARVs in sediment samples are scarce. Analysis conducted by Rimayi et al. (2018), determined various types of ARV drugs present in the Umgeni River, South Africa. There were high concentrations of nevirapine as shown in Table 13.6, at different points on the Umgeni estuary, while efavirenz was also detected near the mouth of the estuary. Other ARVs present in the sediment samples, included: lamivudine, emtricitabine, and tenofovir disoproxil. A study based on the wastewater treatment plant in the town of Machakos, Kenya found traces of ARVs present in sediment samples collected from the Mitheu River. There were high concentrations of lamivudine, 491 ng g^{-1}, and zidovudine, 510 ng g^{-1}, determined upstream of the WWTP (Kairigo et al., 2020). Abacavir and ritonavir were found in the sediment of the Jalle de Blanquefort River in France (Aminot et al., 2015).

13.3.3 Biota

Previous research on phytoremediation of emtricitabine, tenofovir disoproxil, and efavirenz by water hyacinth plants, investigated whether these plants assisted in the removal of selected pharmaceuticals (Mlunguza et al., 2020). Analysis of the hyacinth plant collected near a WWTP revealed the roots to have the highest concentration of emtricitabine, tenofovir disoproxil, and efavirenz, which were 13.4 μg kg^{-1}, 8.7 μg kg^{-1}, and 29.6 μg kg^{-1}, respectively.

In a study conducted in South Africa by Nibamureke et al. (2019a), it was determined that nevirapine levels in surface water had no detrimental effects on the hatching of larvae, survival, or behavior of *O. mossambicus* (Mozambique tilapia) as the highest concentration recorded was 1.48 μg L^{-1}. However, nevirapine may result in adverse health effects in *O. mossambicus* over a long period, as a study revealed hepatocyte apoptosis, vacuolation and fibrosis around the veins and ducts of fish exposed to 1.48 μg L^{-1} and 3.74 μg L^{-1} of nevirapine over 30 days (Nibamureke et al., 2019b).

TABLE 13.6 Total ARV concentration determined in river sediment samples collected on the African and European continents.

Compound	Concentration (ng g^{-1})	Location
Abacavir	0.1	Jalle de Blanquefort[a]
Efavirenz	5	Umgeni River[b]
Emtricitabine	1.6	Umgeni River[b]
Lamivudine	1.0	Umgeni River[b]
	491	Mitheu River[c]
Nevirapine	98	Mitheu River[c]
	92	Umgeni River[b]
Ritonavir	2.6	Jalle de Blanquefort[a]
Tenofovir disoproxil	0.5	Umgeni River[b]
Zidovudine	510	Mitheu River[c]

[a] *Aminot et al. (2015).*
[b] *Rimayi et al. (2018).*
[c] *Kairigo et al. (2020).*

Robson et al. (2017) also conducted studies on the *O. mossambicus* at the Nandoni dam in the Vhembe district of South Africa, exposing them to 10.3 ng L^{-1} and 20.6 ng L^{-1} of efavirenz. The health of the fish exposed to 20.6 ng L^{-1} declined compared to the control sample as it showed an increase in liver damage with evidence of steatosis and frank necrosis.

13.4 Degradation and removal of ARVs

The significant presence of ARVs detected in the environment necessitates its removal or degradation. Since WWTPs are an important direct source of ARV input into the environment, studies have focused on developing suitable degradation processes that can be adopted at WWTPs. One such study looked at the degradation of stavudine and zidovudine using UV_{254} with and without H_2O_2 at different pH values and showed the use of UV with hydroxyl radicals would need a higher UV dose than is normally used in disinfection processes (Russo et al., 2018). Another study looked at using CO_2 produced by bacteria to degrade zidovudine but results showed that it was not degradable (Vaňková, 2010). Other studies looked at photo-transformation of abacavir, zidovudine, and emtricitabine and biotransformation of acyclovir and lamivudine. Photo-transformation was kinetically favored whereas biotransformation was slower (Prasse et al., 2015).

Biological wastewater treatment plants showed oxidation of the terminal hydroxyl-moiety of 5 ARVs, abacavir, emtricitabine, ganciclovir, lamivudine, and zidovudine to form their respective carboxy degradation product. No parent ARV was found in the effluent and concentrations of the carboxy degradation product ranged from 16 to 750 ng L^{-1} (Funke et al., 2016). A study by Abafe et al. (2018) showed almost complete removal of abacavir, zidovudine, and lamivudine from 2 WWTPs using chlorination and a DEWAT plant anaerobic treatment while lopinavir and nevirapine accumulated in all 3 WWTPs plants (Abafe et al., 2018).

Natural degradation using sediment showed the possibility of ARV degradation particularly with increasing concentrations of suspended solids (Aminot et al., 2018). Estuaries are also able to show some benefit in reducing ARV loads based on biodegradation from bacteria present in suspended solids (Aminot et al., 2016).

13.5 Challenges and recommendations

13.5.1 Challenges

The following challenges were identified from the literature that exists on the occurrence and measurement of ARVs in the natural external environment of developing countries:

- It was evident from literature, that studies on ARV residues in the environment from the African continent were limited to only South Africa and Kenya, with a recent study in Zambia, though several other countries have antiretroviral treatment programs in place. The majority of the studies carried out were once-off investigations as opposed to continuous environmental monitoring of the ARV contaminants. Together with this, the majority of studies reporting the occurrence of ARVs in the environment were focused on wastewater effluent and surface water while data on other environmental compartments such as sediments, soil, groundwater, and biota was limited. Hence, the currently limited studies do not provide a clear and true picture of the real status of ARVs in the environment of the African continent.

- Again, ecotoxicological data, which is crucial for conducting an environmental risk assessment of ARVs in the environment, was limited. Apart from two experimental studies from South Africa investigating the ecotoxicological effects of efavirenz and nevirapine on *O. mossambicus* (tilapia fish) no other such data has been reported in other African countries. Hence, risk assessment studies are needed to further address this lack of information. The toxicity of ARVs in wastewater sludge should also be investigated as oftentimes this sludge is applied as fertilizer in crop fields.
- The lack of adequate technical (analytical instrumentation) capacity and provision of research funding in many African countries is a major contributing factor. The implication of this situation is that there is a dearth of knowledge about the true extent of ARV contamination in the environment across Africa.

13.5.2 Recommendations

- In order to build up research and analytical capacity for ARV research, the governments of African countries need to increase funding to research institutions and relevant environmental protection agencies. Collaborations among environmental scientists to share technical and analytical knowledge at the regional and continent-wide level should be encouraged.
- Considering the constraints of limited extensive ecotoxicological data for environmental risk assessment purposes, long-term environmental monitoring programs need to be put in place for the collection of adequate temporal and spatial data to track the distribution of ARVs in the environment. Also, various modeling tools such as the Ecological Structure-Activity Relationships (ECOSAR), Sistema de Tratamento de Ponto (STPWIN), and the University of Minnesota Pathway Prediction System (UM-PPS) can be employed to provide data for prediction to fill in the experimental ecotoxicological data gaps that currently exist.
- To overcome the challenge of low numbers of municipal wastewater treatment plants which contribute to the direct release of ARVs into the environment via untreated sewage, appropriate sewage treatment technologies such as the decentralized wastewater treatment (DEWATS) facility can be adapted for use in rural localities and peri-urban areas. Additionally, alternative sewage management systems such as source separation of urine and fecal matter are viable approaches that can be considered. The separated urine stream, which contains the most amount of ARV residues, can then be broken down by photodegradation via exposure to UV radiation from the sun.

This chapter falls under the section on fate and occurrence of emerging pollutants within aquatic ecosystems with other chapters, e.g., Ajayi et al. (2022), Cristale (2022), Vizioli et al. (2022), Galhardi et al. (2022), Hashemi and Kaykhaii (2022), Madikizela et al. (2022), Mashile et al. (2022), Montagner et al. (2022), Ntshani and Tavengwa (2022), Sanganyando and Kajau (2022), and Yardy et al. (2022) that aims to make an understanding of the different emerging pollutants within the aquatic environment.

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CHAPTER

14

Disinfection byproducts in emerging countries

B.C. Vizioli, Leandro W. Hantao,
and Cassiana C. Montagner

14.1 Background

One of the greatest achievements in public health accomplished by humanity was the chemical disinfection of water (see Mashile et al., 2022, Chapter 8; Tavengwa and Dalu, 2022, Chapter 1). Modern water treatment was incorporated a little more than a century ago with the advent of chemical disinfection (Smith, 2017). However, the concept of water purification for human consumption goes back to ancient civilizations that already were adept at a handful of treatment methods such as filtering, boiling, and sunlight exposure to enhance water's organoleptic characteristics (de Namor, 2007). Despite a few attempts at chlorination of water supplies following major outbreaks of cholera and typhoid fever in the late 1800s, it was not until the early 1900s that chemical disinfection was of regular use in water treatment (National Academy of Sciences, 1977). Before the successful widespread introduction of chlorination, the existing water treatment techniques included filtration, chemical precipitation, and sedimentation, yet there was no assurance of a microbiologically safe water supply using these methods alone (Juuti et al., 2015). Thus, chlorination provided a cheap and reproducible method of ensuring water safety, leading to a significant decrease in waterborne infectious diseases that posed serious public health threats (Black and Veatch Corporation, 2010). At the same time that the use of chlorine and other strong oxidants aids in microbial inactivation, their highly reactive nature also causes them to react with most organic and inorganic compounds present in the source water (i.e., lakes, rivers, reservoirs, or groundwater aquifers from which water is drawn and treated), forming a vast range of undesirable compounds called disinfection byproducts (Krasner, 2009; Richardson, 2011; Richardson and Postigo, 2015a).

14.2 Disinfection byproducts

DBPs form a broad group of emerging contaminants (ECs) that differ from other groups because, while also a result of anthropogenic activity, they are not manmade but rather are formed in situ. DBPs are mainly formed when disinfectants react with dissolved organic matter (DOM) and a few inorganic compounds present in water during the disinfection step of water treatment (Richardson and Postigo, 2015a).

Trichloromethane, or chloroform, was the first DBP detected in 1974 (Rook, 1974). Along with the three most common trihalomethanes (THMs), namely tribromomethane (bromoform), bromodichloromethane, and dibromochloromethane, they were reported present in chlorinated water at much higher concentrations than in raw water. It was then proposed that THMs were produced by the action of chlorine on humic substances comprising natural organic matter in the raw water (Kajino and Yagi, 1980; Medeiros et al., 2019).

After the discovery of THMs as a side reaction of chlorination, the US Environmental Protection Agency (EPA) subsequently conducted surveys confirming the widespread occurrence of THMs in chlorinated water supplies, while toxicological studies supported allegations of chloroform carcinogenicity. In 1979, EPA set a provisional maximum contaminant level (MCL) for the combined concentrations of the four THMs, commonly called total trihalomethanes (TTHM), of $0.1\,\mathrm{mg\,L^{-1}}$. This standard would theoretically serve as a surrogate measure for other chlorination DBPs. However, with the first reports on the adverse effects of haloacetic acids in the 1980s, EPA implemented the Stage 1 Disinfectants and Disinfection Byproducts Rule (Stage 1 D/DBPR, 1998). The Stage 1 Rule, currently in effect, reduced

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the MCL for TTHM to 0.080 $mg\,L^{-1}$ and included chlorite (1.0 $mg\,L^{-1}$), bromate (0.010 $mg\,L^{-1}$), and the total concentration of five priority haloacetic acids (HAAs), including monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid and dibromoacetic acid (0.060 $mg\,L^{-1}$) (Kolb et al., 2017; Krasner, 2009; Richardson, 2011; Wang et al., 2015).

The discovery of THMs in drinking water led to an increasing apprehension about DBP-associated health effects, resulting in extensive research on other compounds formed during water disinfection (Krasner, 2009; Richardson and Postigo, 2015a). Currently, there are over 700 compounds distributed in an array of classes reported in the literature for the major disinfectants used (chlorine, chloramines, chlorine dioxide, ozone, and combinations) (Krasner et al., 2006; Srivastav et al., 2020). However, only a small portion of them has undergone extensive research for their formation, toxicity, and occurrence (Hebert et al., 2010; Wagner and Plewa, 2017). As an outcome of the unpredictably complex constitution of dissolved organic matter, a substantial proportion of DBPs still has not been identified, and it is estimated that these unknown compounds account for the greater part of the total DBP load (Wawryk et al., 2021). On a mass basis, THMs and HAAs are the two most prevalent classes of DBPs in chlorinated drinking water, representing the largest fraction of detected DBPs (Krasner et al., 2006; Richardson, 2011). Yet, the sum of quantified halogenated DBPs typically only accounts for approximately 30%–60% of total organic halides (TOX), meaning that around 40%–70% of halogenated DBPs remain unidentified (Krasner et al., 2006). However, it is suggested that the unknown fraction is most likely predominately constituted of halogenated macromolecules that may not be biologically active (Reckhow et al., 2007).

Most DBPs present relevant toxic properties. Although the most significant toxicological behavior of DBPs is carcinogenicity, several DBPs are also cytotoxic, neurotoxic, mutagenic, teratogenic, and/or genotoxic, having been associated with many long-term adverse outcomes on human health such as neurological, immunological, reproductive, developmental, congenital, respiratory, cardiovascular, hepatic, renal, amongst others (Hebert et al., 2010; Plewa and Wagner, 2015; Richardson et al., 2007; Wagner and Plewa, 2017).

Epidemiological studies in different countries have consistently associated long-term consumption of chlorinated drinking water with an enhanced risk of cancer, particularly of bladder and colorectal cancers (Bove et al., 2007; Cotruvo and Amato, 2019; Evlampidou et al., 2020; Hrudey et al., 2015; Nieuwenhuijsen et al., 2009; Rahman et al., 2010). While the elevated risk for cancer has only been associated with DBPs and not with the disinfectant, the causal agents are still unknown (Diana et al., 2019). With hundreds of DBPs already identified and with the eminent discovery of further compounds soon, it is the scientific community's understanding that DBPs are a group of contaminants that pose several adverse risks to human health. However, the uncertainty about carcinogenic health effects of DBP exposure exists mainly because the assessed compounds in toxicology studies do not fully account for the health risks observed in many cancer epidemiology studies. Thus, toxicological and epidemiological studies are divergent.

This is because either the assessed DBPs do not cause bladder or colorectal cancers in bioassays (DBPs mostly induce kidney, liver, intestine, stomach, and lung cancers in animals), or their carcinogenic potencies along with their commonly found concentration levels in water are not high enough to explain the cases ascribed to DBP exposure (Diana et al., 2019; Krasner, 2009). Over the past decades, research has primarily focused on THMs and HAAs as surrogates for general exposure to chlorinated DBPs in epidemiologic studies (Furst et al., 2019). However, the complexity of chlorinated DBP mixtures prevents the assignment of causation to any single component or class of components. It is plausible that other compounds, or classes of compounds, have stronger associations with the adverse health outcomes; recent toxicological studies reveal that several emerging DBPs (EDBPs), particularly nitrogenous, brominated, and iodinated by-products, are of great concern because they are believed to be more toxic than many of the currently regulated DBPs (Li and Mitch, 2018; Plewa and Wagner, 2015). Thus, the search for the main toxicity drivers needs to be further explored.

However, identifying potentially critical DBPs may not be an easy task for many reasons. Firstly, taking into consideration that the risk that a chemical pose is a function of the intrinsic toxicity (inherent ability to induce a specific toxic effect) and the magnitude of exposure (frequency of detection and level of concentration), there is insufficient systematic toxicological and occurrence data available for the 700+ reported DBPs. Also, for each characterized DBP, several remain uncharacterized (Richardson and Postigo, 2011). Therefore, it is likely that some DBPs with toxicological and/or occurrence significance are yet to be identified. Another aspect is that research on DBP exposure routes suggests that oral ingestion may not be the only primary form of contact. Dermal absorption and inhalation while bathing or during leisure activities may also account for a significant part of total DBP exposure (Ashley et al., 2005; Richardson and Postigo, 2011; Villanueva et al., 2006, 2015). However, there is little data available about other routes of exposure. Hence, they are usually not included in epidemiological studies (Hebert et al., 2010). Finally, toxicological studies typically assess the health effects caused by individual compounds or simple mixtures, whereas in reality, people are exposed to complex mixtures of DBPs in water (Diana et al., 2019). When considering the concentration of each DBP in drinking water alone, none appears to explain the observed risk. However, little is known about the toxicological effects of their interactions (Simmons et al., 2002). As synergistic effects could contribute to the increased risk of cancer, collectively they could be of concern (Stalter et al., 2020). Also, DBP interactions could potentially change the toxicity, the mode of action, and the target organs of individual DBPs (Diana et al., 2019). Thus, both toxicology and epidemiology research on recognizing potentially critical DBPs shall consider their toxicity and occurrence and the impact of complex mixtures and multiple-route exposure.

14.3 Formation of DBPs

Given an ever-growing list of DBPs, DBP formation is a rather complex and largely uncovered topic, yet it is a key point in DBP research. DBP formation (including chemical mechanisms and pathways, rate, speciation, and concentration) is a function of several factors, from the process of water treatment to source water characteristics (Ding et al., 2019; Kimura and Ortega-Hernandez, 2019). However, it is mostly associated with the type of disinfectant used and the source water's organic and inorganic matter character. Other factors that also influence DBP formation are dose, point of addition, contact time and residual concentration of the disinfectant, and pH and temperature of the source water (Hua and Reckhow, 2008; Sadiq and Rodriguez, 2004; Srivastav and Kaur, 2020). Thus, as DBPs occur in complex mixtures that are a function of several factors, the potential health effects will be a function of the exposure to DBP mixtures.

Of all disinfectants, chlorine is the most widely used method of chemical disinfection (Gerba and Pepper, 2019). Today, the majority of water supplies use chlorine-based solutions, either alone or in combination with others. Chlorine's widespread use owes much to its safety, effectiveness against most pathogens, residual protection against recontamination, affordable cost, ease of use, and acceptability (Black and Veatch Corporation, 2010). The multifarious benefits of chlorine made it the smart and preferred method for water treatment, especially in developing countries, where treatment facilities are often costly, distant, or do not exist at all (Treacy, 2019). Chlorine disinfection had been successfully used for many years unquestionably until the 1970s. However, the discovery of chlorinated DBPs brought several doubts regarding the advisability of long-term chlorine use for drinking water disinfection. Shortly after the initial DBP regulations, some water utilities in developed countries changed their disinfection methods to achieve compliance and reduce DBP formation. Thus, they switched to alternative disinfectants (mainly chloramines, chlorine dioxide, and ozone) that reportedly generated significantly lower levels of THMs and HAAs (Shah and Mitch, 2012; US EPA, 2013; Wang et al., 2015). However, as each of the commonly used disinfectants has its advantages and disadvantages in terms of cost, efficacy, stability, and ease of application, it also applies to byproduct formation. All chemical disinfectants produce inorganic and organic DBPs and it is unlikely that any combination of them is free of formation. Moreover, each disinfectant is believed to form its own set of DBPs (Richardson and Postigo, 2011). Thus, while the use of these alternative disinfectants will substantially reduce the levels of THMs and HAAs, several classes of EDBPs are shown to increase in formation (Hua and Reckhow, 2007; Krasner et al., 2006; Richardson, 2011).

The properties of DBP inorganic and organic precursors have been extensively studied and reported to affect DBP formation. The precursors' concentration and character are critical in determining the extent and rate of reaction and DBP speciation. For instance, the disinfection of source waters with a high content of inorganic precursors, such as bromide and iodide, produce reactive species that alter the speciation pattern and enhance the concentration of highly toxic brominated and iodinated DBPs (Dong et al., 2019; Postigo and Zonja, 2019; Sharma et al., 2014; Zhai et al., 2014). Another factor that significantly influences DBP speciation is the content and concentration of the dissolved organic matter initially present in source waters. As DOM is a complex mixture of heterogeneous organic compounds, the diversity of DBPs relies mostly on the characteristics of DOM and its fractions (Deborde and von Gunten, 2008).

The DOM is made of both geogenic and anthropogenic constituents. The DOM that naturally occurs in surface waters, also known as natural organic matter (NOM), is mainly originated from terrestrial (allochthonous NOM) or internal (autochthonous NOM) activities. Allochthonous NOM is produced externally from plant debris and soil organics flushed into surface waters by runoff. Alternatively, autochthonous NOM is formed internally due to algal and microbial productivity (Aitkenhead-Peterson et al., 2003; Bertilsson and Jones, 2003). In pristine waters, the primary sources of DPB precursors are composed of humic and fulvic substances (Gallard and von Gunten, 2002). However, the degradation of water quality from daily human activities plays a major role in DBP concentration and speciation (Alexandrou et al., 2018; Chaukura et al., 2020; Gilca et al., 2020).

The high anthropogenic loads of complex chemical compounds deposited into receiving waters usually increase the concentration and variety of DBP precursors, enabling the formation of an entirely different suite of DBPs with unknown formation mechanisms and toxicities. For example, source waters impaired by wastewater disposal or algal blooms typically feature higher concentrations of dissolved organic nitrogen precursors for highly toxic nitrogenous DBPs (N-DBPs) such as halonitroalkanes, halonitriles, haloamides, and nitrosamines (Bond et al., 2012; Shah and Mitch, 2012). Furthermore, DBPs also form from some anthropogenic contaminants (Fiss et al., 2007; Le Roux et al., 2012). Several groups of ECs, including personal care products, pharmaceuticals, hormones, pesticides, bactericides, UV-filters, dyes, industrial and household chemicals, and countless others represent a myriad of possible precursors to numerous DBPs and transformation products (TPs) from disinfection (Acero et al., 2008; Armbruster et al., 2015; Bulloch et al., 2015; Canosa et al., 2006; Dieter, 2010; Fan et al., 2013; Han et al., 2018; Jaén-Gil et al., 2020; Li et al., 2017; Liberatore et al., 2020; Oliveira et al., 2006; Postigo and Richardson, 2014; Santos et al., 2012; Wang et al., 2014; Wong et al., 2019).

14.4 Analytical methods to determine DBPs

The overall water quality is determined by a broad range of physical, microbiological, and chemical parameters to ensure human health protection (DeMarini, 2020). Monitoring the quality of waters is impacted by a multitude of challenges ranging from local infrastructure to the development of testing methods. In addition, while critical parameters may be tested in remote locations using simple methods and portable instruments, most of the chemical analyses related to the occurrence of ECs and DBPs are dependent on well-equipped laboratories.

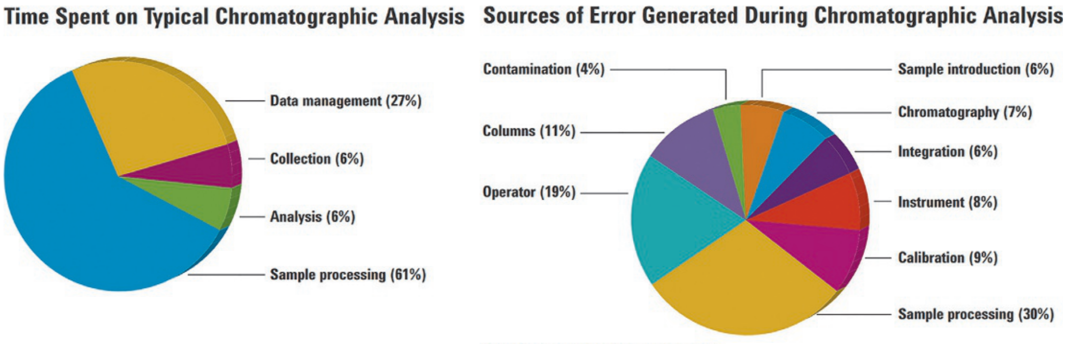
14.4.1 Sample preparation

Sample preparation is a vital part of the analytical method. A recent survey estimated that 6% of the analysis time is spent on sample preparation (Majors, 2014), while up to 30% of the analytical errors originated from sample processing (Fig. 14.1). Hence, proper sampling and sample preparation are mandatory for fast and reliable characterization and accurate and precise quantitation of DBPs.

14.4.1.1 Traditional techniques

Traditional analytical methods used for organic DBP analysis are based on liquid- and solid-phase extractions. The development of such methods is challenging because it requires efficient extraction of the analytes while proving some level of matrix clean-up for qualitative and quantitative analyses. Considering that DBPs may exhibit a broad range of physical and chemical properties, a broad-selectivity extractant phase is required. To illustrate the analytical challenge, more than 700 low-molecular-weight, volatile or semivolatile DBPs have been identified and reported (Richardson, 2011).

Direct analysis of the aqueous sample may be suitable, depending on the concentration levels of the DBPs, matrix effect, and analytical instrumentation. For instance, produced water samples from a Texas gas-charged reservoir were collected in headspace-free high-density polyethylene bottles and subjected to simulated disinfection experiments (Liberatore et al., 2020). For the initial nontargeted DBP screening, the water samples were diluted 10-fold and 10 μL was directly injected into the liquid chromatography coupled to a mass spectrometer (LC-MS).



Data taken from Agilent Technologies survey

FIG. 14.1 Survey of the most important sources for the error generated during chromatographic analysis and typical time spent on the separation method. *Reproduced with permission from Majors, R.E., 2014. Sample Preparation Fundamentals for Chromatography. Agilent Technologies, Inc., pp. 1–356 (Open Access).*

Liquid-liquid extraction (LLE) of DBPs typically involves a separatory funnel, wherein a water-immiscible solvent is selected (e.g., $<10\%$ solubility in water) (Majors, 2014). The principle underlying LLE is the Nernst Distribution Law that describes the distribution constant (K_D) of a solute between two immiscible phases (Majors, 2014). A careful interpretation of Eq. (14.1) indicates that the best extraction efficiency may be attained by selecting a solvent with a large K_D value and performing multiple extractions. In other words, instead of performing a single extraction with 100 mL of solvent, three extractions with 30 mL aliquots provide higher extraction efficiency than the former procedure.

$$E = 1 - [1/(1 + K_D V)] \tag{14.1}$$

where E is the extraction efficiency, K_D is the Nernst distribution constant determined by the ratio of the concentration of the analyte in the extracting phase and aqueous phase (C_o/C_a), and V is the ratio of the volume of the organic solvent and aqueous phase (V_o/V_a).

After the LLE experiment, removal of excess extractant phase may be required to achieve the desired preconcentration levels. This procedure is essential to ensure that the limits of detection and quantitation are met, but it also requires careful sample handling to avoid significant losses of the volatile organic compounds (VOC). For example, THMs, HAAs, and haloacetonitriles (HANs) are common classes of DBPs. The analysis of such analytes by gas chromatography with electron-capture detection (GC-ECD) or mass spectrometry hyphenation (GC-MS) requires LLE under acidic conditions (Ackerson et al., 2020). In this report, the quenched and acidified samples were extracted with methyl *tert*-butyl ether, followed by GC analysis. It is worth noting that HAA analysis requires some form of derivatization like methylation, by converting the hydroxyl of the acid moiety into a methyl ester.

Solid-phase extraction (SPE) is typically carried out using disposable cartridges packed with porous particles loaded with the sorbent phase. The chemical composition of such phases determines the extraction's selectivity, alongside the composition of the clean-up and desorption solvents (Wang et al., 2016a). The SPE procedure is initiated by loading the analytes by percolating the liquid sample through the sorbent bed. The composition of the loading mixture should primarily favor the retention of the analytes. Next, a clean-up step may be executed by passing a cleaning solvent through the SPE cartridge to remove the interfering compounds. Lastly, the analytes must be desorbed using a strong solvent mixture. The preconcentration factor may be determined by the ratio between the original sample volume and the extract's final volume (V_a/V_o). An additional step by online SPE using a valve-based column switching setup is also interesting to reduce matrix effects, depending on the sample's complexity (Tetzner and Rath, 2018).

A preconcentration and clean-up step is required to analyze DBPs, such as nitrosamines in drinking water, as these chemicals may be found at nanogram per liter concentrations in waters (Boyd et al., 2011). In addition, sample clean-up is an important step, especially for source water or wastewater analysis using LC-MS fitted with electrospray ionization (ESI) to eliminate pronounced matrix effects. Traditionally, gas chromatography (GC) has been used for nitrosamine analysis (Boyd et al., 2011; Taguchi et al., 1994). However, newly developed liquid chromatography (LC) methods have exhibited a complementary scope by enabling the investigation of more polar and thermally labile nitrosamines, when compared to GC-based methods (Boyd et al., 2011).

The selectivity offered by SPE sorbents is vast and their combination is highly dependent on the nature of the experiments. Targeted analysis may be carried out using a single sorbent cartridge (Wang et al., 2016b). For instance, the US EPA Method 521 established the use of SPE with activated carbons (e.g., Restek's method-specific SPE Cartridge) for the isolation and preconcentration of seven nitrosamines (Munch and Bassett, 2004). Additional developments have reported other sorbent phases that are also suitable for nitrosamine analysis, such as activated carbons (Ambersorb 572, neutralized activated charcoal) (Plumlee et al., 2008; Zhao et al., 2008), normal phases (Sep-Pak Vac Fluorisil) (Asami et al., 2009), and reversed phases (Oasis HLB, Chromabond C18 Hydra) (Lee et al., 2007; Zhou et al., 2009). Conversely, an untargeted analysis may require the combination of multiple cartridges to ensure broad analyte coverage (Tang et al., 2016). For example, an integrated multiple SPE protocol was developed to improve analyte coverage for untargeted LC-MS analysis. Parallel extractions were carried out with three sorbent phases, namely, Oasis HLB, Bond Elut ENV, and Bond Elut C18 cartridges were used to extract precursors and nonchlorinated/chlorinated peptide DBPs from the water samples (Tang et al., 2016).

14.4.1.2 *Solvent-free techniques*

Sample preparation protocols may use laborious extraction methods, which can alter the original precursor and DBP profiles of the sample by contamination or degradation of labile organic compounds. Awareness of these extraction artifacts, which act as "chemical noise," is generally not perceived, but such artifacts, if not previously assigned, will produce misleading results, especially in nontargeted investigations (Heffner et al., 2007). Hence, automated extraction protocols are ideal companions for DBP analyses using GC-MS and LC-MS. Furthermore, method miniaturization is an exciting playground for separation science and environmental analysis to reduce the consumption of consumables and generation of residues, resonating with the latest guidelines for sustainability and green analytical chemistry (Tobiszewski et al., 2015; Yayayuruk and Yayayuruk, 2019).

Direct access to organic precursors and DBPs present in aqueous matrices using immobilized sorbent-based techniques may potentially bypass conventional laborious steps, like liquid-liquid extractions and solvent evaporation. In this context, microextraction techniques are interesting alternatives to exhaustive solvent extractions. Furthermore, the prospection of micro-scale techniques is fundamental to ensure reduced solvent consumption and method automation (Belinato et al., 2018).

Solid-phase microextraction (SPME) comprises a group of solvent-free microextraction techniques that explores immobilized sorbent phases for sample preparation (Song et al., 2017). The SPME protocol combines analyte isolation and preconcentration into a single step, under relatively mild extraction conditions. Considering the typical SPME formats and sample volumes, the extraction is equilibrium-based and may be carried out through the headspace or direct immersion (Ouyang and Pawliszyn, 2006). The SPME method may be coupled to both LC-MS and GC-MS by solvent-assisted desorption or thermal desorption, respectively. For example, a method was developed for the extraction of seven N-nitrosamine compounds from water using headspace solid-phase microextraction (HS-SPME) (Grebel et al., 2006). The SPME-based method required a total analysis time of only 75 min, considering sampling and GC-MS analysis, compared to at >180 min for traditional solvent-based methods. The reported method detection limits (MDLs) were found in the ng L^{-1} range (Grebel et al., 2006). Another format of SPME is the thin-film solid-phase microextraction (TF-SPME). The TF-SPME has been validated as a novel sampling device, having both an increased extraction phase volume and surface area to volume ratio, compared to conventional fiber-based SPME, making it a convenient and ideal sampling tool for ultra-trace level analysis (Emmons et al., 2019).

14.4.2 Instrument analysis

The analysis of organic DBPs in waters is not a trivial task and it requires the combination of multiple analytical techniques to increase byproduct coverage due to the broad range of physical and chemical properties of the analytes. The diversity of DBPs found in waters is variable, and in numerous cases, unknown since these compounds are highly correlated to water source and treatment process (Li and Mitch, 2018). In other words, these compounds are inadvertently formed through parallel reactions between disinfection agents and chemical precursors initially found in the source water. Therefore, analysis of DBPs is a two-stage protocol that requires both untargeted and targeted approaches, as detailed below.

The initial screening of unknown DBPs in water requires the combination of multiple instrumental platforms to characterize the contaminants. Typical separation-based platforms include GC-MS (Daiber et al., 2016), LC-MS (Pereira et al., 2011), and ion chromatography (IC-MS) (Xue et al., 2016) coupled with mass spectrometry. The instrument requirement and method development necessary to reliably characterize unknown DBPs (i.e., untargeted analysis) are far more demanding than routine monitoring of known contaminants, i.e., targeted analysis (Richardson and Kimura, 2020; Wang et al., 2016a).

In targeted analysis, selectivity and sensitivity are the main parameters sought during method development by exploring highly selective detectors (e.g., ECD, nitrogen-phosphorus detection (NPD)) (Sakai et al., 2016) or parallel reaction monitoring by triple quadrupole mass spectrometry (MS/MS) (Ding and Zhang, 2009; Liu et al., 2015). Methods used for untargeted analysis may be longer than targeted methods employed for routine measurements because the former demands high peak capacity separations to resolve the peaks of isomeric compounds with the same elemental formula. Thus, the triad for untargeted analysis comprises chromatographic separation, mass resolution, and mass accuracy by using high-resolution/accurate mass (HRAM) mass spectrometers.

Let us imagine the following two scenarios for illustrative purposes. At least eight molecules with an elemental formula of $C_2H_6N_2O$ have been reported and indexed by the National Institute of Standards and Technology (NIST). While they exhibit the same monoisotopic mass ($M = 74.048013$ Da), these compounds behave very differently in chromatography, enabling the resolution of their peaks and, therefore, proper qualitative and quantitative analysis. Hence, highly efficient columns and low-dispersion instruments are necessary for untargeted analysis.

Conversely, compounds with distinct monoisotopic mass may show nearly identical retention times in chromatography experiments. For example, *N*-nitrosodimethylamine (NDMA), a highly carcinogenic nitrosamine with formula $C_2H_6N_2O$ and monoisotopic mass of 74.04746 Da, coeluted with an interferent, with the formula $C_3H_6O_2$ and mass of 74.03623 Da. An approximate mass resolution of >15,000 at m/z 74 Th is required to enable the reconstruction of the extracted ion chromatogram for reliable qualitative and quantitative analysis of NDMA in Full MS acquisition mode. While transmission quadrupole and conventional ion trap (3D and 2D/linear) mass analyzers cannot provide this level of mass resolution, Fourier Transform (FT) and some time-of-flight (TOF) mass analyzers are suitable for such chromatography-based measurements.

High-end TOFMS instruments can provide resolutions up to 30,000 for low mass measurements, suitable for most samples (Hanigan et al., 2015; Huang et al., 2017). For more complex matrices, higher mass resolution levels are necessary and are currently offered by FT-ICR (Fourier Transform-Ion Cyclotron Resonance) (Postigo et al., 2021; Zhang and Yang, 2018) and FT-Orbitrap mass spectrometers (Negreira et al., 2015; Phungsai et al., 2018, 2019; Postigo et al., 2016). It is important to highlight that mass resolution behavior is instrument-specific and it is dependent on the measured mass (Schmidt et al., 2018). A general observation is that TOFMS performs better for heavier ions. For instance, a resolution of 36,000 is observed at m/z 554 Th, while a value of less than 20,000 is found for m/z 151 Th. Conversely, modern FT-Orbitrap mass spectrometers exhibit higher resolution values as the measured mass decreases. For example, a resolution value of 140,000 is observed at m/z 200, while much higher levels are attained for smaller ions. Two distinct mass spectra are shown in Fig. 14.2 to exemplify the mass resolution of the most popular mass analyzers for unknown/untargeted analysis.

While chromatographic selectivity and mass resolution contribute to producing pure analytical signals, mass accuracy is critical for reliable assignment of the elemental composition of unknown DBPs. To illustrate the importance of accurate mass measurements, over 8000 possible elemental formulas are available for nominal mass measurement of 308 Da. However, only nine formulas can produce a monoisotopic mass close to 308.1878 Da.

To assign the elemental composition, the analyst must first define the list of expected elements (C, H, O, N, S, P, Cl, Br, I) and their range of occurrence. In addition, the user must also inform the permitted range of unsaturation of the molecule (i.e., double bond equivalent, DBE) to narrow the outcomes and increase the likelihood of finding a feasible formula. The DBE value can be calculated from Eq. (14.2).

$$\mathrm{DBE} = \mathrm{C} + \mathrm{Si} - \tfrac{1}{2}(\mathrm{H} + \mathrm{F} + \mathrm{Cl} + \mathrm{Br} + \mathrm{I}) + \tfrac{1}{2}(\mathrm{N} + \mathrm{P}) + 1 \tag{14.2}$$

where DBE: double bond equivalent, C: number of carbon atoms, Si: number of silicon atoms, H: number of hydrogen atoms, halogen atoms (F, Cl, Br, and I), N: number of nitrogen atoms, P: number of phosphorus atoms in the molecule.

The elemental composition (i.e., molecular formula) generated from the exact mass measurement should limit the combinations that yield structurally meaningful results. To guide this process, the Lewis (Noury et al., 2002) and Senior (Senior, 1951) rules must be satisfied (Kind and Fiehn, 2007):

(i) the sum of valences or the total number of atoms having odd valences is even;
(ii) The sum of valences is greater than or equal to twice the maximum valence;
(iii) The sum of valences is greater than or equal to twice the number of atoms minus 1.

Once a hit list is generated according to the Lewis and Senior rules, an acceptable mass error between the measured monoisotopic mass and theoretical mass should be <5 ppm. The formula to calculate the mass error is shown in Eq. (14.3).

$$\text{Mass accuracy} = 10^6 \times \left[(m_{\text{exp}} - m_{\text{calc}})/(m_{\text{calc}})\right] \tag{14.3}$$

where m_{exp}: measured monoisotopic mass, m_{calc}: calculated monoisotopic mass, with the mass accuracy (error) given in parts per million (ppm).

The confirmation of the selected elemental composition is ascertained by isotopic pattern filtering or matching. In other words, the selected theoretical formula is used to estimate the isotope ratio of the [M], [M+1], [M+2], [M+3] isotope ions and matched against the experimental mass spectrum. An acceptable isotopic abundance value is within 5%.

Lastly, element ratio evaluations must be performed, such as hydrogen/carbon (H/C), nitrogen/carbon (N/C), oxygen/carbon (O/C), phosphorus/carbon (P/C), sulfur/carbon (S/C) (Kind and Fiehn, 2007). Conversely, preliminary information about the precursor composition and disinfection method is very useful to guide the interpretation of the mass spectra, especially for halogenated DBPs (Postigo et al., 2016). Fragmentation patterns are also very useful for validation purposes. Such information is readily available in electron ionization (EI), but it requires additional MS/MS experiments for soft ionization techniques like chemical ionization (CI), ESI, atmospheric chemical ionization (APCI). These rules allow the assignment of the correct formula 98% of the time for compounds present in a database (Peterson et al., 2010).

Recently, a GC-HRAM-MS instrument based on FT-Orbitrap was used to characterize iodinated DBPs (I-DBPs) in chlorinated and chloraminated DBP mixture concentrates (Postigo et al., 2016). The extracts were analyzed in Full MS mode allowing for the integration of high-resolution accurate mass information and fragment rationalization.

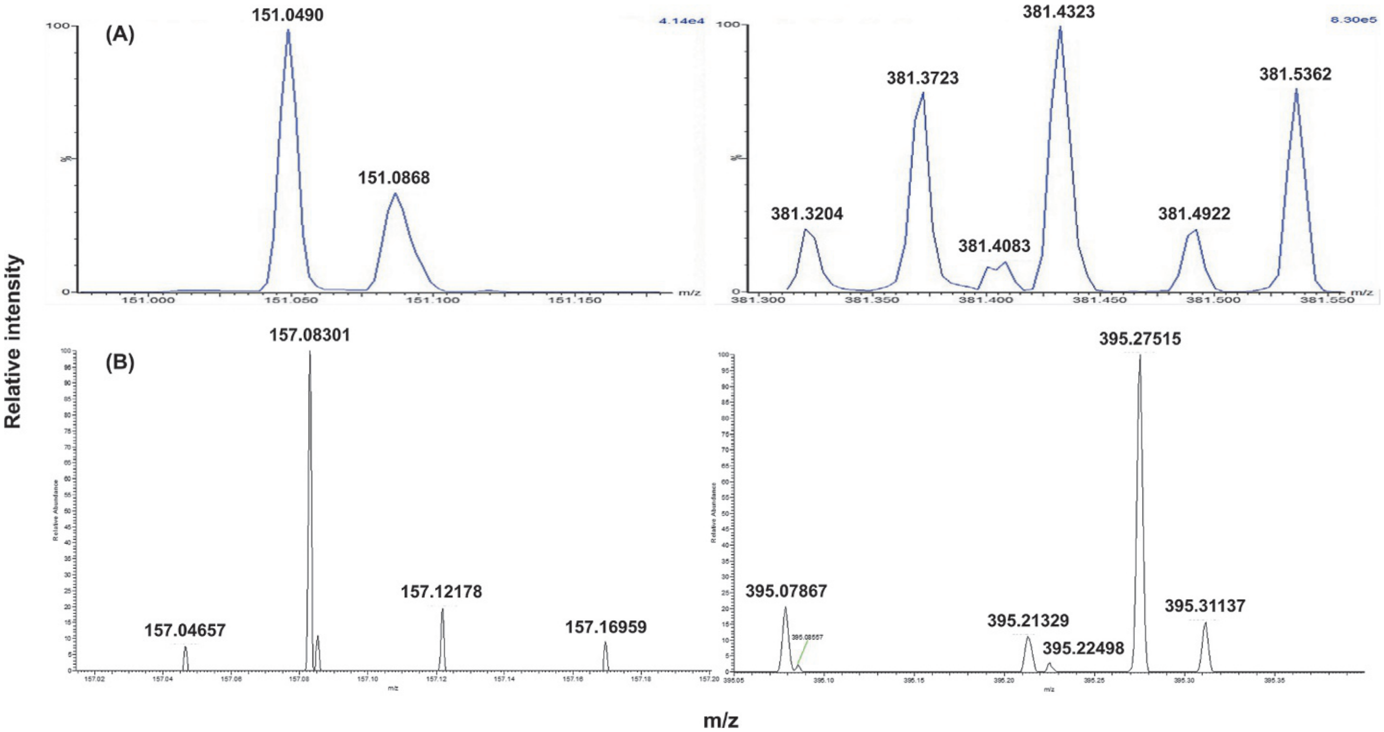


FIG. 14.2 Comparison of distinct mass spectra obtained in Xevo G2-XS QTOF hybrid mass spectrometer (A) and Q Exactive FT-Orbitrap hybrid mass spectrometer (B). Data obtained in our laboratory.

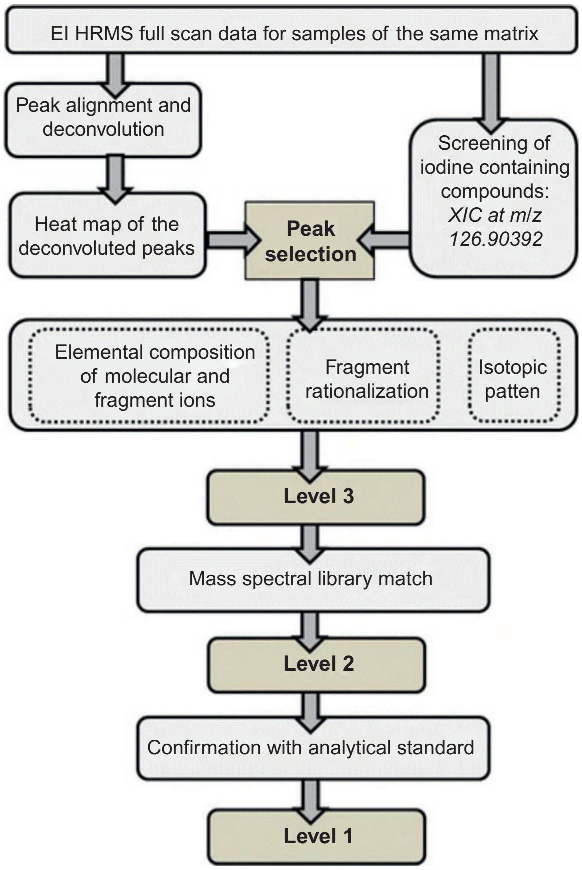


FIG. 14.3 Workflow applied for the identification of I-DBPs and confidence levels of the I-DBP molecular structures proposed. *Reproduced with permission from Postigo, C., Cojocariu, C.I., Richardson, S.D., Silcock, P.J., Barcelo, D., 2016. Characterization of iodinated disinfection by-products in chlorinated and chloraminated waters using Orbitrap based gas chromatography-mass spectrometry. Anal. Bioanal. Chem. 408, 3401–3411.*

As described in Fig. 14.3, this workflow allowed the identification of up to 11 different I-DBPs in the water extracts, including one new I-DBP reported for the first time. The usefulness of the fragmentation patterns further ascertained the characterization of complex DBPs, as shown in Fig. 14.4.

14.5 Status of water and sanitation services in developing countries

Safe water and sanitation are crucial for human health and well-being. The lack of these services negatively affects the quality of life and undermines fundamental human rights (UN, 2010). Yet, water and sanitation conditions worldwide are vastly unequal, as millions of people globally still lack adequate and safely managed services. Although access to clean drinking water and sanitation is amply recognized as a basic need, it is still a major challenge for most developing countries. Contaminated water and poor sanitation are associated with the transmission of waterborne diseases caused by pathogenic microorganisms such as bacteria, viruses, fungi, helminths, trematodes, and protozoa (Gerba, 2015; Griffiths, 2008; Magana-Arachchi and Wanigatunge, 2020).

Absent or inadequate water and sanitation services expose individuals to highly preventable health risks yearly (WHO, 2007). In 2016, roughly 1.9 million deaths were attributed to inadequate water and sanitation services (WHO, 2019). Each year, diarrheal diseases alone kill around 525,000 children under five, being the second leading cause of young children's death worldwide (Bryce et al., 2005). Although waterborne diseases occur worldwide, they are highly endemic in several developing countries and are amongst the leading causes of disability-adjusted life years (DALYs) in such nations (Prüss-Ustün et al., 2019). The World Health Association (WHO) estimates that, of the total

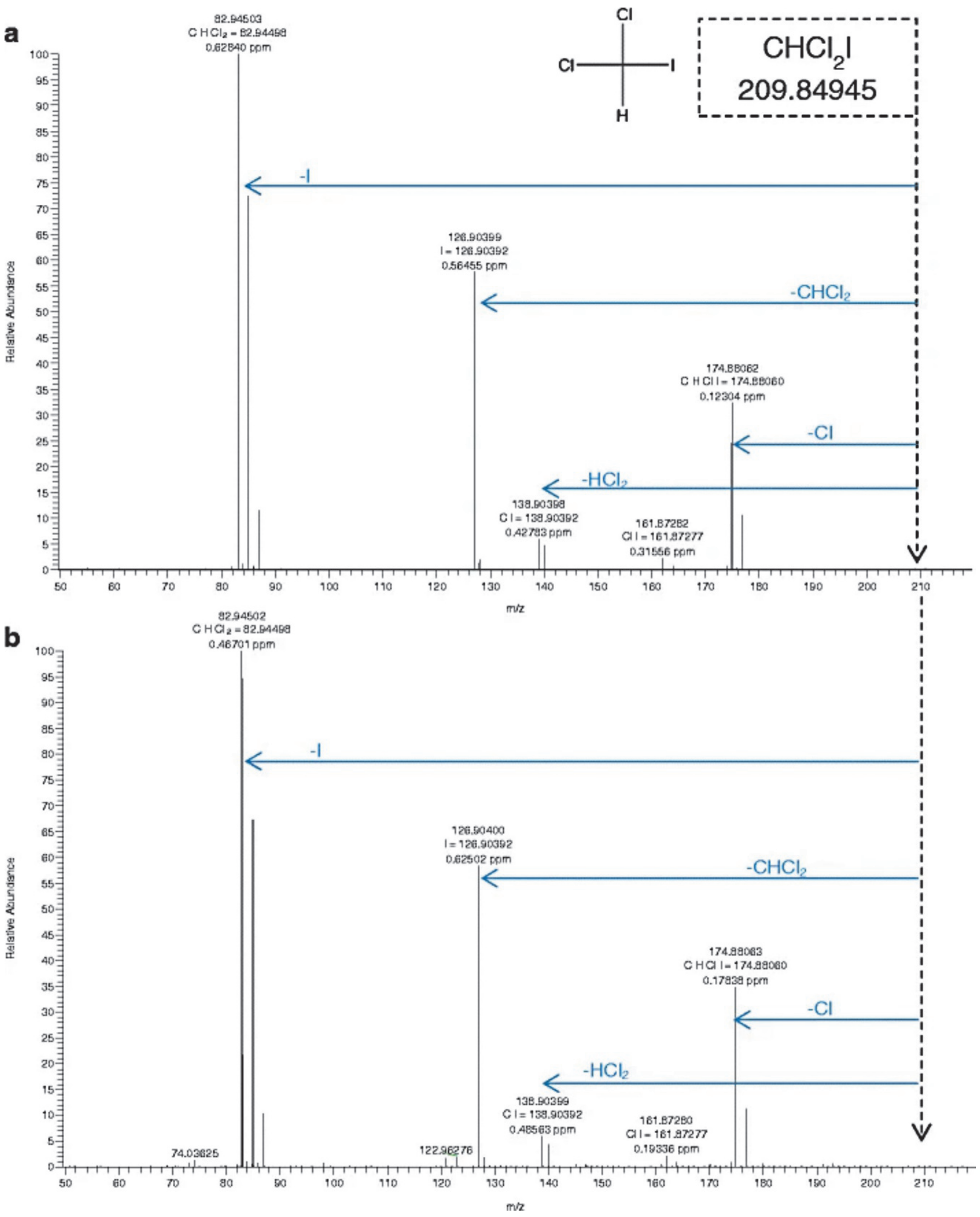


FIG. 14.4 Characterization of I-DBPs in chlorinated and chloraminated waters using GC-HRAM-MS. *Reproduced with permission from Postigo, C., Cojocariu, C.I., Richardson, S.D., Silcock, P.J., Barcelo, D., 2016. Characterization of iodinated disinfection by-products in chlorinated and chloraminated waters using Orbitrap based gas chromatography-mass spectrometry. Anal. Bioanal. Chem. 408, 3401–3411.*

cases of diarrheal diseases, 88% are attributable to unsafe water and inadequate sanitation, in which up to 94% of them are preventable through appropriate services (WHO, 2007).

In 2019, the WHO/UNICEF Joint Monitoring Program for Water Supply, Sanitation and Hygiene released their latest national, regional, and global estimates of 2000–17 (WHO and UNICEF, 2019). According to the report, global aggregates may conceal the large differences between developed and developing nations as water and sanitation vary greatly amongst all countries due to significant existing inequalities. Yet, the global snapshot highlights a few considerations from the water and sanitation crisis. Essentially, there is a strict relationship between wealth and the provision of water and sanitation. Although countries differ widely in the rate at which they convert wealth into water and sanitation services, on average, the coverage levels for water and sanitation rise with income. Simultaneously, one of the most profound disparities in water and sanitation is between urban and rural areas. Part of the rural-urban gap can be traced to differences in incomes and poverty. In addition, delivering services are often more difficult and costly for rural populations than for urban populations. Another highlighted problem is the gap between water and sanitation provision. Although wastewater management and treatment levels vary significantly across countries, there is a global trend of sanitation provision lagging far behind access to water. This is an urgent issue not just because access to sanitation is intrinsically important but also because the benefits of improved access to water and sanitation are mutually reinforcing.

The report shows that, between 2000 and 2017, the population using safely managed drinking water and sanitation services increased from 61% to 71% and 28% to 45%, respectively. From 2000 to 2017, 1.8 billion people gained access to at least basic services, whereas 2.1 billion people gained access to at least basic sanitation services. World rural coverage increased from 39% to 53% for drinking water access and from 22% to 43% for safely managed sanitation services, in which the gap between urban and rural areas decreased from 47 to 32 and 14 to 5 percentage points, respectively. However, in 2017, 8 out of 10 people who still lacked basic water services lived in rural areas, and nearly half lived in the least developed countries. Similarly, 7 out of 10 people who still lacked basic sanitation services lived in rural areas, and one-third lived in the least developed countries.

Globally, water demand is predicted to increase significantly over the coming decades, influenced mainly by population growth and urbanization, industrialization, expansion, and intensification of agriculture and livestock, increasing energy demands, and extreme events aggravated by climate change. However, as the overall water demand grows, so does the pollution of freshwater ecosystems. Agricultural and urban runoff, effluents from mining and extractive industries, industrial spills, algal blooms, sediment loading, solid waste transport into water bodies, and inadequate management of the municipal, hospital, and industrial wastewater account for the main sources of surface water and groundwater pollution. Therefore, discrepancies in water supply and water demand are becoming increasingly exacerbated, especially where supplies are vulnerable or scarce and their use and distribution are poorly managed (UNESCO, 2018). As a result, the gradual reduction of available pristine waters forces drinking water utilities to exploit impaired source waters to meet growing water demands. Although water quality degradation is a widespread phenomenon of worldwide incidence, it is gradually becoming a leading problem throughout the developing world, as a quarter of the world's population lives in regions facing extremely high water stress (UNESCO, 2019). This challenge is particularly relevant for developing countries with highly impaired freshwaters that often serve as open sewers for wastewater disposal and illegal dumping. Thus, water quality degradation translates directly into environmental, social, and economic problems.

Having all the facts considered, providing microbiologically safe drinking water and adequately treating wastewater are still major public health issues in several developing countries, and chemical disinfection plays the main role in it. Although disinfection of drinking water has been very successful in pathogen inactivation and waterborne disease control, it also brought relevant concerns about unintended health hazards associated with DBP exposure. Water disinfection implies a trade-off between microbiological and chemical risks (Li and Mitch, 2018; Wawryk et al., 2020). However, circumventing it brings a much more complex and delicate situational decision that involves balancing two sides of a coin.

The WHO clearly states that infectious diseases caused by pathogenic agents are the most widespread health risk associated with drinking water and, therefore, it is of utmost importance that the biological quality of water always takes precedence over the chemical quality (WHO, 2017). The acute risk related to waterborne diseases due to microbial pathogens are immediate and potentially lethal, while the health concerns associated with the great majority of chemical contaminants, including DBPs, only exert an effect after prolonged periods of exposure, i.e., the risk is associated with chronic intake and the health effects arise in the long term. Therefore, while most developed countries have the resources to meet both microbiological and chemical regulations and follow a precautionary principle, the initial critical need in most developing countries is the provision of microbiologically safe drinking water, especially if we are to consider the current circumstances of water and sanitation services in the great majority of them. Yet, just as efforts to develop efficient, economically, and technologically sound methods to produce clean drinking water and provide adequate sanitation are globally increasing in developing countries, there is also an increasing need to investigate the chemistry, toxicology, and epidemiology of DBPs to understand the health risks they pose comprehensively. Thus, rather than pondering on which risk to abide by, research efforts should be coordinated into both aspects in the interest of decreasing the chemical risk without compromising microbiological quality.

14.6 Legislation of DBPs in drinking waters

Over 40 years after the first regulation of drinking water DBPs, in 1979 in the United States, several countries have adopted similar regulations for the past decades, yet DBP regulations vary worldwide. Many countries from all continents have national or regional standards for a few DBPs, yet not all of them have listed them as mandatory; some countries have advisory values for guidance purposes (Poleneni, 2020).

The THMs and, to a lesser extent, HAAs, are the predominant classes of chlorinated DBPs that are currently regulated in the world. Both classes are often regulated as a total by either following existing guidelines or setting specific values, yet some nations choose to regulate their most representative compounds individually (Poleneni, 2020). Very few countries in the world (developed economies included) provide regulations for inorganic DBPs such as chlorate, chlorite, and bromate (DeMarini, 2020; Wang et al., 2015). The WHO provides the Guidelines for Drinking Water Quality, currently adopted by many countries (WHO, 2017). They cover several different DBPs such as the most representative THMs and HAAs, inorganic DBPs, *N*-Nitrosodimethylamine, 2,4,6-trichlorophenol, dibromoacetonitrile, and dichloroacetonitrile. Other disinfection byproducts such as cyanogen chloride, trichloroacetaldehyde, 3-chloro-4-(dichloromethyl)-5-hydroxy-5H-furan-2-one (MX), chlorocetones, chlorophenols, and brominated acetic acids are also described but with no guideline values inferred, either because the available data are inadequate to permit derivation of health-based values or because the provisional calculated health-based values are significantly above the typical levels of concentration in drinking water.

One of the main purposes of drinking water quality regulations is to establish requirements for compliance monitoring. Yet, the existing regulations do not always result in quality improvement. For instance, while several countries in the developed world, particularly in Europe and North America, have successfully established strict monitoring for DBPs in drinking water, the cost of water treatment in developing countries is often prohibitively high enough to prevent strict monitoring and further research in drinking water quality. It is also noteworthy that countries with water and sanitation issues either have no DBP regulations or mostly follow the existing regulations with little to no enforcement (Poleneni, 2020). The current failure to enforce strict monitoring describes a trend in developing countries, mostly due to jurisdictional, economic, technological, and/or infrastructural issues. In addition, the lack of compliance with regulations usually comes with minimum legal consequence regarding chemical safety, except for situations in which short-term exposure is likely to lead to health impairment (such as arsenic, lead or nitrate, or contamination).

Another great obstacle in the path of progress in regulation is the lack of data for most DBPs in emerging countries. When assessing priority compounds for risk management, chemical and toxicological data are frequently not available. Identification of priority compounds should rely as much as possible on data from the country in question, such as evidence of adverse health effects from exposure through drinking water, an indication of their presence in drinking water, and the plausible chance of human exposure at concerning levels. Indeed, the paucity of accurate, reliable, and timely data has been a recurring issue for the development of regulations and standards. At the same time that the need for information underpins policy action and policymakers are increasingly called on to use evidence-based research, the lack of published research does not allow the identification of key points of concern and make data-driven decisions.

Consequently, several inadequate assumptions are often made when developing or revising regulations and standards. The existing gaps in available data (if any) for DBP occurrence hinder the development of relevant and realistic drinking water quality regulations, causing delays in implementation and potentially resulting in DBPs with greater health impact not having guidelines. Thus, more often than not, it is difficult to ascertain the effectiveness of regulations or whether available resources are being rightfully allocated to address the most urgent issues.

For instance, current DBP regulations and standards address only a relatively small fraction of the overall observed DBP toxicity (Itoh et al., 2011). However, regulations and standards are inevitably limited in what they include. Excessively strict regulations have several constraints and are unlikely to provide health benefits, undermining the credibility and usefulness of the regulations and standards. US EPA's initial regulations assumed that other DBPs might be formed as well during water disinfection, yet TTHM regulation would be an adequate surrogate to DBP formation in general (US EPA, 2016). Unfortunately, over time, it did not prove right (Richardson and Plewa, 2020). While the use of surrogates presents itself as a viable strategy to DBP control, enabling routine monitoring and simplifying future regulations, the selection of these surrogates was inevitably pragmatic because of the existing knowledge about the chemical identity of DBPs and their correlation in formation is considered incomplete. Thus, as THM (and HAA) formation poorly correlates with the formation of other more toxic DBPs, there are current concerns about whether THM and HAA concentrations are an adequate metric of DBP exposure, especially in developing countries with highly impaired water supplies (Furst et al., 2019). Thus, as these countries upgrade drinking water legislations, their first instinct would be to enact DBP regulations focusing solely on THMs and HAAs without considering that other more toxic DBPs might be of greater concern.

14.7 Occurrence of DBPs in drinking waters

While much research effort has been directed toward DBP identification and determination in developed countries, there is a distinct lack of high-quantity data available on the occurrence of DBPs in developing countries. There may be several reasons why data is not available. Partly, the absence of research comes from insufficient government and economic incentives. However, there is the pressing necessity to respond to a much more fundamental agenda of improving water and sanitation access in developing countries.

Background information concerning DBPs and their relationship to environmental conditions is necessary to develop adequate regulations and implementation of public health policies. Furthermore, obtaining DBP exposure estimates in developing countries will also allow the assessment of the health risks on a more global scale.

Historically, research on DBP occurrence has predominately focused on drinking water due to the public health concerns that arise from the toxicity of several DBPs. Worldwide, much effort has been put toward the occurrence and toxicity data on DBPs in drinking water to develop water quality guidelines purposes. However, there is a comparative absence of DBP occurrence data in alternative sources such as wastewaters and impaired source waters, mostly because of a lack of perceived need for this information and the reduced human contact with such waters (Du et al., 2017; Luan et al., 2020; Watson et al., 2012). Nonetheless, there has been an increased use of impaired source waters and reclaimed waters redirected for broader applications, especially in countries prone to water stress with the need for alternative and more sustainable water sources (Gerba and Pepper, 2019; Shah and Mitch, 2012).

Since wastewaters and impaired source waters are expected to contain more organic matter, their disinfection can produce a correspondingly greater amount and variety of DBPs (Krasner et al., 2009; Li and Mitch, 2018; Richardson and Postigo, 2015b). It is then necessary to provide an in-depth insight into the formation mechanisms of impaired and wastewater-associated DBPs, along with a much-needed reference for their occurrence and public health implications.

As with much of the research on DBP occurrence in developing countries, the current studies are highly limited in scope and range. Regional and national assessment of current levels of DBPs are very scarce and the few scattered data is essentially focused on the most commonly regulated DBPs, with very little research on compounds other than THMs and HAAs. Thus, current research does not contemplate the possible occurrence of more toxic species and does not reflect the actual scenario of drinking water chemical safety for the great majority of developing countries. However, in recent years, there has been a slight increase in research conducted on the occurrence of some EDBPs, such as haloacetonitriles, haloketones, and nitrosamines.

For analytical purposes, the United Nations (UN) country classification is adopted herein. The UN classifies all world countries into three broad categories: developed economies, economies in transition, and developing economies (UN, 2020). Thus, Tables 14.1–14.3 show a comprehensive assessment of DBP occurrence in drinking water based on quantitative analysis in developing countries except for China and South Korea. Although both countries are currently classified as developing nations by the UN, China (2nd) and South Korea (10th) are amongst the top 10 most productive countries in DBP research (Tang et al., 2020). Thus, their innovative research in the field is recognized, yet it shall not be presented.

14.8 Mind the gap(s): Conclusions and perspectives

Chemically disinfected water was the leap forward in human progress (see Tavengwa et al., 2022, Chapter 20; Sanganyado, 2022, Chapter 19). The use of strong oxidants to disinfect water has virtually eliminated waterborne diseases in developed countries. Nonetheless, chemical disinfection produces an unintended health hazard associated with DBP formation. DBP subject has been extensively addressed in most developed countries for several decades. Yet, these contaminants represent a rather new and complex aspect of the challenge in water quality in developing countries.

TABLE 14.1 Occurrence of trihalomethanes ($\mu g L^{-1}$) in drinking water in developing countries.

Country	Year	TTHM	TCM	BDCM	DBCM	TBM	Br-THM	DCIM	BCIM	Reference
Brazil	2003	22,500–111,000								Tominaga and Mídio (2003)
	2007		0.7–182.4	1.8–74.4	0.1–40.4	n.d.–5.8				Budziak and Carasek (2007)
	2009		55.6–72.5	28.7–47.2	13.3–21.7	n.d.				Viana et al. (2009)
	2012	3.1–129.3								Ferreira and da Cunha (2012)
	2018	26.0–35.4								Schafer et al. (2018)
Chile	2009	11.4–133.7	9.7–111.6	0.9–29.5	0.1–1.0					Loyola-Sepulveda et al. (2009)
	2013	8.0–213.1	5.4–182.0	0.9–35.2	0.1–0.9					Loyola-Sepulveda et al. (2013)
Cyprus	2014		0.8–43	0.6–44	0.7–46	0.7–17	2–98			Charisiadis et al. (2015)
	2016		1.3–31.1	2.3–28.5	0.1–22.5	0.1–19.9		0.03–1.6	0.1–0.5	Ioannou et al. (2016)
	2019		0.1–13.3	0.9–30.9	1.1–66.2	0.1–100.3	3.1–197.3			Andrianou et al. (2019)
Colombia	2012	190–210								Rosero et al. (2012)
	2015		42.3[a]	1.9[a]	1.6[a]	1.4[a]				Vargas et al. (2016)
Egypt	2013	39.6–80.2								Abdullah and Hussona (2013)
	2014	35–153								Azeem et al. (2014)
	2019		4[b]	4[b]	4[b]	4[b]				Mishaqa et al. (2019)
India	1997		10.5–70.5							Srikanth (1997)
	2002		29.1–231.3	n.d.–87.4	0.6–50.2	n.d.–46.8				Thacker et al. (2002)
	2007		36.5[a]	8.7[a]	7.7[a]	5.1[a]				Sharma and Goel (2007)
	2010		375[b]	110[b]	55[b]	11[b]				Hasan et al. (2010)
	2011		3.9–532.6	n.d.–315.2	n.d.–187.1	9.8–1855				Basu et al. (2011)
	2014	269–594								Mishra et al. (2014)
	2015	231–484	223–461							Kumari and Gupta (2015)
	2015	236–503								Kumari et al. (2015)
	2019		89.2–107.3	36.3–50.0	52.4–77.6	55.2–77.8				Tak and Vellanki (2019)
Iran	2008		57.3							Yousefi and Mohseni-Bandpei (2008)
	2010		6							Hassani et al. (2010)
	2011		10.1							Andalib et al. (2011)
	2011		4.3							Pardakhti et al. (2011)
	2012		20.8							Noshadi et al. (2012)

	2013		36.7				Babaei et al. (2013)
	2014		13				Fazli et al. (2015)
	2016		38.0				Mohammadi et al. (2016)
	2019		6[b]	15[b]	3[b]	8[b]	Kalankesh et al. (2019)
	2019		3–23	3–6	3–6	3–7	Mohammadi et al. (2019)
	2019		1.1–212.3	0.02–228.9	0.02–99.3	0.02–24.0	Sadeghi et al. (2019)
Israel	2003		n.d.–0.4	n.d.–0.6	n.d.–9.4	n.d.–67	Richardson et al. (2003)
Kuwait	2010		0.2[b]	0.8[b]	5[b]	30[b]	Al-Mudhaf et al. (2010)
Lebanon	2007	30[b]					Semerjian et al. (2007)
Malaysia	2003	2.4–136.5	1.5–123.0				Abdullah et al. (2003)
Mexico	1999		n.d.–42.0	0.8–68.4	1.5–27.7	8.0–124.2	Leal-Ascencio et al. (1999)
Nigeria	2017		21.9–999.6	n.d.–0.4	n.d.–0.4	n.d.–0.4	Benson et al. (2017)
Pakistan	2013		20–363	0.3–9	0.3–14	n.a.	Amjad et al. (2013)
	2013	0.6–170.1					Karim et al. (2013)
	2014		32.5–67.3	2.0–6.2	0.6–3.5	0.3–0.4	Siddique et al. (2014)
	2015		23.9–575.9	2.0–33.2	n.d.–18.2	n.d.–7.8	Abbas et al. (2015)
Qatar	2016		n.d.–5	n.d.–26	n.d.–2	1–56	Al-Otoum et al. (2016)
Saudi Arabia	1993	0.1–41.7					Fayad (1993)
	2009		0.2–0.5	0.7–1.5	1.2–2.3	4.3–6.7	Ahmad and Bajahlan (2009)
	2013		1.2–6.1	0.5–3.4	n.d.–1.2	n.d.–0.7	Chowdhury (2013)
	2016	6.4–14.6					Chowdhury (2016)
	2018		1.2–14.4	0.2–6.3	0.1–2.1	0.3–29.7	Chowdhury et al. (2018)
Taiwan	2007		5.9–23.9	3.7–15.4	2.0–16.5	1.4–20.1	Wang et al. (2007)
	2010	n.d.–133.2					Chang et al. (2010)
	2010	1.7–18.3					Lou et al. (2010)
Thailand	2015		9.6–152.6	2.1–22.0	n.d.–4.8	n.d.	Feungpean et al. (2015)
	2019		4–211	n.d.–149	n.d.–64	n.d.–20	Ratpukdi et al. (2019)
Tunisia	2010		3.6–15.6	13.3–25.4	21.1–40.8	9.1–48.9	Bahri and Driss (2010)
	2016	46.0–186.7					Rabhi et al. (2016)

Continued

TABLE 14.1 Occurrence of trihalomethanes ($\mu g L^{-1}$) in drinking water in developing countries—cont'd

Country	Year	TTHM	TCM	BDCM	DBCM	TBM	Br-THM	DCIM	BCIM	Reference
Turkey	2004	110[b]	30.7[a]	n.a.	4.3[a]	n.a.				Tokmak et al. (2004)
	2005		18–29	20–36	23–40	7–12				Toroz and Uyak (2005)
	2005	56.3–147.8	52.0–136.2							Uyak et al. (2005)
	2006		6.4[a]	5.4[a]	3.8[a]	0.9[a]				Kavcar et al. (2006)
	2006		12–42	11–30	6.7–33	1–11				Uyak (2006)
	2008		0.03–98.4	0.01–43.8	0.2–65.9	0.04–19.1				Baytak et al. (2008)
	2008		185.9[c]	74.8[c]	48.5[c]	7.4[c]				Uyak et al. (2008)
	2014		0.7–57.4	0.03–49.1	0.01–54.9	0.04–30.2				Uyak et al. (2014)
Uruguay	2014		1–143							Camponovo et al. (2014)
	2018		75[b]							Borras et al. (2018)
Vietnam	2003		0.3–11.1	0.5–7.3	0.3–22.3	1.2–18.5				Duong et al. (2003)

BCIM, bromochloroiodomethane; *BDCM*, bromodichloromethane; *Br-THM*, brominated trihalomethane; *DBCM*, dibromochloromethane; *DCIM*, dichloroiodomethane; *TBM*, tribromomethane; *TCM*, trichloromethane; *TTHM*, total trihalomethanes; *n.d.*, not detected; *n.a.*, not analyzed.

[a] *Average values.*

[b] *Value obtained from graphic interpretation.*

[c] *Maximum value.*

TABLE 14.2 Occurrence of haloacetic acids ($\mu g L^{-1}$) in drinking water in developing countries.

Country	Year	THAA	MCAA	BCAA	DCAA	TCAA	MBAA	DBAA	TBAA	BDCAA	DBCAA	DALAPON	Reference
Egypt	2019		<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	Mishaqa et al. (2019)
Iran	2016				4.8–39.1	3.4–19.0							Ghoochani et al. (2017)
	2019		2[a]		22[a]	22[a]	17[a]	8[a]					Kalankesh et al. (2019)
Israel	2003		n.d.	n.d.–3.9	n.d.	n.d.	n.d.	n.d.–38.7	n.d.	n.d.	n.d.		Richardson et al. (2003)
Kuwait	2011	5.7–42.0											Al-Mudhaf et al. (2011)
Malaysia	2009			1.0[b]	5.7[b]	4.0[b]							Sadia and Pauzi (2009)
	2010		0.5[a]	2[a]	10[a]	8.5[a]	n.d.	1.5[a]		1[a]			Waseem and Abdullah (2010)
Saudi Arabia	2018	6.4–9.9											Chowdhury et al. (2018)
Tunisia	2013		1.6–12.4	3.3–17.5	3.0–19.2	2.1–18.4	3.2–9.4	1.1–11.6	2.6–10.7				Hammami and Driss (2013)
	2014		6.7–34.1	2.1–13.8	2.8–23.2	3.9–26.3	3.0–9.8	4.4–289	1.6–9.4				Hammami et al. (2014)
Turkey	2008		12[c]	7.1[c]	149.6[c]	149.0[c]		31.5[c]					Uyak et al. (2008)
	2014		1.4–16.8	0.02–10.5	0.9–35.6	0.02–44.1	0.03–13.8	0.01–22.7	0.1–6.5	0.03–6.9	0.05–6.3		Uyak et al. (2014)

BCAA, bromochloroacetic acid; *BDCAA*, bromodichloroacetic acid; *DALAPON*, 2,2-dichloropropionic acid; *DBAA*, dibromoacetic acid; *DBCAA*, dibromochloroacetic acid; *DCAA*, dichloroacetic acid; *MBAA*, monobromoacetic acid; *MCAA*, monochloroacetic acid; *TBAA*, tribromoacetic acid; *TCAA*, trichloroacetic acid; *THAA*, total haloacetic acids; *n.d.*, not detected; *n.a.*, not analyzed.

[a] *Value obtained from graphic interpretation.*

[b] *Average values.*

[c] *Maximum value.*

TABLE 14.3 Occurrence of other disinfection byproducts in drinking water in developing countries.

DBP class	Country	Year	DBPs	Concentration level	Range	Reference
Aldehydes	Israel	2003	Formaldehyde	$\mu g\,L^{-1}$	2.9–31.0	Richardson et al. (2003)
			Acetaldehyde		2.6–4.5	
			Glyoxal		n.d.–4.9	
			Methylglyoxal		n.d.–4.2	
Halogen Acetonitriles	Thailand	2019	DCAN	$\mu g\,L^{-1}$	0.4–11.0	Ratpukdi et al. (2019)
			BCAN		n.a.	
			DBAN		n.d.–6.0	
			TCAN		0.1–14.0	
	Turkey	2008	DCAN	$\mu g\,L^{-1}$	n.d.–20.8	Baytak et al. (2008)
			BCAN		0.01–11.9	
			DBAN		n.d.–16.4	
			TCAN		n.d.–54.6	
Haloketones	Turkey	2008	1,2-DCP	$\mu g\,L^{-1}$	0.01–7.8	Baytak et al. (2008)
			1,1,1-TCP		0.01–7.8	
			CP		0.08–9.3	
Halofuranones	Iran	2020	MX	$ng\,L^{-1}$	15–38	Bagheban et al. (2020)
Inorganic DBPs	Qatar	2016	Chlorate	$\mu g\,L^{-1}$	11–280	Al-Otoum et al. (2016)
			Chlorite		13–440	
	Saudi Arabia	2012	Bromate	$\mu g\,L^{-1}$	3.4–75.0	Alsohaimi et al. (2012)
Nitrosamines	Taiwan	2016	NDMA	$ng\,L^{-1}$	n.d.–10.3	Chen et al. (2016)
			NMEA		n.d.	
			NPYR		n.d.–5.1	
			NDEA		n.d.–16.5	
			NDPA		n.d.	
			NDBA		n.d.	

BCAN, bromochloroacetonitrile; *CP*, chloropicrin; *DBAN*, dibromoacetonitrile; *DCAN*, dichloroacetonitrile; *MX*, 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone; *NDBA*, *N*-nitrosodi-n-butylamine; *NDEA*, *N*-nitrosodiethylamine; *NDMA*, *N*-nitrosodimethylamine; *NDPA*, *N*-nitrosodi-n-propylamine; *NMEA*, *N*-nitrosomethylethylamine; *NPYR*, *N*-nitrosopyrrolidine; *TCAN*, trichloroacetonitrile; *n.d.*, not detected; *n.a.*, not analyzed.

Sharp geographic, socio-cultural, and economic inequalities persist between developed and developing countries. Most developed countries use advanced water treatment methods and have strict DBP regulations or guidelines to minimize health risks associated with DBP exposure, while most developing countries still struggle with microbiologically safe drinking water and adequate sanitation. Although the primary goal is to ensure all people's access to sufficient, safe water and proper sanitation, DBPs pose a chemical risk that demands measures to limit their production. However, it is important to stress that when attempting to control total DBP exposure, the beneficial public health role of disinfection should not be compromised. Thus, future research is needed to minimize DBP formation while accomplishing pathogen reduction standards.

While it seems like a long path before DBPs are regularly monitored and regulated in developing countries, the potential chronic health risks associated with the consumption of chemically disinfected water demand immediate action for ensuring the overall safety of drinking water. However, the main challenges in improving water quality are financing research and infrastructure and regulatory enforcement.

Firstly, water and wastewater treatment receive a low and often poorly targeted share of development aid and investment in developing countries, whereas most drinking water and wastewater facilities are outdated and not designed to meet local guidelines, with appropriate technologies mostly limited to developed countries.

Secondly, policy action is highly dependent on information. Government and institutions need to plan accurately, fund, and evaluate development actions based on comprehensive data collection. Occurrence data in developing countries are scarce and scattered. Despite the slight rise in research and publications regarding DBPs in the aquatic environments over the past years, the lack of information continues to be a major constraint to the effective monitoring and evaluation of DBP exposure.

Thirdly, the lack of political commitment, accountability, and transparency in complying with existing standards, together with the limited (or nonexistent) enforcement, remain common practice, preventing the implementation of adequate public health policies.

Finally, as existing regulations worldwide limit specific DBPs that cannot account adequately for the potential health impacts, refinement of regulatory limits is of great importance moving forward, increasing the list as needed. Yet, the selection of parameters for inclusion in regulations and standards should prioritize them according to the actual risks they pose in the local context. Thus, future research must enable the identification and prioritization of possible toxicity drivers, whereas new or improved regulations must follow a more realistic yet attainable approach.

In conclusion, there is a demand for more research into the toxicological effects and occurrence of a broader range of occurring DBPs, especially the ones expected to occur in drinking water from impaired sources and reclaimed waters. In addition, the complexity and variety of DBP formation also imply that there are further compromises when it comes to reducing the production of certain DBPs such as the regulated THMs and HAAs. Therefore, while research continuously develops efficient and cheap methods to sustain clean water and adequate sanitation for developing countries, it is necessary to evaluate the viability and economics of novel treatment systems that adequately address the general lack of water resources and water quality degradation, ensuring that both microbiological and chemical risks are safely managed.

This chapter falls under the section on fate and occurrence of emerging pollutants within aquatic ecosystems with other chapters, e.g., Ajayi et al. (2022), Cristale (2022), Galhardi et al. (2022), Hashemi and Kaykhaii (2022), Madikizela et al. (2022), Mashile et al. (2022), Montagner et al. (2022), Moodley et al. (2022), Ntshani and Tavengwa (2022), Sanganyando and Kajau (2022), and Yardy et al. (2022) that aims to make an understanding of the different emerging pollutants within the aquatic environment.

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CHAPTER

15

Azo dyes: Sources, occurrence, toxicity, sampling, analysis, and their removal methods

Sayyed H. Hashemi and Massoud Kaykhaii

15.1 Introduction

The continuous growth of the pharmaceutical (Madikizela et al., 2022, Chapter 10), over years may in chemical and agricultural industries several pollutants including steroid hormones, pesticides (Montagner et al., 2022, Chapter 12), antibiotics (Ntshani and Tavengwa, 2022, Chapter 11) or synthetic organic dyes entering into water bodies (Tavengwa and Dalu, 2022, Chapter 1). Due to the mutagenic and carcinogenic character of some of these compounds, such as azo dyes, contamination of aquatic media with these pollutants is hazardous and of great concern worldwide as a serious (Hashemi et al., 2018a, b, 2019a, b, c).

Mauveine, the first synthetic dye, was introduced by Perkin in 1856 (Cova et al., 2017). This finding led to a revolution in the industry of dyestuff on a global scale and the production of dye has increased tremendously since then. Today, besides the main suppliers of fabrics worldwide, China and India are the largest producers of dyes in the world (Tkaczyk et al., 2020). It is estimated that more than 100,000 dyes exist commercially worldwide (Tkaczyk et al., 2020). Chemical Economics Handbook (Tkaczyk et al., 2020) is a good source that presents full information about the worldwide consumption of dyes.

Azo dyes are the main group of synthetic dyes which are major environmental contaminants because of their wide use. It is estimated that the annual global production of them is over 1,000,000 tons. They are general in the world because of their large-scale generation and their usage in many industries such as leather, tanning, textile, printing and paper, pharmaceutical, cosmetics food processing, pharmacologically active substances and human, and veterinary medicine (Hashemi et al., 2018a). Azo dyes are regarded as micropollutants because of their occurrence in low concentrations (ng/L to μg/L) in the aqueous environment. The presence of these dyes has negative effects on the absorption and reflection of sunlight reaching aqueous media which has effects on the growth and biological activity of aquatic living organisms. Moreover, these dyes can decrease dissolved oxygen in the stream and destroy aquatic life via biological and chemical changes (Hashemi et al., 2018a, b, 2019a).

Obviously, due to the massive production of azo compounds, a huge volume of colored wastewater and various types of post-generation waste is generated. The textile industry is a significant source of dyes in aqueous media. Dye wastage can be in the possibility of 5%–50%. About 200 billion liters of such colored effluents are produced in a year. Since biodegradation of these compounds are slow or is not performed, contamination with azo dye may persist for very long periods. Therewith, with currently commercially available techniques in sewage treatment plants, clean-up of wastewater contaminated with these dyes' is almost impossible (Hashemi et al., 2018b).

15.2 Dyes' classification

Dyes' chemical structures are diverse, consist of azo and nitro groups (for example), phthalocyanine, and diarylmethane dyes by very various chemical and physical properties. Dyes are complex unsaturated materials that absorb light and give color to the visible region. Also, a dye is a material having the property of absorbing part of the visible spectrum (chromophore). The color is given using the fraction of light not absorbed with the dye but reflichie. The

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conjugated double bonds constitute a chemical structure favorable to the absorption of light. So, colorants often including aromatic amines. Dyes are characterized by their capacity to absorb light radiation in the visible spectrum from 380 to 750 nm. The transformation of white light into colored light with reflection on a body or with transmission or diffusion results in the selective absorption of energy with certain groups of atoms named chromophoric groups (Benkhaya et al., 2020a).

The three main groups that exist in dye molecules: chromophore, matrix, and auxochrome. The chromophore is the active site of a dye that absorbs light. These include a series of atoms, such as azo (—N=N—), nitro ($—NO_2$), nitroso (—N=O), thiocarbonyl (—C=S), carbonyl (—C=O), and alkene (—C=C—). While due to the excitation of electrons chromophores can absorb electromagnetic radiations in special wavelengths, when mixing with other groups of atoms (auxochrome), their absorption wavelengths can be shifted and so, the color of the compound will be changed. Auxochromes may include acidic (—COOH, $—SO_3$, and —OH) or basic (NHR, NH_2, and NR_2) groups. The remaining atoms in a dye molecule are called the matrix (Benkhaya et al., 2020a).

The dyes include an assembly of chromophoric, auochromic groups and conjugated aromatic structures (benzene rings, anthracence, perylene) When the number of aromatic nuclei increases, the conjugation of the double bonds increases. The energy of the p-bonds decreases while the activity of the electrons π or n increases and generates a displacement towards the long lengths wave. Also, when an electron-doner auxochromic group such as amino, hydroxyl, alkoxy, is placed on a conjugated aromatic system, the group joins the conjugation of the p-system, there may be hyperconjugation and the dye absorbs in large wavelengths and obtains darker colors (Benkhaya et al., 2020a).

The azo dyes are distributed based on the number of azo linkages that are in the same molecule of the dye including monoazo, disazo, trisazo, polyazo, and azoic. In the color index (CI) system, azo dyes are supplied by numbers ranging from 11,000 to 39,999 in correspondence by the chemical structure as shown in Table 15.1. The color index number, developed with the society of dyes and colorists, is utilized for dye classification (Benkhaya et al., 2020b; Gürses et al., 2016). Azo dyes can be classified according to their structure, as shown in Table 15.2 into classes including anthraquinone, acridine, azo, azine, indigoid, diphenylmethane, methine, nitroso, nitro, oxazine, phthalocyanine, thiazine, triphenylmethane, and xanthene dyes; they can also be classified according to their usage including, direct, basic, disperse, fiber, reactive, vat, and mordant (Table 15.2). Generally, spectrophotometric determination of dyes is performed in a wavelength with maximum absorbance in their spectrum ($\lambda_{\max}$). The formal names of colorants based on their chemical structures are difficult and so their general names are used instead. Chemical Abstract Service Number, each colorant is explained by a Color Index classification (characterized with its color and a unique number) and Color Index Constitution Number (Society of Dyers and Colorists 2013) (Tkaczyk et al., 2020). For example, methylene blue is explained with the classification of Color Index as CI basic blue 9 and CI 52015 (Table 15.2). Coloring materials in Europe are defined based on their number of Color Index (CI), and they are ordered for their application in the cosmetic generation on except products of hair dye with the Regulation (EC) NO 1223/2009 (Guerra et al., 2015) introduced in force in 2013 and its next amendments (Annex IV) (Guerra et al., 2015).

15.3 Azo dyes and their applications in textile and cosmetic industries

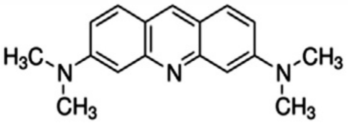
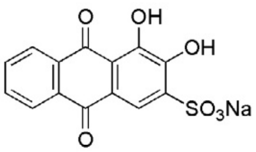
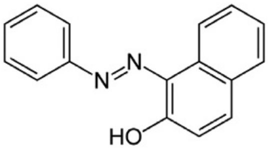
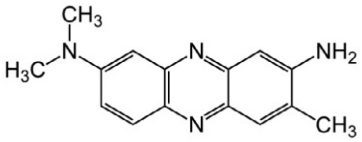
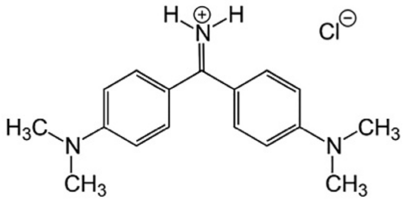
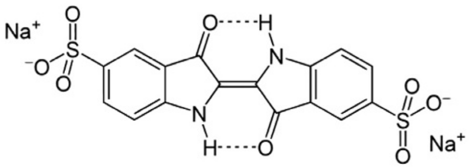
The industry of textile dyeing has been existing for the past 4000 years and the dyes were being produced from natural sources only until the last 150 years. For coloring different textiles, large volumes of various dyes are in use in the textile and tannery industries including clothes, bedding, leathers, carpets, or soft furnishings. Moreover, these dyes are also in use in the industry of printing as pen and printing inks. Approximately 7×10^7 tons of various textile dyes are produced yearly and about 10% of this is introduced to water bodies as effluent from textile industries. Among them, azo, anthraquinone, and phthalocyanine dyes are the most significant that are obtained of production. Crystal violet, ethyl violet, methyl violet 2B, methyl violet 6B, victoria blue B, and victoria pure blue BO are usually existing in the constituents of pen ink dyes. A significant group of nitrogen-including heterocycles applied in the preparation of textile dyes is quinoxaline and its derivatives. It is estimated that up to 50% of the dyes utilized for textile remain as a contaminant in the liquid phase (Benkhaya et al., 2020a). Use of azo dyes in the textile industries in the European Union (EU) is permitted and they are not placed on the list of EU Ecolabel Textile Restricted Substances.

Another use of coloring material is their addition to cosmetics and personal care products formulations for their coloring and decorative goals. These materials can be categorized into pigments (both mineral and organic) and soluble synthetic organic dyes. Pigments stay as particles and are found in toothpaste, shadows eye and decorative makeup and are insoluble in water. In personal care products like creams or shampoos, hydro- or oil-soluble synthetic organic dyes are used. These dyes are very sensitive to UV light, pH, and oxidative or reducing chemicals and consist of carboxylic ($—COO^-Na^+$) or sulfonic ($—SO_3^-Na^+$) groups as their water-soluble part (Guerra et al., 2015).

TABLE 15.1 Classification of dyes in Color Index.

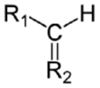
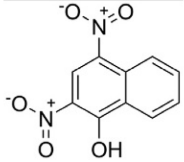
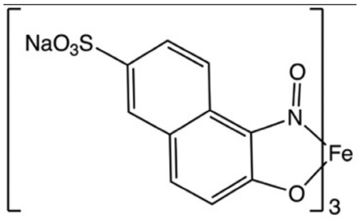
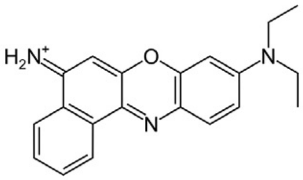
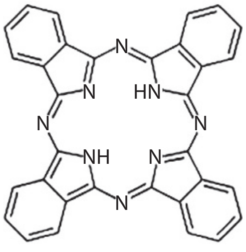
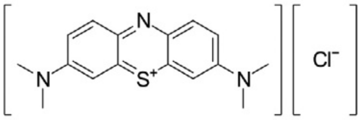
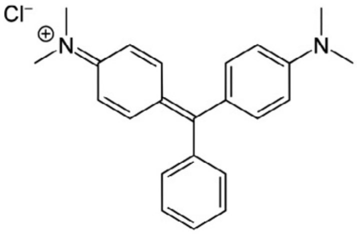
Chemical class	Color Index
Monozo	11,000–19,999
Disazo	20,000–29,999
Trisazo	30,000–34,999
Polyazo	35,000–36,999
Azoic	37,000–39,999

TABLE 15.2 The classes of dyes and their examples based on their structural formula.

Dye class	Color Index Generic Name/ Color Index Constitution Number	CAS No.	Common name	Structural formula of dye	λ_{max} (nm)
Acridine	CI basic orange 14 CI 46005	10127-02-3	Acridine orange		500
Anthraquinone	CI mordant red 3 CI 58000	72-48-0	Alizarin red s		609
Azo	CI solvent yellow 14 CI 12055	842-07-9	Sudan I		476
Azine	CI basic red 5 CI 50040	553-24-2	Neutral red		530
Diphenylmethane	CI basic yellow 2 CI 41000	2465-72-2	Auramine O		432
Indigoid	CI acid blue 74 CI 73015	860-22-0	Indigo carmine		612
Methine	CI disperse blue 74 CI 48480	104137-27-1	Methylidyne		610

Continued

TABLE 15.2 The classes of dyes and their examples based on their structural formula—cont'd

Dye class	Color Index Generic Name/ Color Index Constitution Number	CAS No.	Common name	Structural formula of dye	λ_{max} (nm)
Nitro	CI acid yellow 24 CI 10315	605-69-6	Martius yellow		432
Nitroso	CI acid green 1 CI 10020	19381-50-1	Naphthol green B		714
Oxazine	CI basic blue 12 CI 51180	3625-57-8	Nile blue A		638
Phthalocyanine	CI direct blue 199 CI 74190	12222-04-7	Phthalocyanin, Pigment Blue 16		610
Thiazine	CI basic blue 9 CI 52015	61-73-4	Methylene blue		660
Triphenylmethane	CI basic green 4 CI 42000	2437-29-8	Malachite green		615
Xanthene	CI acid red 52 CI 45100	81-88-9	Rhodamine B		550

λ_{max}, maximum absorption wavelength.

The main route of human exposure to cosmetic dyes is dermal exposure, excluding oral products in which ingestion is the main route. Azo-dyes are the most used dye in cosmetics because of their low price. Their chromophore can be reduced to carcinogenic amines and some investigations emphasized their carcinogenic, genotoxic, and mutagenic effect. Other investigations concerning triarylmethane dyes have reported that these can be found in human blood.

15.4 Sources of azo dyes in the environmental waters and their toxicity to aquatic organisms and human health

Due to the large production and wide use of dyes, these pollutants may enter the aquatic environment. While the tannery and paper industries use huge amounts of water and are accountable for pollution by discharging large volumes of wastewater to the aqueous environment (20% of industrial aqueous contamination is accounted to textile industry), the most significant direct source and dyes in the environment is the textile industry. As an example, the tanneries in the Jammu district, India discharge $9000\,m^3$ of untreated sewage into the Ganges River daily (Hashemi et al., 2018b). Based on the type of fabrics and groups of dyes, wastewater including dye is produced in various dyeing steps and dye loss happens heavily. For example, textile sewage from dyeing cellulose fabrics is mainly consisting of sulfur (10%–40%) and reactive dyes (10%–50%). 200 billion liters of colored effluent is released by the textile industry yearly into the ecosystems and about 280,000 metric tons of dyes are lost yearly, which means unbelievable amounts of dyes are released in water directly (Tkaczyk et al., 2020).

Another source of the dyes in the aqueous media is household wastewater resulting from the disposal of unapplied hair dyeing, colored cosmetics, or household chemical and dye-derived drugs. Another house source of dye compounds is detergents such as shampoos, soaps, or laundry. In additional, some of the dyes such as tartrazine and brilliant blue are food dyes. In sewage treatment plants (STPs), wastewater passes via primary, secondary, and tertiary treatments based on different physical, chemical, and biological processes. The main byproducts of wastewater treatment are sewage sludge, which is stored mainly on landfills, and effluents directly discharged into the aqueous media. These by-products consist of many pollutants including heavy metals, antibiotics, and dyes. Effluent sludge contaminated by dyes may cause groundwater and soil pollution. The usage of sewage sludge as fertilizer and the utilization of raw industrial wastewater to irrigate farmlands is a major soil and crop pollution by dyes (Tkaczyk et al., 2020).

The pharmaceutical factories and hospitals release large volumes of dangerous wastewater that is full of disinfectants, pharmaceuticals, dyes, and pigments. Aquaculture could be another source of dyes in the aqueous media. While the use of malachite green, crystal violet, and methylene blue dyes in the fish industry became illegal, still many aquaculture farms are still using them. The use of pharmaceuticals in the fish industry is unavoidable they are necessary for the prevention and treatment of parasitic, fungal, or bacterial infections in fish (Tkaczyk et al., 2020).

It is well known that dyes have a toxic effect on aquatic life. Novotny et al. (2006) reported (see Table 15.3) the toxicity of azo and anthraquinone dyes on various organisms including bacteria, microalga, and ciliates. Disperse Blue 3 was the most toxic among tested dyes. For *Selenastrum capricornutum*, EC_{50} of the dyes was 0.5 mg/L and for *Vibrio fischeri*, EC_{50} was 488 mg/L (Tkaczyk et al., 2020). The observations indicated that algae were more sensitive to this dye than bacteria. Disperse blue 3 affected and caused growth inhibition and cell deformation of *Tetrahymena pyriformis*. Toxicity of a range of 42 dyes on green algae and daphnia was reported by Croce et al. (2017). Achieved results indicated which algae are more sensitive for the most of 30 selected materials and showed that most of the dyes were toxic to crustaceans (Table 15.3) (Novotny et al., 2006; Croce et al., 2017).

Dyes are applied in human and veterinary medicine in three main application areas such as biological staining, medical therapy, and pharmaceutical colorants (Wainwright, 2011). Dyes are utilized as colorants in the pharmaceutical industry to increase the attractiveness of drugs. Dyes are applied due to their low cost of production and stability. They are commonly added to hard or soft capsules, syrups, tablets, and lozenges (Šuleková et al., 2017). The use is regulated by EU law. Another important application for dyes is as stains in biology where they are classified as anionic (e.g., acid fuchsine), cationic (e.g., Sudan red) or fluorescent (e.g., acridine orange) dyes. Biological staining by dyes is important in diagnostics of fungi, bacteria, protozoa, and virus infections, exemplified with Gram-positive bacteria staining with crystal violet, the most applied dye (Bamfield, 2001). Some of the dyes are utilized as vital stains in some surgical methods, for instance in cancer imaging (e.g., indocyanine green) (Farah et al., 2009). Additionally, dyes including brilliant green and gentian violet are applied in surgical pens (Susarla et al., 2017). In human medical therapy, dyes may be utilized as active pharmaceutical ingredients (where methylene blue is seen in the treatment of methemoglobinemia, malaria (Schirmer et al., 2011), encephalopathy (Pelgrims et al., 2000), and antipsychotic therapy (Wainwright, 2008), aseptic agents (which gentian crystal and methyl violet (Maley and Arbiser, 2013), brilliant green and fuchsin (Balabanova et al., 2003), thionine (Mohr and Redecker-Klein, 2003), and acriflavine (Wainwright, 2008)

TABLE 15.3 List of dyes by aqueous toxicity.

Taxon	Species	Dye name	Class of dye	ErC_{50}/EC_{50} LC_{50} (mg/L)	Toxicological effects
BACTERIA					
Bacteria	*Vibrio fischeri*	Acid orange 7 food yellow reactive black 5 procion yellow procion navy procion crimson	Azo	15.7 22.1 27.5 71 18.9 34.7	–
Bacteria	*Vibrio fischeri*	Remazol brilliant blue R disperse blue 3 reactive orange 16 Congo red	Anthraquinone azo	94 488 1 375 1 623	–
PROTISTS					
Ciliates	*Tetrahymena pyriformis*	Remazol brilliant blue R disperse blue 3 reactive orange 16 Congo red	Anthraquinone Azo	NM[a]	Growth inhibition, rounding off effect on the cells (disperse blue 3), decrease ingestion capability (Congo red, disperse blue 3)
PLANTS					
Algae	*Chlorella vulgaris*	Reactive red 141 basic red 14	Azo methane	95.55 10.88	Decrease dry weight, decrease in cell size, accumulate in cells
Algae	*Selenastrum capricornutum*	Reactive black 5 Acid orange 7 Food red 17 Food yellow 3 Vat green 3	Azo Anthraquinone	29 >100 61 72 5.6	
Algae	*Selenastrum capricornutum*	Remazol brilliant blue R disperse blue 3 reactive orange 16 Congo red	Anthraquinone Azo	81.1 0.5 7.8 4.8	Growth inhibition (Disperse blue 3)
Algae	*Selenastrum capricornutum*	Vat blue 20 vat green 1 vat green 9 acid blue 324	Anthrone Anthraquinone	96.21 142.28 96.48 11.55 123.88	–

TABLE 15.3 List of dyes by aqueous toxicity—cont'd

Taxon	Species	Dye name	Class of dye	ErC_{50}/EC_{50} LC_{50} (mg/L)	Toxicological effects
		acid blue 80 acid violet 48 direct blue 293 acid black 1 acid black 24 acid black 26 acid black 94 acid blue 113 acid brown		102.46 146.77 54.20 67.30 42.99 14.64 78.21 6.32	
		235 acid brown 354 acid green 111 acid green 68 acid orange 33 acid orange 7 acid orange 95 acid red 119 acid red 131 acid red 266 acid red 374 acid yellow 42 acid yellow 49 acid yellow 61 direct blue 71 direct green 26 direct red 227 direct red 23 direct red 81 disperse blue 79 Br disperse blue 79 Cl disperse orange 30 disperse	Azine azo	92.25 71.82 39.05 65.95 56.50 70.17 11.91 84.76 21.79 7.57 77.27 65.13 58.33 66.10 48.94 125.88 106.61 78.44 112.71 127.58 44.90 84.80 116.43 1.12 12.92 135.32 152.76 120.46 11.01	–
		orange 61 mordant yellow 10 mordant black	Sulfur	35.71	

Continued

TABLE 15.3 List of dyes by aqueous toxicity—cont'd

Taxon	Species	Dye name	Class of dye	ErC_{50}/EC_{50} LC_{50} (mg/L)	Toxicological effects
		11 reactive black 5 reactive red 120 reactive red 195 reactive red 83 reactive yellow 15 Sulfur black 1			
Seed plants	*Lemna minor*	Brilliant blue R brilliant red 5 B 150 Yellow GR	Anthraquinone	7 270.3 – –	Growth inhibition
INVERTEBRATES					
Cnidaria	*Hydra attenuata*	Disperse red 1	Azo	1.9	–
Crustaceans	*Astacus leptodactylus*	Remazol brilliant blue R Congo red	Azo	NM	–
Crustaceans	*Ceriodaphnia dubia*	Reactive black 5 acid orange 7 food red 17 food yellow 3 vat green 3	Azo Anthraquinone	25 33 410 250 0.5	–
Crustaceans	*Daphnia magna*	Direct blue 218	Azo	3.6–6	–
Crustaceans	*Daphnia magna*	Disperse red 1 disperse red 13	Azo	0.127 0.0187	–
Crustaceans	*Daphnia magna*	Remazol parrot green remazol golden yellow	Azo	55.32 46.84	–
Crustaceans	*Daphnia magna*	Acid violet 48 acid black 24 acid orange 33 acid orange 7	Anthraquinone Azo	32.85 58.22 22.34 4.27 22.46 65.92 0.55	–

TABLE 15.3 List of dyes by aqueous toxicity—cont'd

Taxon	Species	Dye name	Class of dye	ErC_{50}/EC_{50} LC_{50} (mg/L)	Toxicological effects
		acid orange 95 acid yellow 61 disperse orange 30 disperse orange 61 mordant black 11		3.03 24.32	
Crustaceans	*Daphnia pulex*	Fluorescein phloxine B	Xanthene	337 0.423	Sublethal effect, reduction in reproductive potential
Crustaceans	*Daphnia similis*	Disperse red 1	azo	0.13	–
Crustaceans	*Daphnia similis*	Reactive black 5 acid orange 7 food red 17 food yellow 3 vat green 3	Azo Anthraquinone	36 87 >1000 >1000 6.9	–
Crustaceans	*Desmocaris trispinosa*	Mordant black 17 direct red 2 direct blue 14 reactive red 4 reactive yellow 2	AZO	2.48 4.96 11.33 11.47 732.75	–
Crustaceans	*Moina macrocopa*	Reactive red 141 basic red 14	Azo methane	18.26 4.9	–
VERTEBRATES					
Fish	*Carassius auratus gibelio*	Reactive red 120	Azo	NM	Increase number of micronuclei in erythrocyte cells
Fish	*Catla catla*	Reactive red 120	Azo	NM	Gills damage, kidney dysfunctioning or failure
Fish	*Cirrhinus mrigala*	Bismarck Brown Acid leather	azo	NM	Induce leukocytosis
Fish	*Channa punctatus*	Vat blue 4	Anthraquinone	148	Decrease in lipid and protein content, histopathological changes
Fish	*Cyprinus carpio*	Vat green 1	Anthraquinone	180	Decrease in lipid and protein content, histopathological changes
Fish	*Heteropneustes fossilis*	Malachite green	Triphenylmethane	1	Hyperactivity, erratic swimming, breathing difficulties; liver damage
Fish	*Ictalurus punctatus*	Rhodamine B Fluorescein	Xanthene	526 2267	–

Continued

TABLE 15.3 List of dyes by aqueous toxicity—cont'd

Taxon	Species	Dye name	Class of dye	ErC_{50}/EC_{50} LC_{50} (mg/L)	Toxicological effects
Fish	*Lepomis macrochirus*	Rhodamine B fluorescein	Xanthene	379 3433	–
Fish	*Oncorhynchus mykiss*	Rhodamine B fluorescein	Xanthene	217 1372	–
Fish	*Oreochromis niloticus*	Malachite green	Triphenylmethane	0.437	Respiratory distress, erratic swimming
Fish	*Poecilia reticulat*	Methyl red	Azo	16.6–33.4	Dye deposition on gills and lateral line, blackish–brown spot over the brain
Fish	*Poecilia reticulata*	Methyl red	Azo	27.2	Faster swimming and opercular movements, jumping of fish, poikilocytosis

[a] *Analytical methods:* HPLC-DAD, *high-performance liquid chromatography–diode array detection;* HPLC-PB/MS, *high-performance liquid chromatography–particle beam mass spectrometry;* HPLC-MS/MS, *high-performance liquid chromatography-tandem mass spectrometry;* HPLC-UV, *high-performance liquid chromatography–ultraviolet detection;* HPLC-FLD, *high-performance liquid chromatography–fluorescence detection;* UPLC-MS, *ultra-performance liquid chromatography-mass spectrometry;* ND, *not detected;* NM, *not mentioned.*

and photosensitizers in skin cancer therapy (which apply rose Bengal, methylene blue, toluidine blue (Ormond and Freeman, 2013) and rhodamine (Campolmi et al., 2016).

Some of the dyes are pharmacologically active substances and indicate efficiency in treatment against pathogenic fungi, protozoan ectoparasites, and bacteria. Dyes including acriflavine, methylene blue, and malachite green are applied as disinfectants in ornamental fish disease treatment, especially in water treatment to combat mold infections of eggs or fish (Noga, 2010). The most effective is malachite green that has never been registered as a veterinary medicinal product for food-producing animals because of its carcinogenetic, mutagenic, and teratogenic potential (Tkaczyk et al., 2020). With the reason of the toxic properties of these dyes, they should be applied only in animals not intended for human consumption. But, low cost, effectiveness, and easy availability cause their continued illegal utilization in fish (Mitrowska et al., 2007), shrimp (Uddin and Kader, 2006), and turtle farming (He and Cui, 2016). Other dyes, crystal violet, have been applied in poultry farming for years to control fungi in poultry feeds to prevent feed molding (Clark et al., 1993; Roybal et al., 1989).

The aqueous toxicity on the crustacean *Daphnia pulex* of two xanthene dyes gives details that 0.423 mg/L was LC_{50} for phloxine B and 337 mg/L was for fluorescein. LC_{50} of Rhodamine B and fluorescein on fishes *Lepomis*, *Ictalurus punctatus*, *Macrochirus*, and *Oncorhynchus mykiss* was >100 mg/L. 0.437 and 1 mg/L were LC_{50} of malachite green for *Oreochromic*, *niloticus* and *Heteropneustes fossilis*, respectively. Application of dyes in a textile factory on tadpoles of *Xenopus laevis* was investigated and the most toxic of these materials for tadpoles was astrazon blue FGRL dye that is a composition of azo including basic blue 159 and oxazine such as basic blue 3 dyes by LD_{50} of 0.76 mg/L (Tkaczyk et al., 2020).

15.5 Methods of removal of azo dyes from water, wastewater, and water decolorization

There are a wide variety of techniques used to remove dyes of aqueous sample or sewage. Most of them can be classified as biological, chemical, and physical purification processes. Of the method, absorption is considered to be the most well-known process. Since chemical methods generate foul odor and byproducts and are expensive. Adsorption seems the simplest and fast method to delete the aqueous contaminants. The mechanism of removal by sorbents such as 3A zeolite, alumina, and activated carbon as follows: the sorbent was placed in water media and then the dyes can be absorbed on the adsorbent. Finally, the sorbent was separated from the water sample. The absorbance phenomena are of interest for dye removal due to its low cost and flexibility in design. Moreover, this process does not generate any harmful substances after the removal of the target dyes. The first attempt for applying the adsorption process for the removal of unwanted analytes was started in 1550 BC with Egyptians who applied charcoal to adsorb odorous vapors of wounds and intestines. Phoenicians indicated the application of charcoal filters in 460

BC purify water. For the removal of dyes of different samples, various sorbents have been applied. The commonly used are zeolites which are effective sorbents that can be found in the environment and can also be prepared in the laboratory. Zeolites are highly porous and their charges are negative. Application of 3A zeolite to remove RB is common and the sorbent can remove ~90% of the pollution of industrial wastewater. Application of 3A zeolite in the removal of dyes such as malachite green and RB of environmental water sample was reported with Rahmani et al. (2018). The method was suitable to remove dyes. Also, effective, simple, keeping the experimental cost at a minimum level, reducing time of the experimental cost at a minimum level, reducing the time of experimental investigation were other advantages of the method (Rahmani et al., 2018). The low selectivity was the disadvantage of it. Alumina is a special crystalline gel that is prepared in different sizes and its appearance is granule with a surface area of 200–300 m^2/g. It is a good sorbent for removal (because of high surface area) of dyes such as disperse dyes in water. Silica gel is a porous (advantage of the sorbent) and non-crystalline granule. It has a larger surface area (900 m^2/g) than alumina. The sorbent has no selectivity for dyes (disadvantage of it). Silica gel is synthesized with the coagulation of colloidal silicic acid. A maximum adsorption capacity of 1101 mg/g for modified silica gel was reported for the removal of sulfur dyes of water solutions (Kaykhaii et al., 2018). Since silica gel carbon for dye removal is expensive, some sorbents with features similar to it but environmentally friendly have been applied, such as activated carbon. Activated carbon is the oldest well-known sorbent with quite a high surface area (approximately 200 m^2/g) and can be easily obtained from lignite, coconut shell, wood, and coal. Despite this sorbent is effective; it is not selective (Kaykhaii et al., 2018).

Industrial and wastewater undergo various stages of treatments at STPs to remove harmful compounds from them before their discharge into the environment. Initial treatment of wastewater helps to remove organic and inorganic solids with chemical and physical means such as grinding, sedimentation, and coagulation/flocculation. By sedimentation, suspended materials such as silts and clays settle (chip sedimentation is not effective for the removal of colloidal particles; however, other techniques such as coagulation can be used. Coagulants including alums, ferric sulfate, and ferric chloride are mixed with wastewater to clot and sediment materials that are subsequently accumulated as mud. Coalescence is a suitable technique used in the dye removal of water samples. The goal of biological degradation, generally in use as a secondary step, is the utilization of organic matters in aerobic or anaerobic conditions by using micro-organisms (bacteria, fungi, and algae) under controlled conditions. The disintegration of organic substances occurs via biological processes including biological oxidation and biosynthesis. End-products include minerals, suspended in water solution are discharged with the sewage of biological oxidation. The transformation of dissolved organic particles into dense biomass is due to biosynthesis which can be easily stopped up by sedimentation. Secondary treatment is mainly depending on aerobic conditions where primary effluent is applied. The usual techniques for this purpose are aerated lagoons and activated mud systems. Aerated lagoons are tanks consisting of initial treatment effluent aerated for 3–8 days followed by removal of sludge formed by bacterial biomass. During tertiary treatment, ion exchange, adsorption, reverse osmosis, and advanced oxidation processes (AOPs) are applied to remove dyes. One of the best techniques here is removing dyes by their adsorption of samples. The technique is dependent on the adsorption of samples onto a sorbent. The efficiency of this process is based on many parameters including the interaction between dye and sorbent, size and porosity of sorbent, pH, and temperature. The most effective sorbent is activated carbon but due to its high cost other inexpensive alternative sorbents are obtained from various types of wastes including bamboo. The membrane process is another interesting method that can be used in reverse osmosis mode, where wastewater is pumped via a penetrable membrane that has the capability to retain azo dyes such as acid orange 7 (Pan et al., 2017). Wastewater treatment in anaerobic conditions was insufficient and lead only to partial degradation of azo metabolites (Ekici et al., 2001). AOPs are the most effective of the tertiary treatment techniques and can treat non-easily removable dyes from wastewater (Sharma et al., 2011; Vaiano and Iervolino, 2018). These processes include irradiation operation, electrochemical oxidation, Fenton reactions, ozonation, electrical discharge, sonolysis, and wet air oxidation (Hisaindee et al., 2013; Nidheesh et al., 2018). Their mechanism is based on the generation of highly reactive oxidants that attack pollutants and resulting in their dehydrogenation, redox, and hydroxylation. Oxidation is done until the pollutants are completely demineralized (Nidheesh et al., 2018). One of the best AOPs in the treatment of dye is the Fenton process (a reaction between H_2O_2 and Fe^{2+} salts), which occurs through the electro-Fenton process (reduction of O_2 in the presence of ferrous ion) or by UV degradation in the presence of H_2O_2 (photo-Fenton process) (Sharma et al., 2011; Zaharia and Suteu, 2012). Dyes undergo a transformation in treatment and degradation processes and the compounds have very diversified patterns of transformations kinetics. Some Fenton processes use toxic materials as parent materials, and some may initially be transformed into more toxic products but then be converted to non-toxic products (Bouasla et al., 2010; Garcia-Segura et al., 2011; Vaiano and Iervolino, 2018; Vaiano et al., 2015). Utilization of degradation in biological wastewater is not enough to remove dyes of wastewater mainly because of dye resistance to aerobic biodegradation and lack of necessary enzymes in micro-organisms for dye removing during secondary treatments in STPs (Vaiano et al., 2015). As a result, dyes are not degraded and maybe adsorbed with the mud during primary treatment and secondary degradation (Nidheesh et al., 2018; Zaharia and Suteu, 2012). The amount of mud generated poses a disposal problem thus sludge is often burnt or applied as fertilizer on farmlands (Samer, 2015). Due to this, the terrestrial environment may get contaminated with dyes from STPs. Efficient dye removal from water samples may be achieved only using a combination of biological and physicochemical treatment techniques. It is worth underlining which AOPs constitute a promising approach in the efficient degradation of dyes of wastewater. Also, this technique produces less waste than other available protocols (Ghaly et al., 2013).

15.6 Occurrence, presence Analytical methods (including extraction techniques) for azo dye determination in aquatic samples in various parts of the world

The occurrence of various dyes in the environment including drinking water, rivers, ponds, wastewater, soil environment, sediments, seafood, and fish in various parts of the world are summarized in Table 15.4. In two reports, Ghasemi and Kaykhaii (2016a, b) determined the presence of azo dyes including orange G, methyl orange, acid red 18 (AR), malachite green (MG), crystal violet, and rhodamine B (RB), in tap water and wastewater samples (from the recycling wastewater system of the University of Sistan and Baluchestan (Iran). The reported results showed that there was no dye pollution in both media (Ghasemi and Kaykhaii, 2016a, b). In two studies, Hashemi et al. reported concentration of similar dyes including MG, RB, methyl red (MR), methyl orange (MO), and AR in seawater samples of Chabahar Bay (Iran). Concentrations of these dyes were found to be: 1.1–3.1 μg/L for MR, 1.12–3.50 μg/L for MG, 0.60–2.77 μg/L for RB, 0.5–3.02 μg/L for MO and 0.53–2.87 μg/L for AR (Hashemi et al., 2018a, b, 2019a, b, c).

For the first time, dyes were found in water samples including mud and influents and effluents of sewage treatment plants (STPs) located close to the carpet manufacturing in 1980 with Nelson and Hites who determined leucomalachite green and leucocrystal violet in sediment and soil around to a riverbank where a dyestuff manufacture waste dump was located. The unpremeditated dump caused the permeation of dyes in the soil and river. In 1992, 15 azo dyes were detected in the aquatic environment and sediment in the Yamask a River in Canada and 3 of the dyes were determined as dispersing red 60, disperse blue 26 and disperse blue 79. 2-Bromo-4,6-dinitroaniline (BDNA), a mutagenic product of the cleavage of disperse blue 79, was determined in sediment samples in a concentration range of 100–1900 μg/kg. Dyes were also found in water media in Italy, Brazil, Canada, China, Germany, and Belgium.

Interesting results were reported by Carneiro et al. (2010) who indicated the presence of three azo dyes such as disperse blue 373, disperse orange 37, and disperse violet 93 not only in river water and sediment samples, but also in drinking water samples. The dyes occurrence in the samples was reported to be directly connected to the close location of the textile industry. In addition, to evaluate the possible risk to humans due to consumption of the potentially contaminated drinking water, the treated effluent of the dye processing plant was given to rats. The observation indicated an increased number of abnormal crypts in the colons of the treated animals, which is considered a marker for colon carcinogenesis (Carneiro et al., 2010).

The majority of the textile industry in Brazil is located in Sao Paulo State and causes serious water environment contamination. Zocolo et al. (2015) identified disperse dyes including dispersing red 1, disperse blue 373 and disperse violet 93 in the water of the Cristais and Piracicaba rivers (0.0844–3.45 μg/L) (Zocolo et al., 2015). These dyes were also determined by Vacchi et al. (2017) in other environmental aquatic media of the Piracicaba and Quilombo rivers in a concentration range of 0.01–6.81 μg/L. Other dyes detected in this research are dispersed blue 291, disperse yellow 3, and disperse orange 30 (Vacchi et al., 2017).

Dyes present in the environment can reach other various ecosystems. So far, only Zhou (2001) has indicated dyes passing via different ecological units in the terrestrial environment. Research on dyes occurrence in the vicinity of printing and dyeing plants in China included samples taken from water bodies located near these plants and soil samples that were collected from places where industrial wastewater was applied to irrigate farmlands. The study included the determination of 18 dyes including reactive X-3B red, basic brown, indigo, mordant black 2B red, and basic green. The results indicate serious dye contamination of the local environment in high concentrations. Dyes were detected in water bodies and in surface soils and concentration ranges from 1 to 706,000 μg/L and of 10 to 3,114,000 μg/kg, respectively. Dye-containing wastewater applied to irrigate cultivated lands led to contamination of agricultural soil (Zhou, 2001).

Dyes in soils can be absorbed by cereals (including wheat and rice), fruits, and vegetables. In addition, research on dyes seepage through the soil was conducted. Results indicated which dyes easily and deeply permeate in the soil; based on the type of the soil and selected dyes. For example, in Shaoxing, Keqiao Town (China) reactive X-3B dye was found in pond water in a concentration range of 629–933 μg/L, whereas in surface soils concentrations were

TABLE 15.4 Analytical methods applied for the determination and geographical distribution of azo dyes in various parts of the world.

Matrix	Dyes' name	Extraction method	Analytical instrument	Concentration determined (μg/kg or μg/L)	LOD (μg/L)	Ref.
Drinking water	Disperse orange 37, disperse violet 93, disperse blue 373	–	HPLC-DAD	0.00165–0.00886	4.5–42.0	Carneiro et al. (2010)
Pond water	Azo dyes	–	GC	X-3B: 1–1232 Σ (organic dyes): 6000–706,000	NM	Zhou (2001)
River water	Disperse blue 26, disperse blue 79	–	HPLC-PB/MS	Σ: 3–17	NM	Maguire (1992)
River water	Disperse orange 37, disperse violet 93, disperse blue 373	–	HPLC-DAD	Σ: 0.0118–0.397	4.5–42.0	Carneiro et al. (2010)
River water	Disperse blue 373, disperse red 1, disperse violet 93	–	HPLC-MS/MS	Σ: 0.0844–3.453	0.002	Zocolo et al. (2015)
River water	Disperse blue 291, disperse blue 373, disperse red 1, disperse orange 30, disperse violet 93, disperse yellow 3	–	HPLC-MS/MS	Σ: 0.01–6.81	0.0003–0.0128	Vacchi et al. (2017)
River sediment	Disperse orange 37, disperse violet 93, disperse blue 373	–	HPLC-DAD	Σ: 3.38–41.00		Carneiro et al. (2010)
River suspended particulate matter	Disperse blue 26, disperse blue 79	–	HPLC-PB/MS	Σ: 400–1500		
Celery, lotus root, potato, rice, radish, soybean, watermelon, wheat	Azo dyes	–	GC	Celery: X-3B: Σ (organic dyes): 100–2800 lotus root: X-3B: – Σ (organic dyes): 8300–126,400 potato: X-3B:10–100 Σ(organic dyes): 4300–29,700 rice: X-3B:10–2300 Σ(organic dyes): 600–7900 radish: X 3B: 10–2800 Σ(organic dyes): 16,300–39,900 soybean: X-3B: 700–1600 Σ(organic dyes): 10–5700 watermelon: X-3B: 6700–11,300 Σ(organic dyes): 60,300–78,700 wheat: X- 3B: –Σ (organic dyes): 100–2800	NM	Zhou (2001)
Seawater	Methyl red	Molecularly imprinted polymer in pipette-tip	Spectrophotometry	1.2–3.1	0.5	Hashemi et al. (2018a)
Seawater	MO and AR	Pipette tip micro-solid phase extraction (sorbent = graphite based magnetic $NiFe_2O_4$ decorated exfoliated)	Spectrophotometry	1.1–2.4 (MO)–1.0–2.6 (AR)	0.9 and 1.0	Hashemi et al. (2019b)

Continued

TABLE 15.4 Analytical methods applied for the determination and geographical distribution of azo dyes in various parts of the world—cont'd

Matrix	Dyes' name	Extraction method	Analytical instrument	Concentration determined (μg/kg or μg/L)	LOD (μg/L)	Ref.
Aqueous samples	Orange G, MO, and AR	Micro-cloud point extraction	Spectrophotometry	0	0.6–111	Ghasemi and Kaykhaii (2016a)
Tap water samples	MR and MO	Mixed hemimicelle solid-phase extraction (sorbent = magnetic halloysite nanotubes and ionic liquids)	HPLC-DAD	ND	0.042	Liu et al. (2018)
Textile wastewater	Disperse blue 183, CI disperse blue 79, CI disperse red 82, CI disperse red 65, CI disperse yellow 211 and CI disperse orange 25	–	UV-vis spectrophotometry	0	NM	Sxahin et al. (2009)
Food samples	Ponceau 4R and Sudan Orange G	Sea sponge column	UV–vis spectrophotometer	7–131 μg/g for ponceau 4R and 28–136 for Sudan Orange G	0.002 μg/L and 1.9×10^{-4} μg/L for Ponceau 4R and Sudan Orange G dyes, respectively	Karatepea et al. (2016)
Diesel fuel	Blue dye Solvent Blue 35	SPE (sorbent = modified silica)	HPLC with UV-vis detection	200	10	Tomić et al. (2018)
Wastewater	Nylosan Red N-2RBL-azo and Optilan Blue MF-GL-anthraquinone	SPE cartridges (sorbent = C18)	LC-MS	12.16 for Nylosan Red N-2RBL and 42.00 for Optilan Blue MF-GL	0.285 for Nylosan Red N-2RBL and 0.433 for Optilan Blue MF-GL	Copaciu et al. (2013)
River water	Disperse blue 1, disperse blue 3, disperse blue 7, basic red 9, basic violet 14, disperse blue 102, disperse blue 106, disperse blue 124, disperse yellow 1, disperse yellow 3, disperse yellow 9, disperse yellow 39, disperse yellow 49, disperse brown 1, disperse red 1, disperse red 11, disperse red 17, disperse orange 1, disperse orange 3, disperse orange 11 and disperse orange 37	SPE (sorbent = magnetic chemically modified graphene oxide)	LC-MS	7.02–11.2 ng/L	0.3–10.2 ng/L	Zhao et al. (2016)

1800–3400 μg/kg. The dye also permeated the soil and was found at the depth of 35–65 cm at a concentration of 600 μg/kg. Reactive X-3B dye was also detected in crops (rice, 50–600 μg/kg, root vegetable (radish, 1200–2800 μg/kg) and cucurbit vegetables (watermelon, 6700–11,300 μg/kg) (Zhou, 2001).

Dye-containing industrial wastewater is difficult to treat with commercially available techniques and the problem has been well known for years (Tkaczyk et al., 2020). Research on wastewater from different dye manufacturing plants indicated the hazardous potential of effluents because of the presence of 314 chemical compounds, of which 32 have mutagenic activity (Alaimo et al., 1990). Oliveira et al. (2007) conducted a study on the presence of azo dye in raw effluents of a dye processing plant where dyes including disperse blue 373 and disperse orange 37 were found in the concentration range of 57.9–316 μg/L. Moreover, treated effluent still contained dyes in a range of 67–126 μg/L (Oliveira et al., 2007). Results of Lou et al. (2018) who investigated wastewater from textile industry for the presence of dyes found out that these samples contained dyes including disperse brown 1, disperse red 1, disperse red 17, disperse orange 3, disperse orange 37/76, disperse yellow 1, disperse yellow 49 in the concentration range of 12–428 μg/L (Lou et al., 2018). Khan et al. (2019) tested wastewater of different industries for malachite green. The dye was found in wastewater from paper (620 μg/L), printing (790 μg/L), and textile (1680 μg/L) industries. Moreover, wastewater of laundries also contained malachite green (1320 μg/L) (Khan et al., 2019).

So far, dyes including disperse blue 291, disperse blue 373, disperse red 1, disperse violet 93, rhodamine B, rhodamine 6G were found in treated effluents (Chiang et al., 2011; Vacchi et al., 2017; Zocolo et al., 2015). Also, dyes including disperse orange 37, disperse violet 93, and disperse blue 373 were obtained in sewage sludge produced with an STP in Brazil (Carneiro et al., 2010). In 2008, insufficiently treated municipal sewage effluents were the reason for media pollution of wild eels with malachite green, crystal vio, and their leuco form as triphenylmethane dyes in the vicinity of STPs in Berlin accumulation. It was the first report on pollution of wild fish caused by the legal utilize of dyes generally applied illegally in aquaculture (Schuetze et al., 2008a, b).

In 2013, malachite green was detected in natural surface water media in Germany. The dye was obtained in suspended particulate matter and sediments in a concentration range of 4.7–543 μg/kg of various water sites in Germany (Ricking et al., 2013). After that, a large-scale research performed in Belgium found out that more than 77% of wild fish were dye contaminated, mainly with malachite green, crystal violet, brilliant green, Victoria blue B, and Victoria pure blue BO (Reyns et al., 2014). All these research studies show which dyes are mostly detected in aquatic ecosystems.

Till today various analytical techniques have been utilized for the determination of azo dyes in various environmental samples as shown in Table 15.4. The detection methods include spectrophotometry and chromatography. Since azo dyes have an intense color due to their high extension coefficient in the visible region of light, they can be easily determined using a simple photometric device. However, for the detection of trace amounts of these pollutants in complex matrices, a sample preparation procedure has to be done before instrumental detection. Solid-phase extraction (SPE), liquid-liquid extraction (LLE), and cloud point extraction (CPE) are commonly in use for the clean-up of dyes from various complex matrices.

One of the most widely used sample preparation techniques is SPE based on adsorption of dyes on a solid phase allowing for their effective extraction. Solid-phase extraction (SPE) is an extractive method in which dyes (target compounds, such as congo red, Sudan dyes, sunset yellow, allure red, tartrazine, ponceau 4R, Sudan orange G, methylene blue, rhodamine B, malachite green, and brilliant green) that are dissolved or suspended in a liquid sample are separated from other compounds according to their physical and chemical properties. Analytical laboratories utilize SPE to concentrate and purify samples for analysis. First, the column is conditioned by a suitable solvent (Fig. 15.1, condition step). Then, in the loading step the sample including desired and undesired analytes passed on sorbent and compounds absorbed. In the washing step, the sorbent is washed by suitable solvent for deleting undesired analytes. In the elution step, the sorbent on column SPE is eluted by elution solvent and then send for analysis (Fig. 15.1, elution step) (Alexandra Sandoval Riofrio, 2016). Ponceau 4R and Sudan Orange G dyes utilizing a glass column (10 cm length and 1.0 cm diameter) filled with 500 mg of sponge as a solid phase (Karatepea et al., 2016). In another research, the SPE method employing 3A zeolite as a sorbent was used for the removal of RB and MG dyes of water samples. The size of the column is not mentioned (Rahmani et al., 2018). Also, SPE on the silica-based solid-phase extraction was applied for the separation of Solvent Blue 35 dye in diesel fuel. Since the selection of elution solvent is very important for successful SPE, mixtures of various solvents were investigated. Among studied elution solvents, the mixture composed of chloroform and heptane in the volume ratio of 1:0.75 (v/v) provided the best recovery (Tomić et al., 2018). Copaciu et al. (2013) reported a method for the analysis of two dyes including Nylosan Red N-2 RBL-azo and Optilan Blue MF-GL-anthraquinone) in wastewater with SPE. Four types of Strata SPE cartridges (500 mg/6 mg C_{18}-U C_{18}-E, WAX/NH_2 (best cartridges) and SAX with particle size 10 μm and 25 cm × 0.46 cm size of column). Desorption of the analyte of the column was performed by 1% ammonia: ethanol (1:1, v/v) mixture (Copaciu et al., 2013).

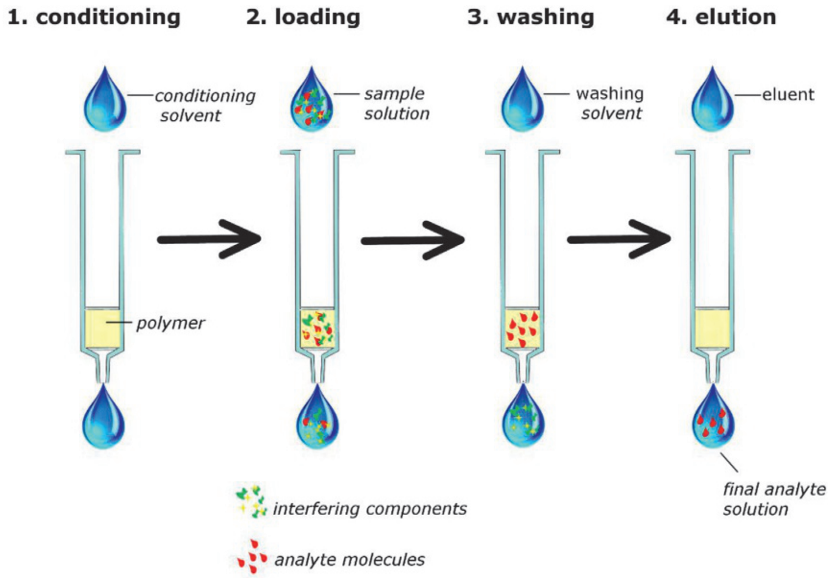


FIG. 15.1 General steps for SPE (Alexandra Sandoval Riofrio, 2016).

Pipette tip microsolid-phase extraction (PT-μSPE) is a miniaturized version of the general SPE. The dyes are micro-extracted by repeated sample loading and elution. PT-μSPE provides attributes such as low cost, simplicity, significant reduction in the consumption of reagent, time, adsorbent and organic solvents, good extraction factors, and possibility of integrating extraction. PT-μSPE of the dyes with MIP and their analysis was performed. MIPs have been employed in solid-phase extraction (SPE) of dyes in real media because of their low cost, stability, ease of preparation, and high selectivity. In MIP, cross-linked polymers are formed with free-radical copolymerization of functional monomers with an excess of cross-linker around template dyes (target analyte). After elution of dyes, the MIP can be used as a selective binding structure for these analytes. MIP was synthesized by the bulk polymerization method by adding template molecules (each dye), monomer, ethylene glycol dimethacrylate, and initiator dissolved in porogen. Next, the solution was deoxygenized utilizing a nitrogen stream and then polymerization was performed in a water bath (Hashemi et al., 2018a, b, 2019a).

Graphene oxide/zinc oxide nanocomposite-based pipette tip micro-solid-phase extraction for the analysis of dyes in water media. Graphene including a single carbon atom densely packed into a benzene ring structure used as an adsorbent for μSPE because of its high sorption capacity, chemical stability, strong hydrophobicity, excellent thermal stability, high specific surface area, and large delocalized π-electron system. Graphene oxide (GO) has many oxygen atoms in the basal plane and edge of its sheets in the form of epoxy, hydroxyl carboxyl groups and can bind positively charged organic analytes via coordination and electrostatic interaction. Zinc oxide nanoparticles (ZnO NPs) using different morphologies have various desirable attributes consist of high electron mobility, good transparency, wide bandgap, and ambient temperature luminescence, and are semiconductors. Subsequently, binding of ZnO NPs on GO obtains a higher absorbance capacity and surface area that can be applied for the extraction, enrichment, and removal of dyes (Hashemi et al., 2018b).

Pipette tip solid-phase extraction for dyes analysis in water matrix utilizing graphite-based magnetic $NiFe_2O_4$ decorated exfoliated as adsorbent was carried out. Expanded graphite (EG) is a highly porous worm-like and very light particle and is a sorbent of growing significance due to numerous actual and potential applications. The adsorbing spaces of graphite can be divided into two kinds. One is the absorbance space constructed utilizing graphite on each other and the second is the pores in each graphite worm-similar segment. Expanded graphite is well adsorbent by high capacity because of its pore particle. EG has high selectivity extraction for dyes. Combining magnetic materials on EG is practiced that could yield new composites of high value for absorption of dyes because of having high adsorption capacity and simple handling to extraction efficiency. $NiFe_2O_4$ is one of them that has high electrical resistivity, low magnetic coactivity, low eddy current loss, and excellent chemical stability and can be used for absorbance of dyes (Hashemi et al., 2019b).

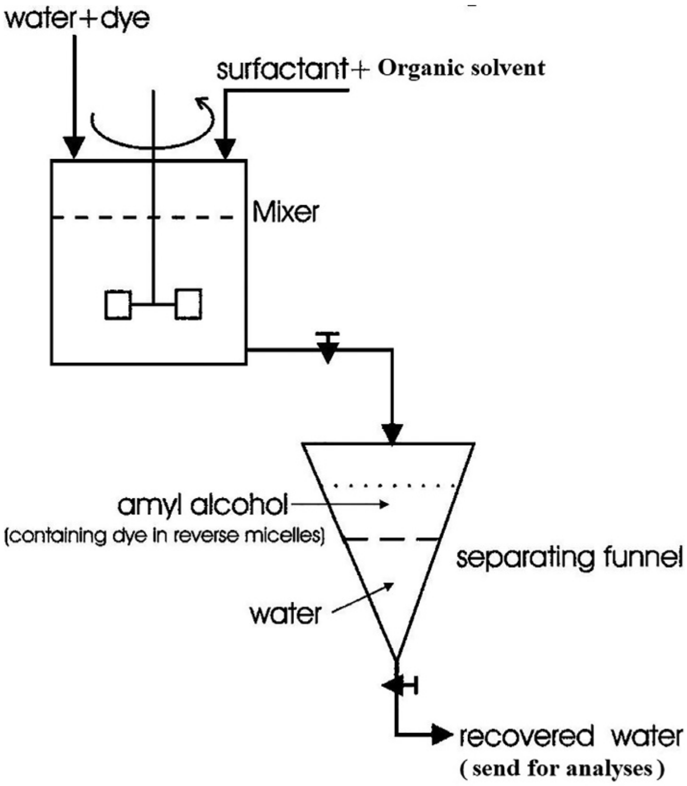


FIG. 15.2 Schematic setup for liquid-liquid extraction for the removal dye from water (Pandit and Basu, 2002).

Optimization of metal-organic framework (MOF) based pipette-tip solid-phase extraction of dyes of aqueous media was applied. Three-dimensional crystalline porous particles, various geometries, and functional compounds within the channels/cavities exist in MOF. MOF is prepared by adding organic linker and metal salts, often under hydrothermal or solvothermal factors. The unique properties of MOFs are adjustable pore sizes and controllable structural characteristics, extraordinarily large porosity, high surface areas, and low density and can be applied for removal, separation, absorption, and extraction of different analytes such as dyes (Hashemi et al., 2019c). Obtained MOF has a specific surface area of 3000 m^2/g. Liquid-liquid extraction or solvent extraction is a technique where the separation of dyes depends on their relative solubility in two immiscible liquids, generally water (polar) and an organic solvent (non-polar) are used (Fig. 15.2).

This is a transfer of one or more species (dyes such as methyl orange, methylene blue, astacryl blue BG, and astacryl golden yellow) from one liquid into other liquid phases usually of water to an organic solvent such as amyl alcohol (Muthuraman, 2011). A liquid-liquid extraction technique was employed for purifying and enriching the sample of dyes including Para red, Sudan red G, Sudan I, Sudan II, Sudan III, Sudan IV, Allura Red AC, Red 2G, Azorubine, and Fast Green FCF) (Long et al., 2011; Smirnova et al., 2021).

In recent years, various methods of microextraction (the techniques applied to minimal volume of organic solvent) have been applied for enrichment goals of dyes. Among the various microextraction, dispersive liquid-liquid microextraction (DLLME) indicates excellent enrichment characteristics and the technique is very fast. In DLLME, target compound extraction is practically instantaneous due to the enormous contact surface between the receptor and donating solvents. To obtain dispersion, a third solvent can be applied in both solvents. In DLLME, after adding a proper volume of extraction and dispersive solvent in the aquatic sample, a cloudy solution consists of three solvents (water solution, extraction, and dispersive solvent) is formed. After extraction of the target analyte of the water sample in fine droplets of extraction solvent, the technique is followed by centrifugation, the organic phase was taken and injected into the analytical instrument for analysis (Fig. 15.3a) (Nassiri et al., 2018; Mirmoghaddam et al., 2019; Ghasemi and Kaykhaii, 2016a, b). Cloud point extraction (CPE) is a simple method for the pre-concentration of target analytes such as azo dyes (Sudan I, II, III, and IV; red B; black B; red G; metanil yellow and rhodamine B) (Ates et al., 2011). In CPE a surfactant is an extracting media instead of organic solvents. The method consists of three steps which

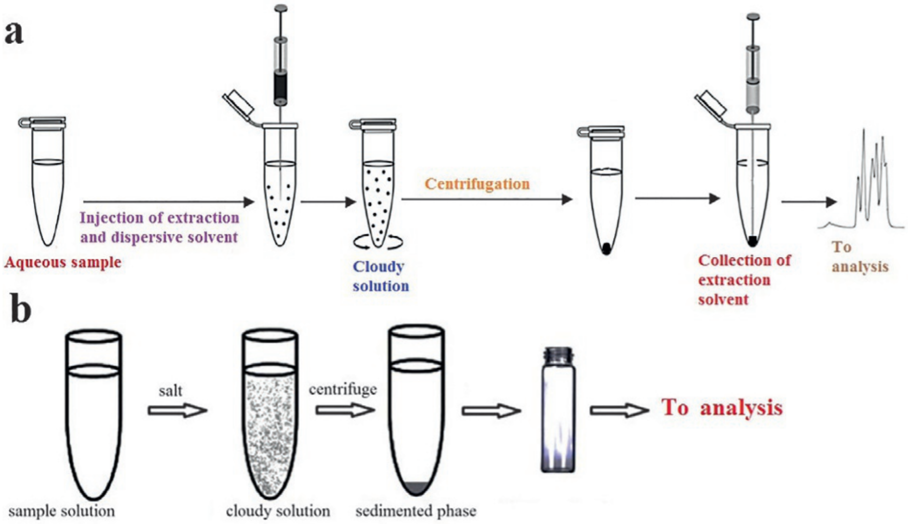


FIG. 15.3 DLLME (A) and MCPE (B) setup (Ghasemi and Kaykhaii, 2016b; Mirmoghaddam et al., 2019; Nassiri et al., 2018).

include—mixing surfactant with water samples—for creation of cloudy solution and micelle with the surfactant, collect one of the pre-concentrated micellar phase of water sample with centrifugation. CPE has some disadvantages such as large volumes of the water sample and it is time-consuming. In addition, there is the necessity of diluting the pre-concentrated micellar phase prior to analysis and it not in agreement because in comparison with microextraction methods, CPE consumed larger volumes of solvent. Micro cloud point extraction (MCPE) technique and minimization of volume of solvent. The MCPE is fast, simple, inexpensive, and compliant with green chemistry principles. The MCPE setup is indicated in Fig. 15.3 (Ghasemi and Kaykhaii, 2016a, b).

An effective mixed hemimicelles magnetic solid-phase extraction (MHMSPE) depending on magnetic halloysite nanotube (MHNTs) and ionic liquid (IL) is used for the extraction of dyes in the water sample. In the MHMSPE, the creation of C_{16} mim Br by mixed hemimicelles on the surface of MHNTs leads to the retention of dyes with strong hydrophobic, p-p, and electrostatic interactions. Halloysite nanotubes (HNTs) is clay aluminosilicate mineral that chemical properties are similar to the structure of kaolinite. A greener, rapid, sensitive, and simple SPE technique is of the advantages of the method (Liu et al., 2018).

The template-free fabrication of three-dimensional hierarchical nanostructures, i.e., three-dimensional interconnected magnetic chemically modified graphene oxide (3D-Mag-CMGO), via a simple and low-cost self-assembly process applying one-pot reaction depend on solvothermal technique. 3D-Mag-CMGO nanocomposite has been synthesized with a simple and environmentally friendly one-pot technique. The excellent 3D-Mag-CMGO nanocomposite that is applied as an adsorbent in Mag- dispersive solid-phase extraction (dSPE) protocol, has been employed for the extraction of dyes of water. The method was simple, rapid magnetic separation, a high enrichment factor, acceptable recoveries, and environmentally friendly. The disadvantage of the method was the low productivity of 3D-Mag-CMGO (Zhao et al., 2016).

This chapter falls under the section on fate and occurrence of emerging pollutants within aquatic ecosystems with other chapters, e.g., Ajayi et al. (2022), Cristale (2022), Vizioli et al. (2022), Galhardi et al. (2022), Madikizela et al. (2022), Mashile et al. (2022), Montagner et al. (2022), Moodley et al. (2022), Ntshani and Tavengwa (2022), Sanganyando and Kajau (2022), and Yardy et al. (2022) that aims to make an understanding of the different emerging pollutants within the aquatic environment.

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CHAPTER

16

Flame retardants in tropical regions: Sources, fate, and occurrence in the aquatic environment

Joyce Cristale

16.1 Flame retardants and environmental concern

Flame retardant is the term used for substances that are incorporated in materials with the aim to decrease the ease of ignition, flame spread, and smoke released when the material is exposed to an ignition source. Flame retardants are used in the construction of materials such as the polymers used in electric and electronic equipment, construction and furniture materials, polyurethane foam, textiles, and some chemical formulations (pants, resins). The flame retardants can be classified as reactive or additive. Reactive flame retardants are added during the polymerization processes and are chemically bound to the final material. Additive flame retardants are added after the polymerization process and are physically attached to the final material, occupying spaces in the tridimensional polymeric chain and interacting with the material through intermolecular forces (see Sanganyando and Kajau, 2022, Chapter 7; Tavengwa and Dalu, 2022, Chapter 1).

Flame retardants have been used since ancient times, with their use recorded as early as approximately 450 BC, when alum was used by Egyptians to reduce wood flammability. Other examples are the use of clay and gypsum to reduce the flammability of theater curtains (1638), borax and ferrous sulfate used in textiles and wood (1735), and the use of alum for reducing balloon flammability (1783) (Hindersinn, 1990). With the development of petroleum-based polymers and the vast application possibilities that emerged, the development of new substances was necessary to produce fire-safe products. Currently, the most commonly used flame retardants include organic and inorganic substances of different chemical structures based on bromine, chlorine, phosphorus, boron, nitrogen, and metallic hydroxides. The choice of the most suitable flame retardants will depend on the material, application type, and required performance.

Although the use of flame retardants represents an advance in terms of fire safety, which is associated with a reduction in deaths and injuries related to accidental fires, some substances deserve attention due their toxicity to humans and biota, bioaccumulation potential and persistency. The high production volumes and wide use of flame retardants has resulted in the ubiquitous presence of some families of substances in all the environmental compartments, with the aquatic system being particularly sensible to these substances. Some flame retardants are classified as persistent organic pollutants (POPs) by the Stockholm Convention, and the signatory countries are expected to make efforts to monitor and protect the environment from these substances, in addition to restricting or eliminating their use (Sharkey et al., 2020). Other flame retardants not included in the POPs list also deserves attention due to their presence in the aquatic environment and their potentially toxic properties. Four flame retardant families of environmental concern are described below.

16.1.1 Polybrominated diphenyl ethers

The polybrominated diphenyl ethers (PBDEs) are a family of additive flame retardants used in many construction and building, furniture, vehicle, and electrical and electronic equipment (EEE) applications. According to the number of bromines (ranging from 1 to 10) and their position in the aromatic rings of the molecule, a total of 209 substances are

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possible. A numerical-based nomenclature has been used to refer to each PBDE congener, which consists of the term "BDE" plus an identification number. For example, the substance 2,2′,4,4′,5 pentabromodiphenyl ether ($C_{12}H_5Br_5O$) is called BDE-99, the substance 2,2′,4,4′,6 pentabromodiphenyl ether ($C_{12}H_5Br_5O$) is called BDE-100, and the decabromodiphenyl ether ($C_{12}Br_{10}O$) is called BDE-209. During the synthesis reaction, some structural configurations are mostly formed, resulting in a lower number of PBDE congeners present at high concentrations in commercial formulations (Alaee et al., 2003). Three main formulations were marketed, which are classified according to the bromination degree of the most abundant substances, i.e., penta-BDE, octa-BDE, and deca-BDE.

The penta-BDE formulations contain BDE-47 (38%–42%), BDE-99 (45%–49%) and BDE-100 (8%–13%) as the main constituents, while BDE-153, BDE-154, and BDE-85 are minor constituents (2%–5%) (La Guardia et al., 2006). This formulation was mainly used in polyurethane foam for furniture, seat cushions, mattresses, and rigid insulation. Other applications include epoxy resins, laminates, coatings, adhesives, and unsaturated polyester (WSU, 2006).

The octa-BDE formulations have a variable composition according to the manufacturer. The formulation DE-79 (Great Lakes Chemical Corp., United States) presents BDE-183 as its major component (approximately 40%) followed by BDE-197 (22%), while BDE-196, BDE-207, BDE-153 are present at lower concentrations (9%–12%). Regarding Bromkal 79-8DE (Chemische Fabrik Kalk, Germany), the major constituent is BDE-209 (49.6%), while BDE-183, BDE-197, BDE-207, BDE-203, and BDE-206 are present at lower concentrations (8%–12%) (La Guardia et al., 2006). Octa-BDE formulations were most used in acrylonitrile-butadiene-styrene (ABS) and high impact polystyrene (HIPS), which are typically used in electronic enclosures, kitchen appliance casings, and automobile trim. Other uses include thermoplastic elastomers, nylon, polyolefins, polyamide, and polybutylene terephthalate (WSU, 2006).

The deca-BDE formulation contains BDE-209 (91%–96%) as the principal component, and the minor constituents are BDE-206 and BDE-207 (2%–5%). Deca-BDE is mainly used in HIPS for electric and electronic enclosures, with some use in textiles and construction materials. This formulation was also used in nylon, unsaturated polyester, epoxy, polypropylene, polybutylene terephthalate, low-density polyethylene, ethylene-propylene terpolymer, and ethylene-propylene-diene rubber (WSU, 2006).

PBDEs are toxic to humans and wildlife, persistent, bio-accumulative, and can undergo long-range transport, resulting in their ubiquitous presence in the environment. Due to these characteristics, the production and use of PBDEs were banned in several countries worldwide. In 2004, the tetra- and pentabromodiphenyl ether constituents of penta-BDE commercial formulations, as well as the hexa- and heptabromodiphenyl ether components of the octa-BDE formulations were classified as POPs and listed in Annex A of the Stockholm Convention. Recently, in 2019, deca-BDE was also listed in the Stockholm Convention (Sharkey et al., 2020).

16.1.2 Hexabromocyclododecane

Hexabromocyclododecane (HBCDD) is a substance with the molecular formula $C_{12}H_{18}Br_6$ that consists of a cyclic carbon structure containing six bromine atoms. There are 16 possible stereoisomers for HBCDD, but three main diastereomers (α, β, γ) are the most abundant and are commonly found in the commercial mixtures. The compositions of HBCDD formulations vary depending on the manufacturer and consist of 70%–95% of γ-HBCDD and 3%–30% of α- and β-HBCDD. HBCDD is an additive flame retardant mainly used in expanded polystyrene (EPS) and extruded polystyrene (XPS) insulation boards. Other uses of HBCDD include back-coatings in textiles, HIPS, latex, adhesives, and paints. Thus, materials containing HBCDD include insulation boards used in building and transport vehicles, textiles used in furniture, vehicle interiors, mattresses, wall coverings, and HIPS used in electric and electronic appliances (UNEP, 2010). HBCDD is one of the most produced flame retardants worldwide and is considered a ubiquitous environmental contaminant. In 2013, HBCDD was listed in Annex A of the Stockholm Convention (Sharkey et al., 2020).

16.1.3 Chlorinated paraffins

Chlorinated paraffins (CPs) are complex mixtures of chlorinated *n*-alkanes with the chemical formula $C_xH_{(2x-y+2)}Cl_y$. The commercial formulations consist of mixtures of alkanes with different chlorine content (30%–70% by weight) and carbon-chain lengths (from 10 to 30 carbon atoms). These substances are classified as short-chain chlorinated paraffins (SCCPs; C10–C13), medium-chain chlorinated paraffins (MCCPs; C14–C17), and long-chain chlorinated paraffins (LCCPs; >C17). The properties of CPs vary according to the chain length and chlorination degree, conferring to these substances a versatility that allows their use for multiple purposes, and consequently, CPs are present in a wide range of consumer goods. CPs are used in natural and synthetic rubbers to meet the flammability standards required for some applications (e.g., conveyor belting, cable covers, industrial roller coverings, pipe seals, industrial sheeting, etc.). CPs are used as flame retardants in textiles, paints, coatings, adhesives, and sealers. These substances are also used as plasticizers, softeners, antiincrusting agents, fatliquoring agents, waterproofing materials, etc. CPs are used in metalworking fluids for lubricating and cooling effects and as lubricant additives (UNEP, 2019).

Some CPs have been recognized as persistent contaminants distributed throughout all the environmental compartments, and SCCPs deserve more attention than MCCPs and LCCPs in terms of bioaccumulation and toxicity. Consequently, in 2017, the SCCP mixtures with a chlorine content greater than 48% by weight were listed in Annex A of the Stockholm Convention. Other CP mixtures containing SCCPs at concentrations higher than 1% (by weight) were also listed (UNEP, 2019).

16.1.4 Organophosphate esters

Organophosphate esters (OPEs) are a family of substances used as flame retardants and plasticizers in a wide variety of materials and chemical formulations (Wei et al., 2015). These substances deserve attention due to their high production volumes, their wide environmental distribution, and their potentially toxic properties, including neurotoxicity, endocrine disruption, and carcinogenicity (Chokwe et al., 2020a). The OPEs can be classified as a type of phosphorus-based flame retardant, a major group that includes different chemical substances containing phosphorus (e.g., red phosphorus, phosphonates, phosphinates, phosphates, etc.). These substances can be classified according to the type of carbon chain bound to the phosphate group, and the most studied substances are described below:

Haloalkyl phosphates: The main OPEs in this group contain chlorine or bromine in the alkyl chain, resulting in flame retardants that combine the action modes of phosphorus- and halogen-based substances. Among the chloroalkyl-OPEs, the main substances used are tris(2-chloroethyl) phosphate (TCEP), tris(2-chloroisopropyl) phosphate (TCIPP), and tris(1,3-dichloroisopropyl) phosphate (TDCIPP). TCEP is mostly used in furniture and construction materials based on polyurethane, polyacrylates, polyester resins, and other polymers. TCEP is also used in textiles, lacquers, and paints. TCIPP is most often used in the rigid and flexible polyurethane foam used in construction (e.g., rigid insulation) and furniture (e.g., upholstery, matrasses, and textiles). TDCIPP is mainly used in the polyurethane foam in transport vehicles, with some use in furniture. Tris(2,3-dibromopropyl) phosphate (TDBPP) is a bromoalkyl-OPE used in textiles.

Aryl-OPEs: Triphenyl phosphate (TPHP), tris(methylphenyl) phosphate (TMPP), also called tricresyl phosphate, and 2-ethylhexyl diphenyl phosphate (EHDPHP) are flame retardants with plasticizer properties that are used in polyvinylchloride (PVC) (e.g., wire cables), adhesives, coatings, rubbers, and other polymers. These compounds are also used in hydraulic fluids.

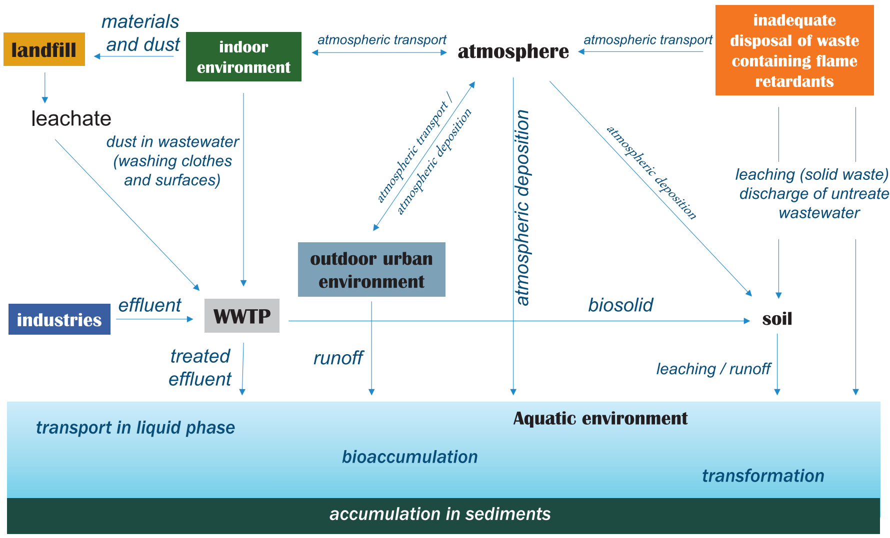
Alkyl-OPEs: Used as plasticizers with flame retardants properties. The most used substances include tris(ethyl) phosphate (TEP), tris(butyl) phosphate (TNBP), tris(isobutyl) phosphate (TIBP), tris(2-ethylhexyl) phosphate (TEHP), and tris(2-butoxyethyl) phosphate (TBOEP), which are used in a wide variety of materials and chemical formulations, including cellulose-based plastics and synthetic resins, hydraulic fluids, rigid polyurethane foam, unsaturated polyester resins, PVC, lacquers, paints, glues, and rubbers. The TBOEP is also often used in floor waxes and vinyl flooring.

16.2 Sources and fate of flame retardants in the aquatic environment

The sources of flame retardants in the aquatic environment can be both punctual and diffusive. The main punctual sources include discharges from the industries that produce/use these substances, discharges from wastewater treatment plants (WWTPs), and emissions from inadequately disposed wastes. The diffuse sources are mainly related to emissions from materials containing flame retardants and their subsequent transport in the atmosphere. Once the FRs reach the aquatic environment, their fate will depend on the physical and chemical properties of the substances, which will affect their water/suspended particle partition, biological, photo, and chemical degradation, the degree that these compounds can be transported far away from their sources, and their accumulation potential in sediments and organisms. Fig. 16.1 illustrates the sources and distribution pathways of flame retardants in the aquatic environment.

Release from consumer goods: The additive flame retardants are not chemically bound to the host materials, and these substances interact with the material through intermolecular forces. Since this type of interaction is weak, these compounds are continuously released from the material to the surrounding environment during the entire life-cycle of the consumer product. The transferring of flame retardants from the material to the surrounding environment can occur by different mechanisms, such as material-to-dust migration (direct contact), abrasion, volatilization, and leaching

FIG. 16.1 Sources and distribution of flame retardants in the aquatic environment.



(Rauert et al., 2015, 2016; Stubbings and Harrad, 2018). As a consequence of these mechanisms, and due to the high number of consumer goods (e.g., EEE, upholstered furniture, rugs, curtains) and construction materials containing additive flame retardants, these substances are present at ng/g to μg/g levels in indoor dust (e.g., homes, workplaces, schools, and public places). In addition, the worldwide occurrence of these substances in house dust evidence that consumer products containing flame retardants are globally distributed, including in tropical countries (Brits et al., 2019, 2020; Cristale et al., 2018; Li et al., 2019).

Indoor dust particles are transferred from the indoor environment to sewages as a result of washing clothes and indoor surfaces, which is an important source of flame retardants to WWTPs and receiving waters (Schreder and La Guardia, 2014). The indoor-to-outdoor transferring of dust, suspended particles, and substances in the gaseous phase are important sources of semivolatile organic compounds to the outdoor environment, including flame retardants (Harrad, 2019). Once in the atmosphere, flame retardants can reach the aquatic environment by wet and dry deposition. Concerning urban surface waters, stormwater runoff also contributes to the input of these substances by carrying the flame retardants from outdoor dust to receiving waters (Burant et al., 2018; Gasperi et al., 2014).

The final disposal of consumer goods and construction materials containing flame retardants is also an important issue since these substances continue to be released after their disposal. The inadequate final disposal of consumer products (e.g., mattresses, upholstered furniture) can lead to groundwater contamination, as observed for chloroalkyl-OPEs in Brazil (Cristale et al., 2019). Municipal dumping sites were suggested as significant sources of PBDEs in tropical Asian countries (Cambodia, Vietnam, Indonesia, India, and Malaysia) due to the higher concentrations observed in the soil from these locations (ranging from 0.12 to 430 ng/g dw) in comparison to reference sites (Eguchi et al., 2013). Other studies performed in tropical countries also evidence the presence of flame retardants in landfill leachate (Cristale et al., 2019; Kwan et al., 2013a; Odusanya et al., 2009; Sibiya et al., 2019), which can be a source of these substances in the aquatic environment if not properly treated.

Effluents: Domestic and industrial effluents are significant sources of flame retardants in the aquatic environment. Concerning conventional secondary treatment in WWTPs, more lipophilic substances, such as PBDEs, HBCDD, and CPs, tend to be associated with the particulate phase and accumulate in the sludge, frequently resulting in significant removals from the aqueous phase (higher than 80%) (Been et al., 2018; Ichihara et al., 2014; Wang et al., 2019a). On the other hand, the behavior of OPEs in WWTPs vary according to the chemical structure of the substance; chloroalkyl-OPEs are hardly removed from the aqueous phase, alkyl-phosphates are partially removed, while aryl phosphates and hydrophobic alkyl-phosphates (e.g., TEHP) are more efficiently removed (Cristale et al., 2016; Woudneh et al., 2015). Although some compounds have high removal rates in WWTPs, total removal is not achieved using conventional primary and secondary treatment, and even effluents containing flame retardants at low concentrations (pg/L to ng/L) are a significant source of these compounds in the aquatic environment due to high discharges rates. It is also important to mention that many tropical countries do not have in their territories a wide sewage collection and treatment system, which can aggravate the flame retardant contamination of their water bodies even more. In addition, the flame retardants accumulated in sewage sludge reach agricultural lands when the biosolids are applied as a soil amendment (McGrath et al., 2020). Although the impacts of this practice as flame retardant sources are still to be elucidated, some studies indicate the potential for aquatic contamination due runoff and leaching (Gottschall et al., 2017; Gray et al., 2017).

Partition and transformation: PBDEs are hydrophobic compounds, and the higher the bromination level is, the higher their hydrophobicity is. As a result, the low brominated PBDEs are more easily transported far away from their sources in the dissolved phase than are the high brominated PBDEs, which have a tendency to accumulate in the sediments. However, suspended particles have an important role in the transportation of high brominated PBDEs (e.g., BDE-209) in the water column (Zarnadze and Rodenburg, 2008). PBDEs have a high affinity to dissolved organic carbon (DOC), which implies that, to some extent, DOC can stabilize the high brominated PBDEs in the water column, contributing to the transportation of PBDEs in the water body (Wang et al., 2011). The PBDEs absorb ultraviolet radiation and undergo photodegradation, thus generating lesser brominated PBDEs (due to the sequential loss of bromines) and other substances, such as polybrominated dibenzofurans (PBDFs), hydroxylated PBDEs, hydroxylated PBDFs, and bromophenols (Qu et al., 2017; Wang et al., 2018). Lower brominated PBDEs tend to have lower photodegradation rates than high brominated PBDEs (Eriksson et al., 2004). This fact is of concern regarding the high brominated congeners, such as BDE-209, that can generate lower brominated products in the aquatic environment, which can be more mobile, persistent, and toxic than the precursor substance. Regarding PBDEs accumulated in sediments, anaerobic biodegradation is expected to be the most important transformation route, which can also generate lesser brominated BDEs (Tokarz et al., 2008; Chen et al., 2015).

The HBCDD is also a hydrophobic compound, and similarly to PBDEs, this compound tends to accumulate in sediments and adsorb onto suspended particles. The α-, β-, and γ-HBCDD diastereomers have different physicochemical properties that affect their distribution in the aquatic compartment. The α-HBCDD tends to be the most abundant in the water phase, attributed to its higher water solubility, while γ-HBCDD is the less soluble diastereomer and is often the most abundant in sediments. In addition, α-HBCDD presents a higher bioavailability and bioaccumulation potential, and the percentual contribution of α-HBCDD in relation to the γ- and β-diastereomers tends to increase with the trophic levels (Wu et al., 2010). Hydrolysis is not considered an important transformation route since the HBCDD concentration is expected to be low in the dissolved phase due to its low water solubility and high affinity to organic carbon. In addition, the HBCDD molecular structure lacks hydrolyzable functional groups (UNEP, 2010). HBCDD biodegradation in sediments occurs at higher rates in anaerobic than in aerobic conditions (Davis et al., 2005).

The CPs are hydrophobic substances, and high concentrations in the dissolved phase are not expected. Despite the tendency for accumulation in sediments, SCCPs and MCCPs were detected in the water phase at ng/L to μg/L levels in urban rivers under high anthropogenic pressures (Wang et al., 2019b). Hydrolysis is not expected to be an important transformation route for CPs in the aqueous phase, and slow biodegradation is expected for the CPs accumulated in sediments (UNEP, 2015). Thus, due to the high persistence and high hydrophobicity of PBDEs, HBCDD, and CPs, the sediments can be considered a sink of these flame retardants in the aquatic environment.

Concerning the OPEs, their behavior in the aquatic environment varies substantially among compounds due to their different chemical structures and physical-chemical properties. TEP, TCEP, and TCIPP have water solubility higher than 1 g/L and $\log K_{ow} < 3$, and transportation in the aqueous phase tends to occur. TDCIPP, TBOEP, TNBP, and TIBP can be considered as having intermediate hydrophobicity ($3 < \log K_{ow} < 4$), while aryl phosphates (e.g., TPHP, EHDPHP, TMPP) and long-chain alkyl-phosphates (e.g., TEHP) are hydrophobic, tending to be associated with particles and sediments (Cristale et al., 2013). Although OPEs are susceptible to undergoing hydrolysis, it is expected to occur at a slow rate in environmental conditions (EURAR, 2008). OPEs can undergo indirect photolysis in the aquatic environment, and the photodegradation rates follow the trend aryl-OPEs > alkyl-OPEs > chloroalkyl-OPEs, with TCEP being the most resistant compound (Cristale et al., 2017). Chloroalkyl phosphates are resistant to biodegradation, and aryl phosphates tend to be degraded easier than alkyl phosphates (Reemtsma et al., 2008). Thus, chloroalkyl phosphates are the most persistent OPEs in the dissolved phase of aquatic systems, followed by alkyl phosphate, while aryl phosphates are more readily transformed by biotic and abiotic mechanisms.

16.3 Environmental analysis

The PBDEs, HBCDD, CPs, and OPEs are contaminants widely present in the aquatic environment, as evidenced in different environmental studies performed in areas affected by punctual sources (e.g., points downstream from WWTP discharge points, urban and industrial areas, etc.) and/or areas under low anthropogenic pressure (e.g., national parks, polar regions). The highest levels occur in urban and industrial areas, but these substances have also been detected in remote zones, evidencing their long-range transport (Klinčić et al., 2020; Pantelaki and Voutsa, 2019; van Mourik et al., 2016). Monitoring studies have been conducted using grab and passive sampling of waters and sediments. Since these flame retardants can bio-accumulate in aquatic organisms, analyses of biological samples (plankton, fish, mussels, etc.) have been used to evaluate the degree of contamination of a location and to provide information regarding the exposure of aquatic organisms. Flame retardants are present in indoor environments, including vehicles and laboratories, and thus, the collection and manipulation of environmental samples must be performed with care to avoid contamination. Field blanks and procedural blanks are necessary to evaluate if contamination is occurring during the collection and extraction of samples. Some precautions can be taken to avoid this contamination, such as the use of high purity solvents, baking glass materials and filters at high temperatures (>400°C), and solvent-rinsing glassware and sorbents before use. In this section, an overview of the most used techniques for extraction and analysis of flame retardants in environmental matrices is presented.

The analysis of flame retardants in aqueous samples (e.g., river water, seawater, wastewater) generally requires extraction and preconcentration to allow the detection of these substances at levels ranging from pg/L to μg/L according to the solubility of the analyte and the matrix type. The most used technique is solid-phase extraction (SPE) due to its efficiency in retaining the analytes, removing interferents from the matrix, and its versatility in terms of sorbents (e.g., C18, hydrophilic-lipophilic balance—HLB, etc.) and configurations (e.g., cartridge, disks). In addition, solid-phase extraction has been used for the simultaneous extraction of a large number of compounds, including different flame retardant families, saving time and costs and allowing a comprehensive contamination assessment. SPE cartridges based on HLB, Amberlite XAD-2, C18, and Strata-X (polymeric reversed-phase) sorbents have been used for the extraction of brominated and organophosphate flame retardants (Chokwe et al., 2015; Cristale et al., 2013; Gustavsson et al., 2018; Khan et al., 2016; Lorenzo et al., 2016). Liquid-liquid extraction (LLE) using organic solvents has also been successfully used for extracting flame retardants from water and wastewater. Dichloromethane was used for the extraction of PBDEs, CPs, and OPEs (Daso et al., 2013; Lee et al., 2018; Zeng et al., 2011), and toluene was efficient for the extraction of several OPEs (TIBP, TNBP, TCIPP, TDCIPP, TPHP), except for TCEP (Andresen et al., 2004), and hexane was efficient for the extraction of SCCPs (Rubirola et al., 2018). Miniaturized methods, such as solid-phase microextraction (Kaziur-Cegla et al., 2020; Lana et al., 2010) and liquid-liquid microextraction (Chang et al., 2016), have also been used.

The extraction of flame retardants from sediments and biotic matrices is performed using organic solvents and with the assistance of different techniques to enhance the extraction efficiency. Soxhlet extraction is a classic technique that has been used for the extraction of PBDE, HBCDD, CPs, and OPEs. The disadvantages of the Soxhlet extractor are that it consumes large amounts of solvents (frequently >200 mL) and requires a long extraction time (typically >6 h). Ultrasound-assisted extraction (UAE), microwave-assisted extraction (MAE), and pressurized liquid extraction (PLE) have also been largely used (Lorenzo et al., 2018; Yuan et al., 2019).

Together with target compounds, other substances are extracted from the matrix during the extraction of sediments and biological tissues, frequently causing interferences in the chromatographic analysis. Examples of extractives that need removal are sulfur from sediments and sewage sludge and lipids from biotic matrices. Thus, a clean-up step after extraction is necessary. Sulfur can be removed by adding copper powder before or after extraction (Chokwe et al., 2019; Ferrari et al., 2019). Concerning the elimination of fat, both destructive and nondestructive methods can be used. Many halogenated organic compounds, such as PBDEs, HBCDD and CPs, are stable under strong acid conditions, and sulfuric acid treatment is a destructive clean-up technique that has been largely used for removing fat and other organic interferents. For this, sulfuric acid is added to the sample extract, followed by sequential LLE and centrifugation steps (Chokwe et al., 2020b; Polder et al., 2008). Another option is using a column containing silica impregnated with sulfuric acid (Wu et al., 2020; Krätschmer et al., 2019). OPEs are not stable under strong acid conditions and so the use of sulfuric treatment is not recommended. Gel Permeation Chromatography (GPC) has been successfully used for the elimination of fat and other interferents from sediments and biological matrices (Lorenzo et al., 2018). SPE clean-up is also widely used for environmental samples, with the aim of retaining as many interferents as possible in the sorbent, while eluting the target substances. Concerning the analysis of flame retardants, the most used clean-up sorbents are florisil, silica, alumina, PSA, and HLB, which are placed in glass columns or cartridges (Iqbal et al., 2017; Pantelaki and Voutsa, 2019).

The principal instrumental technique used for flame retardant determination in environmental samples is gas chromatography (GC) or liquid chromatography (LC) coupled with mass spectrometry (MS) due to their high separation efficiency and detection selectivity. Both techniques have been used for the flame retardant families considered in this chapter, but GC-MS is more frequently used for PBDEs and CPs, while both techniques (GC-MS and LC-MS) are widely used for HBCDD and OPEs (see Kebede et al., 2021, Chapter 5; Kumar et al., 2022, Chapter 6). Concerning HBCDD, the LC-MS methods using reversed-phase columns (e.g., C18) allow chromatographic separation of α-, β-, γ-HBCDD diastereomers, while a limitation of the GC methods is the impossibility of separating HBCDD isomers due to the interconversion of HBCDD diastereomers above 160°C (Covaci et al., 2007; Köppen et al., 2008).

A variety of mass spectrometers differing in terms of resolution, ionization mode, and mass analyzer type have been used for the determination of flame retardants in environmental matrices. Regarding GC, other detectors have also been used, such as electron capture detector (ECD) for halogenated flame retardants, and nitrogen phosphorus detector (NPD) for OPEs, but these detection techniques are less selective, and identification confirmation using MS is recommended. More information regarding sample preparation and instrumental techniques for the determination of flame retardants in environmental matrices can be found in the reviews reported in the literature (Brits et al., 2016; Covaci et al., 2007; Pantelaki and Voutsa, 2019; Yuan et al., 2019).

16.4 Occurrence of flame retardants in the aquatic environments of tropical countries

Data on the occurrence of flame retardants in tropical aquatic environments are limited, although after the 2010s an increase in studies addressing this issue has been observed. Inadequate management of residues containing flame retardants is still frequent in tropical countries. Thus, knowledge on the occurrence of these substances in these countries is important to identify their sources and environmental risks, with the aquatic systems deserving attention because flame retardants can reach this compartment by different routes. In this section, the levels and profiles of flame retardants in the aquatic environments of tropical countries are reviewed, including biotic and abiotic matrices. The countries that have a portion of their territories in the tropics were included, except China and Australia.

16.4.1 Brominated flame retardants in abiotic matrices

16.4.1.1 Africa

Discharges from WWTPs are important sources of flame retardants in the aquatic environment. In a WWTP equipped with a membrane bioreactor in Cape Town, South Africa, the total levels observed for the eight PBDE congeners ($\sum PBDE_8$) ranged from 369 to 4370 ng/L in raw water, from 19.2 to 2640 ng/L in the secondary effluent, and from 90.4 to 15.100 ng/L in the final effluent (after disinfection unit), while the concentrations in sewage sludge ranged from 13.1 to 652 ng/g dry weight (dw) (samples were collected bimonthly between April 2010 and February 2011) (Daso et al., 2012). In this study, the most abundant PBDE congeners were BDE-209 (deca-BDE formulation), BDE 47, and BDE 99 (penta-BDE formulation). Another study demonstrated the impact of WWTP effluents on the PBDE levels in surface water. Surface water samples collected from the Diep River (South Africa) presented mean $\sum PBDE_8$ concentrations of 2.60, 4.83, and 4.29 ng/L upstream, at the discharge point and downstream from a WWTP (Daso et al., 2013).

In surface water samples from different rivers in South Africa, the $\sum PBDE_6$ concentration (BDE-209 not evaluated) ranged from 90 to 260 ng/L in the water samples and from 10.5 to 24.5 ng/g wet weight (ww) in the sediment samples collected from the Vaal River in locations downstream from WWTP discharges. Concerning the HBCDD, the concentrations ranged from 510 to 1770 ng/L in the water samples and from 15 to 52 ng/g ww in the sediment samples (Chokwe et al., 2015).

The occurrence of brominated flame retardants in sediments from inland and coastal areas of Durban Bay and in 13 rivers in the eThekwini metropolitan municipality (South Africa) was assessed. A total of 45 sediment samples were analyzed, and PBDEs were detected in 93% of the samples, while HBCDD was detected in 69% of the samples. Concerning the distribution profile of PBDEs, BDE-209 (deca-BDE) was detected in 93% of the samples and penta-BDE congeners were detected in 67% of the samples. Concerning HBCDD, γ-HBCDD was the most abundant diastereomer (57.1%), followed by α-HBCDD (33.3%) and β-HBCDD (9.6%). In most of the sediment samples, the $\sum PBDE$ levels exceeded the $\sum HBCDD$ levels, with median concentrations of 1390 ng/g total organic carbon (TOC) and 349 ng/g TOC, respectively. This study evidenced the influence of anthropogenic sources on the contamination level, since the highest concentrations of brominated flame retardants were observed in sites near urban and industrial areas (e.g., automotive industries, electric and electronic equipment waste recycler), while the lowest concentrations were observed in rural areas. The levels observed in this South African region were considered high in comparison to other parts of the world, such as San Francisco Bay (United States of America) and the Pearl River Estuary (China) (La Guardia et al., 2013).

In Uganda, the presence of PBDEs was verified in surface sediment samples collected from Murchison Bay in Lake Victoria, a site affected by industrial and municipal discharges from Kampala City. The $\Sigma PBDE_{11}$ (BDE-209 not included) levels ranged from 0.0608 to 0.179 ng/g dw, with BDE-47 being the most abundant compound, followed by BDE-99 and BDE-100 (Ssebugere et al., 2014).

The PBDEs were also detected in sediments from the Congo River Basin (Democratic Republic of Congo), a relatively pristine place. Samples were collected from the mid-Congo between Kisangani and Bumba and included two locations in the Congo River (near Isangi and Kisangani) and three tributaries (Itimbiri, Aruwimi, and Lomami). Concentrations of $\sum PBDE_8$ up to 1.9 ng/g dw were observed, with BDE-209 being the most dominant compound (about 90% of $\sum$PBDE) followed by BDE-47 (5% of $\sum$PBDE) and BDE-99 (3% of $\sum$PBDE) (Verhaert et al., 2013).

16.4.1.2 America

In sediments from the Saibro Lagoon (Ribeirão Preto, Brazil), located in a recharge area of the Guarani Aquifer (one of the world's largest freshwater reservoirs), $\sum PBDE_{10}$ levels up to 5.4 ng/g dw were observed. The most abundant compound was the BDE-47, which was responsible for more than 50% of the total PBDE content, while BDE-209 was not detected in any of the samples (Ferrari et al., 2019). The PBDEs in the area were attributed to well-known PBDE sources, such as atmospheric deposition and sewage discharges, and to the evidenced inadequate waste disposal habit of the surrounding population, as half a ton of garbage (mostly furniture and electronics) was removed from the lake some weeks after sampling. The BDE-47 (BDE-209 not assessed) was also the most abundant PBDE congener detected in Paranoá Lake (Brasília, Brazil) (Annunciação et al., 2017).

The PBDEs were detected in all the sediment samples (river areas, estuary, and coastal bays) from the Biobio Region (South Central Chile). The concentrations ranged from 0.03 to 2.43 ng/g dw ($\sum PBDE_6$), and the highest levels were observed in the Lenga estuary and Coronel bay, where a high contribution of the penta-BDE formulation was observed on the contamination profile (Barón et al., 2013). This same study also analyzed sediments from 13 sites under the influence of the Magdalena River at its intersection with the Caribbean Sea (Colombia). Although a lower frequency of detection was observed (5 out of 13 samples), the concentrations in the Colombian sediment samples were higher than those of the Chilean samples, with levels up to 143 ng/g dw, and the only compound detected was BDE-209, which indicates a great contribution of the deca-BDE formulation in the area. The high levels observed were attributed to the discharge of untreated domestic waste, the influence of industrial zones, and inadequate e-waste management (Barón et al., 2013).

The occurrence of PBDEs in sediments of coastal lagoons in Yucatan state (Mexico) was studied. A total of 40 samples were collected in 2012 in Ria Lagartos, Ria Celestun, Bocas de Dzilam, and Chelem. The HBCDD levels ranged from 0.035 to 7.457 ng/g dw and $\sum PBDE_{11}$ ranged from 117.63 to 428.588 ng/g dw, with BDE-209, BDE-100, BDE-47, and BDE-99 being the most abundant congeners. The highest levels were observed in Ria Lagartos and Chelem attributed to their higher water residence times that are 450 and 400 days, respectively (Valenzuela-Sánchez et al., 2018). In Lake Chapala (Central Mexico), 39 PBDEs were determined in sediment core and surface sediment samples but only lower brominated congeners were detected, such as BDE-28, BDE-47, BDE-99, and BDE-100. The BDE-47 was the only PBDE detected in all core sections (ranging from 0.2 to 2.5 ng/g dw) and in surface sediments (up to 0.6 ng/g dw) (Ontiveros-Cuadras et al., 2019).

The occurrence of PBDEs in the water phase was reported for the Mendoza River Basin (Argentina), with total PBDE levels up to 2.4 ng/L and with BDE-47 as the most abundant PBDE congener (Lana et al., 2010).

16.4.1.3 Asia

A study evaluated the occurrence of 23 PBDEs in 44 sediment samples collected between 2000 and 2010 from canals and rivers of highly populated urban areas in the following tropical countries in Asia: Lao PDR, Cambodia, Vietnam, India, Indonesia, Thailand, the Philippines, and Malaysia. Marine sediments were collected from the Philippines and Japan. The $\sum PBDE_{23}$ levels varied greatly among the sampling points and ranged from 0.83 (Lao PDR) to 3140 ng/g dw (Philippines), while in the marine sediments from Japan (Tokyo), it ranged from 34.1 to 465 ng/g dw. The most abundant PBDE congener was BDE-209, accounting for 43%–97% of total PBDE content, and higher levels were observed in the Philippines, Thailand, Cambodia, and Malaysia. Penta-BDEs were also detected in sediment samples but at lower levels than deca-BDE. The occurrence of BDE-209 debromination was indicated in this study, which was attributed to the different (higher) ratios observed for BDE206/209, BDE207/209, and BDE208/209 in the samples in comparison to that observed for the deca-BDE formulation (Kwan et al., 2013b).

The PBDEs were evaluated in sediments samples collected in 2014 from Thane creek (Mumbai, India). The $\sum PBDE_{15}$ concentrations ranged from 15.98 to 132.72 ng/g dw, and the most abundant compound was BDE-209, followed by BDE-47 (Tiwari et al., 2018).

The occurrence of PBDEs (BDE-47, 99, 100, 153, 154, and 183) was evaluated in the dissolved and particulate phases of seawater samples collected between 2011 and 2012 from coastal areas of Singapore Island (east coast, Johor Strait, Jurong Island, and Pasir Ris). The BDEs 47, 99, and 100 were occasionally detected in the dissolved and particulate phases, with concentrations up to 0.009 ng/L in the dissolved phase and up to 0.186 ng/L in the particulate phase (Zhang et al., 2015).

16.4.2 Brominated flame retardants in biotic matrices

Compared to aquatic abiotic samples, a higher number of studies evaluated the occurrence of brominated flame retardants in biotic matrices. Different abiotic matrices were studied, including bird and crocodile eggs, and the tissue of mussels, fish, birds, and cetaceans.

16.4.2.1 Africa

Two different studies concerning bioaccumulation of brominated flame retardants in fishes from the Vaal River (South Africa) were reported. The first study evaluated the levels of PBDEs and HBCDD in the muscles of fish (common carp) collected in 2013. The levels of PBDEs (BDE-209 not evaluated) ranged from 4.63 to 33 ng/g lipid weight (lw), with the most abundant compounds being the congeners of the penta-BDE formulation (BDE-47 and 99), and the levels of HBCDD ranged from 10 to 13 ng/g lw (Chokwe et al., 2015). A second study, regarding samples collected in 2017, evaluated the PBDE levels in the fish muscles of different species, i.e., moggel (*Labeo umbratus*), mudfish (*Labeo capensis*), common carp (*Cyprinus carpio*), and catfish (*Clarias gariepinus*). BDE-209 was the most abundant compound in common carp (57.5%, up to 8.51 ng/g ww) and catfish (52.1%, up to 12.08 ng/g ww) but was not detected in the other species. On the other hand, penta-BDEs presented a high contribution in mudfish (56%) and moggel (28%), and lower contributions in carp (14%) and catfish (23%). Several reasons can be related to the different PBDE patterns observed for the different fish species observed in this study, including differences in the PBDE metabolization, age, and lipid content of the species (Chokwe et al., 2020b).

The PBDEs were also detected in fish samples from Tanzania, including farmed fish (milkfish—*Chanos chanos*) collected from Unguja Island, Pemba Island and Mtwara (Tanzania mainland), and wild fish (mullet—*Mugil cephalus*, and milkfish) collected from the ocean in sites close to the sampled fish farms. PBDEs were detected in 29 out of the 32 farmed fish samples at $\sum \text{PBDE}_{11}$ levels ranging from 0.01 to 0.39 ng/g ww. Concerning wild fish, PBDEs were detected in 100% of samples ($n = 15$) and $\sum \text{PBDE}_{11}$ levels ranged from 0.01 to 0.24 ng/g ww. The most abundant and frequently detected compounds were BDE-47 (>80%), BDE-209 (>60%) and BDE-100 (>27%). HBCDD was detected only in four wild fish samples (mullets from Pemba Island) at levels up to 0.86 ng/g ww (Mwakalapa et al., 2018).

In Uganda, the occurrence of PBDEs in Nile perch (*Lates niloticus*, top-predator species) and Nile tilapia (*Oreochromis niloticus*, detritivorous) collected from the Murchison Bay (Lake Victoria) was studied. The $\sum \text{PBDE}_{11}$ (BDE-209 not included) concentrations ranged from 0.0593 to 0.495 ng/g ww, with BDE-47 and BDE-99 being the most abundant compounds, as also observed for sediment samples collected from the same region (Ssebugere et al., 2014). Another study reported PBDE levels in invertebrate (*Caridina africana*, *Macrobrachium* sp.) and fish samples (*Marcusenius* sp., *Schilbe marmoratus*, *Schilbe grenfelli*, *Synodontis alberti*, *Brycinus imberi*, *Distichodus fasciolatus*) collected from the Congo River Basin, and also in apple snail samples (*Lanistes* cf. *ovum* and *Pila* sp.) purchased from the local population. The $\sum \text{PBDE}_7$ (BDE-209 not included) up to 0.11 ng/g ww was observed in invertebrate samples, and levels up to 0.11 ng/g ww was observed in fish samples, with BDE-99 being the most abundant compound, followed by BDE-47 and BDE-154 (Verhaert et al., 2013).

Birds are exposed to flame retardants through their diet, accumulating these substances in adipose tissues, and females transfer part of this contamination to their eggs. Thus, the analysis of flame retardants in bird eggs provides information on environmental contamination and the exposure level of birds to these contaminants. Table 16.1 summarizes the levels of PBDEs and HBCDD in bird eggs (aquatic, marine, and terrestrial species) from South Africa reported in different studies. Penta-BDEs, octa-BDEs, and deca-BDEs were detected in bird eggs from South Africa, but the distribution profile varied according to the bird species (Polder et al., 2008; Quinn et al., 2020). The detection of brominated flame retardants in the different studies shows the ubiquitous presence of these contaminants in South Africa, and the concentration in bird eggs from areas under high anthropogenic pressure tends to be higher than that in more remote areas. The concentration and distribution profile of these flame retardants in bird eggs differed according to the species, which is related not only to the degree of environmental contamination but also to differences among species regarding feeding habits, the position in the food web, migratory behavior, and metabolization of flame retardants. It is interesting to notice that both Polder et al. (2008) and Quinn et al. (2020) observed higher concentrations of brominated flame retardants in the eggs of the African sacred ibis, attributed to the dietary habits of this species. Besides insects, frog, and fish, this bird is adapted to a scavenging diet in urban areas, feeding in localities where

TABLE 16.1 Concentrations of PBDEs and HBCDD in bird eggs from South Africa.

Sampling site (date)	Common name (scientific name)/feeding habitat	*n*	Compound	mean	median	min	max	(Ref.) Concentration unit
Parys (2004–05)	African darter (*Anhinga rufa*)/ Aquatic	14	∑PBDE[a]	17		7	40	(Polder et al., 2008) ng/g lw
			∑HBCDD	3		< LOD	11	
	Reed cormorant (*Phalacrocorax africanus*)/Aquatic	3	∑PBDE[a]	14		8.8	22	
			∑HBCDD	< LOD				
	Cattle egret (*Bubulcus ibis*)/ Mainly terrestrial	9	∑PBDE[a]	3.7		< LOD	8.9	
			∑HBCDD	< LOD				
	African Sacred ibis (*Threskiornis aethiopicus*)/ Aquatic and terrestrial	2	∑PBDE[a]	228.5[b]		61	396	
			∑HBCDD	37.9		4.8	71	
Barberspan (2004–05)	Cattle egret (*Bubulcus ibis*)/ Mainly terrestrial	11	∑PBDE[a]	2.3		< LOD	13	
			∑HBCDD	< LOD				
Koppies (2004–05)	Crowned plover (*Vanellus coronatus*)/Aquatic and terrestrial	1	∑PBDE[a]	120				
			∑HBCDD	1.6				
Koppies (2004–05)	Little grebe (*Tachybaptus ruficollis*)/Aquatic	1	∑PBDE[a]	19				
			∑HBCDD	< LOD				
Velddrif (2004–05)	White-fronted plover (*Charadrius marginatus*)/ Aquatic and marine	1	∑PBDE[a]	7.1				
			∑HBCDD	< LOD				
Velddrif (2004–05)	Kelp gull (*Larus dominicanus*)/ Aquatic and marine	1	∑PBDE[a]	9.4				
			∑HBCDD	< LOD				
Limpopo Province (2009–10)	Gray heron (*Ardea cinerea*)/ Aquatic	1 p.s.	∑PBDE[c]			3.1		(Bouwman et al., 2013) ng/g ww
	Cattle egret (*Bubulcus ibis*)/ Mainly terrestrial	3 p.s.	∑PBDE[c]			< LOD	0.7	
	House sparrow (*Passer domesticus*)/Terrestrial	6 p.s.	∑PBDE[c]			< LOD	2.6	
Penguin eggs/Marine Robben Island (2011 – 12)	10		∑PBDE[d]	2.3	0.034	0.18	20	(Bouwman et al., 2015) ng/g ww
		10	∑HBCDD	0.12	0.12	0.1	0.13	
Bird Island (2011–12)	Penguin eggs/Marine	10	∑PBDE[d]	0.41	0.38	0.21	0.71	
		10	∑HBCDD		0.15			
Bird Island (2011–12)	Kelp gull (*Larus dominicanus*)/ Aquatic and marine	1	∑PBDE[d]		2.3			
		1	∑HBCDD		0.34			

TABLE 16.1 Concentrations of PBDEs and HBCDD in bird eggs from South Africa—cont'd

Sampling site (date)	Common name (scientific name)/feeding habitat	*n*	Compound	mean	median	min	max	(Ref.) Concentration unit
Bird Island (2011–12)	Cape gannet (*Morus capensis*)/ Marine	1	$\sum$PBDE[d]		0.33			
		1	$\sum$HBCDD		< LOQ			
Industrial center: Sasolburg, Vanderbijlpark, Soweto, Kempton Park, and Pretoria (2008–09)	Sacred ibis (*Threskiornis aethiopicus*)/Aquatic and terrestrial	16	$\sum$PBDE[e,b]	50	43	3.6	221	(Quinn et al., 2020) ng/g ww
			$\sum$HBCDD	2.7[b]	2.8	0.92	4.8	
	Cattle egret (*Bubulcus ibis*)/ Mainly terrestrial	6	$\sum$PBDE[e,b]	5.8	5.8	1.9	9.6	
			$\sum$HBCDD	0.32[b]	0.15	0.15	1.17	
	African darter (*Anhinga rufa*)/ Aquatic	13	$\sum$PBDE[e,b]	8.1	4.2	2.0	20	
			$\sum$HBCDD	1.7[b]	0.56	0.15	9.6	
	White-breasted cormorant (*Phalacrocorax carbo*)/Aquatic	4	$\sum$PBDE[e,b]	6.2	6.2	4.2	8.1	
			$\sum$HBCDD	0.62[b]	0.61	0.31	0.96	
	Heron sp./Aquatic	6	$\sum$PBDE[e,b]	18	13	2.2	52	
			$\sum$HBCDD	0.27[b]	0.15	0.15	0.61	
	Crowned lapwing (*Vanellus coronatus*)/Terrestrial	6	$\sum$PBDE[e,b]	4.6	4.2	3.0	0.40	
			$\sum$HBCDD	0.22[b]	0.15	0.15	0.40	
	Red-knobbed coot (*Fulica cristata*)/Aquatic	6	$\sum$PBDE[e,b]	42	8.7	6.1	208	
			$\sum$HBCDD	0.76[b]	0.37	2.2	0.15	
	Cape turtle dove (*Streptopelia capicola*)/Terrestrial	1	$\sum$PBDE[e,b]		11			
			$\sum$HBCDD		0.34			
	Cape sparrow (*Passer melanurus*)/Terrestrial	3	$\sum$PBDE[e,b]	23	14	13	44	
			$\sum$HBCDD	0.37[b]	0.37	0.36	0.39	
	Southern masked weaver (*Ploceus velatus*)/Terrestrial	4	$\sum$PBDE[e,b]	51	26	3.5	150	
			$\sum$HBCDD	0.59[b]	0.37	0.33	1.3	

LOD, limit of detection; *LOQ*, limit of quantification; *lw*, lipid weight; *n*, number of samples analyzed; *p.s.*, pooled samples; *ww*, wet weight.

[a] *$\sum$PBDE (28, 47, 99, 100, 153,154,183, 209).*

[b] *Calculated by the author based on reported data.*

[c] *$\sum$PBDE (47, 99, 100, 153, 154, 183, 206, 207, 208, 209).*

[d] *$\sum$PBDE (47, 99, 100, 153, 154, 183, 206, 207, 208, 209).*

[e] *$\sum$PBDE (28, 47, 99, 100, 153, 154, 183, 206, 207, 208, 209).*

the concentration of flame retardants in the environmental matrices are expected to be high, such as landfills and WWTPs.

PBDEs were also detected in egg samples collected in 2008 from the island of Rodrigues (Indian Ocean) located 560 km east of the island of Mauritius. A pool of 10 egg samples of common noddy (*Anous stolidus*) and 10 egg samples of sooty tern (*Sterna fuscata*) was analyzed. Only BDE-47 and BDE-100 were detected, and the total PBDE content was 0.08 ng/g ww for the common noddy pooled sample, and 0.06 ng/g ww for the sooty tern pooled sample (Bouwman et al., 2012). Another study revealed the occurrence of PBDEs in the eggs of Nile crocodiles collected from the Kruger National Park (South Africa) (Bouwman et al., 2014). The concentrations of total $\sum PBDE_6$ ranged from 0.023 to 0.63 ng/g ww, with BDE-28, 47, 99, 100, 154, and 183 being the most detected congeners, while BDE-206, 207, 209, and HBCDD were not detected in the crocodile eggs.

16.4.2.2 America

The PBDE concentrations (BDE-209 not included) in the fat tissue of pelagic birds (26 white-chinned petrels—*Procellaria aequinoctialis*, and three spectacled petrels—*Procellaria conspicillata*) from the Rio Grande do Sul (Brazil) were determined. The fat tissue (subcutaneous fat) samples were collected from birds found stranded ashore or resulted from the bycatch on longline fishing vessels. PBDEs were detected in 13 out of the 29 samples and the $\sum PBDE_7$ levels ranged from 0.78 to 72.7 ng/g ww. The most frequently detected congeners were BDE-99 and 153. The levels observed in this study were lower than the reported concentrations for seabird samples from the northern hemisphere (Cipro et al., 2013).

The presence of PBDEs in the liver samples of 51 cetaceans stranded on the beaches of Rio de Janeiro state (Brazil) from 1994 to 2006 was studied. The $\sum PBDE_9$ (BDE-209 not included) concentrations ranged from 3 to 5960 ng/g lw. The most abundant congener was BDE-47, which contributed to 32%–80% of total PBDE content, while BDE-183 was not detected in any of the samples. The levels observed in this study were in the same range as those observed for dolphins from northern hemisphere (Dorneles et al., 2010).

The presence of PBDEs (BDE 209 not included) was evaluated in the tissue of fish and dolphins from the estuary of the Paraíba do Sul River (Southeastern Brazil). The study included samples of silver scabbardfish (*Lepidopus caudatus*, $n = 10$) and Whitemouth croaker (*Micropogonias furnieri*, $n = 10$) collected by local fishermen in a river near Campos dos Goytacazes and Tucuxi dolphins (*Sotalia guianensis*, $n = 14$) found stranded along the North Coast of Rio de Janeiro. The liver and muscles were analyzed from the fish samples, while the liver, muscle, and kidneys were analyzed from the dolphins. BDE-47 and BDE-83 were detected in all the samples, with BDE-47 being the most abundant compound. The levels observed in the liver were higher than those in the other tissues. The mean BDE-47 levels in the liver were 4.05 ± 1.94 ng/g ww, 1.52 ± 0.70 ng/g ww, and 11.0 ± 12.7 ng/g ww for scabbardfish, croaker, and dolphins. The higher levels in dolphins compared to fish evidenced the biomagnification of PBDEs in the food chain. The presence of BDE-47, 99, and 100 in the livers of estuarine dolphins indicates the use of the penta-BDE formulation in Brazil (Quinete et al., 2011).

The PBDEs were found in the livers and muscles of Guiana dolphins (*S. guianensis*) and rough-toothed dolphins (*Steno bredanensis*) incidentally caught in fishing nets or found stranded in the central-northern coast of Rio de Janeiro (Brazil) between 2003 and 2012. Concerning both the liver and muscle levels, the concentrations of PBDEs were higher in *S. guianensis* (29–280 ng/g lw) than in *S. bredanensis* (31–1300 ng/g lw), which was attributed to their feeding habits since the latter feeds on larger pray. The same trend was observed by Dorneles et al. (2010) for these same species. The levels in the liver were higher than those in the muscle for both species, and the most abundant congeners were BDE-47, 100, and 99. The levels in this study were lower than those reported by Dorneles et al. (2010) and Quinete et al. (2011) for *S. guianensis*, indicating a lower level of PBDE contamination in the studied area (Lavandier et al., 2015).

Different studies reported the PBDE levels in blubber from marine mammals, and the data are presented in Table 16.2. The PBDEs were frequently detected in the bubbler of different species, showing that marine mammals from coastal areas in Brazil and the Gulf of Guayaquil (Ecuador) are exposed to PBDEs. BDE-47, 99, and 100 were the most abundant congeners, indicating the predominant use of the penta-BDE formulations, but the presence of BDE-209 (deca-BDE) was not evaluated in these samples. Concerning the different studies in Brazil, higher PBDE levels were observed in samples from highly populated and industrialized regions (Sao Paulo state and Rio de Janeiro state), highlighting the anthropogenic impact on the PBDE levels in aquatic biota.

Another study evaluated the levels of PBDEs in the muscles of Whitemouth croakers (*M. furnieri*) from the state of Rio de Janeiro (Brazil). Samples were acquired from commercial fisheries located in Guanabara and Sepetiba Bay. This region is recognized as the most anthropogenically impacted coastal area in Brazil. A total of 35 PBDE congeners were evaluated but only the following 10 presented detection frequencies higher than 50%: BDE-47, 100, 154, 49, 71, 153, 66, 99, 28, and 183. BDE-47 and BDE-100 were detected in 100% of samples, and BDE-47 was the most abundant congener. This study also evaluated the presence of BDE-209 (deca-BDE), and although it was quantified in only 40% of the samples, its contribution to the total PBDE content reached 78% of these samples. The $\sum PBDE$ levels ranged from 0.0076 to 0.326 ng/g ww (mean 0.091 ng/g ww) (Pizzochero et al., 2019). On the other hand, no PBDEs were detected in three fish species collected from Ilha Grande (Rio de Janeiro State, Brazil) (Lavandier et al., 2013). This study analyzed

TABLE 16.2 Concentrations (ng/g lw) of PBDEs in the bubbler of marine mammals collected from Brazil and Ecuador.

Ref.	Sampling site (date)	Common name (scientific name)	*n*	mean	median	min	max
Yogui et al. (2011)	The Coast of Sao Paulo State (1996–2003)	Guiana dolphin (*Sotalia guianensis*)	9	65.6 ± 59.3[a]			
		Franciscana dolphin (*Pontoporia blainvillei*)	8	60.3 ± 74.8[a]			
		Atlantic spotted dolphin (*Stenella frontalis*)	2	770 ± 86.4[a]			
		Rough-toothed dolphin (*Steno bredanensis*)	1	475[a]			
		Bottlenose dolphin (*Tursiops truncatus*)	1	64.2[a]			
Leonel et al. (2012)	Coast of Santa Catarina, Parana and Sao Paulo states (2004–07)	Atlantic spotted dolphin (*Stenella frontalis*)	9	628.9[b]		23[b]	1347[b]
Leonel et al. (2014)	The Coast of Sao Paulo state (2002–05)	Franciscana dolphin (*Pontoporia blainvillei*)					
		All samples	41			67.8[c]	736.7[c]
		Adult males	11		289.3[c]	67.8[c]	763.7[c]
		Adult females	10		64.8[c]	<0.65	227.8[c]
		Juveniles	8		198.6[c]	72.8[c]	500.9[c]
		pups	12		65.1[c]	31.1[c]	210.4[c]
	Coast of Rio Grande do Sul state (1994–2004)	All samples	73			7.99[c]	65.02[c]
		Adult males	22		26[c]	7.9[c]	65[c]
		Adult females	6		18.1[c]	<0.65	43.39[c]
		Juveniles	37		13.9[c]	<0.65	144[c]
		pups	7		10.88[c]	<0.65	124.43[c]
	El Morro Mangrove Wildlife Refuge (REVISEM), Gulf of Guayaquil, Ecuador (2018)	Bottlenose dolphins (*Tursiops truncatus*)					
		Adult males	3	430 ± 120[d]	0.375[d]	355[d]	572[d]
		Adult females	2	170 ± 95[d]		102[d]	236[d]
		Subadult female	2	480 ± 150[d]		375[d]	581[d]

n, number of analyzed samples.

[a] *$\sum$PBDE (BDE-1, 2, 3, 7, 8, 10, 11, 12, 13, 15, 17, 25, 28, 30, 32, 33, 35, 37, 47, 49, 66, 71, 75, 77, 85, 99, 100, 116, 118, 119, 126, 138, 153, 154, 155, 166, 181, 183, and 190).*

[b] *$\sum$PBDE (BDE-28, 47, 99, 100, 153, 154, and 183).*

[c] *$\sum$PBDE (BDE-1, 2, 3, 7, 8, 11, 10, 12, 13, 15, 17, 25, 28, 30, 32, 33, 35, 37, 47, 49, 66, 71, 75, 77, 85, 99, 100, 116, 118, 119, 126, 138, 153, 154, 155, 166, 181, 183, and 190).*

[d] *$\sum$PBDE (BDE 15, 28, 33, 49, 47, 66, 75, 99, 100, 153, 154, 155, 183).*

61 samples of different organisms. The nondetection of PBDEs was attributed to the low level of anthropogenic contamination on this island.

The PBDEs and HBCDD were frequently detected in the liver of checkered puffer (*Sphoeroides testudineus*) from Ria Lagartos (Yucatan, Mexico). A total of 28 fish samples were collected in 2012 during dry ($n = 13$) and rainy ($n = 15$) seasons. The HBCDD was detected in fish liver samples at levels up to 509.4 ng/g, and the detection frequency was higher for the samples collected in the dry season (84.62%) than in the rainy season (33.33%). BDE-47 (up to 68.16 ng/g) and BDE-100 (up to 65.08 ng/g) were detected in 100% of samples, and the uncommon BDE-85 showed a high detection frequency (92.31%—dry season; 86.67—rainy season) and levels ranged from 1.31 to 10.16 ng/g (Valenzuela-Sánchez et al., 2019).

The occurrence of PBDEs was also verified in fish samples (*Salmo salar*) collected from five farming areas in Southern Chile, showing average total PBDE content of 1.46ng/g ww, with BDE-47 being the most abundant compound (Montory and Barra, 2006). In this study the PBDE profile in fish tissue and feed samples collected from the farms was similar, indicating the feed as the principal PBDE entry source for farmed fish.

16.4.2.3 Asia

Three different studies used mussels for evaluating the environmental contamination of brominated flame retardants in Asian tropical countries. From the Singapore coast, a total of 146 green mussels (*Perna viridis*) samples were collected in 2002. The levels of $\sum PBDE_7$ ranged from 2.0 to 38ng/g dw, and the most abundant compounds were BDE-47 and BDE-99 (BDE-209 was not studied). The highest concentrations were observed in the industrial area of Tuas, a location where electronic industries and waste recycling plants are placed (Bayen et al., 2003). Another study evaluated the presence of PBDEs in mussels collected between 2003 and 2005 from Asian coastal areas, including several tropical countries (Cambodia, India, Indonesia, Malaysia, Philippines, and Vietnam), in addition to China, Korea, and Japan. The $\sum PBDE_{14}$ levels ranged from 0.66 to 440ng/g lw, and the levels in China, Korea, and Philippines were higher than those in the other locations. The most abundant congeners in most of the samples were BDE 47, 99, and 100. Concerning the PBDE levels in the tropical countries, the $\sum PBDE_{14}$ levels ranged from 2.3 to 66ng/g lw in Cambodia, from 1.4 to 14ng/g lw in India, from 0.84 to 16ng/g lw in Malaysia, from 0.66 to 5.4ng/g lw in Vietnam, and were detected at 69 and 140ng/g lw in the two samples collected from the Philippines. (Ramu et al., 2007). A third study evaluated the occurrence of HBCDD in green mussels (*P. viridis*) and blue mussels (*Mytilus edulis*) collected between 2003 and 2008 from different Asian countries. The HBCDD concentrations ranged from 2 to 51ng/g lw in Cambodia, from 0.26 to 16ng/g lw in India, from 2.2 to 15ng/g lw in Malaysia, from 6.6 to 17 in the Philippines, and from 0.03 to 140ng/g lw in Vietnam. The levels observed in Japan (from 10 to 1400ng/g lw) were much higher than those from the other Asian countries, which is attributed to increasing demand for HBCDD in Japan, but the detection in Asian countries indicated a wide use of this flame retardant (Isobe et al., 2012).

Three other studies also indicated penta-BDEs as ubiquitous contaminants in aquatic biota in Singapore. BDE-47, BDE-99, and BDE-100 were the most abundant congeners (BDE-209 was not evaluated) in organisms from different areas in Singapore, including the followings: algae, polychaetes, mollusks, crustaceans, and fishes collected in 2004 from mangrove sites (Sungei Buloh and Sungei Khatib Bongsu) (Bayen et al., 2005); in marine catfish and pike conger eel collected between 2011 and 2012 from Singapore Strait (Zhang and Kelly, 2018); and in fish (tilapia and peacock bass), snails and plankton collected between 2014 and 2016 from a catchment close to urban areas (Wang and Kelly, 2018). Concerning HBCDD, the isomer α-HBCDD was detected in pike conger eel (average 0.03 ng/g ww) and marine catfish (average 0.051 ng/g ww) collected from the Singapore Strait (Zhang and Kelly, 2018).

16.4.3 Chlorinated paraffins (CPs)

To the best of the author's knowledge, to date, only one study reported data regarding the occurrence of CPs in the aquatic environments of tropical countries. In this study, a passive sampler was used for assessing SCCPs and MCCPs, among other contaminants, in the waters from Lake Victoria (Africa) and in the Three Gorges Reservoir (China). The sampling technique used in this study was referred to as a virtual organism, since it can uptake the freely dissolved (bioavailable) nonpolar substances in water, simulating the exposure of aquatic organisms. The virtual organism consists of a lay-flat tube made of semipermeable polyethylene membrane enclosing a thin film of triolein of high molecular weight. During deployment, nonpolar substances from the aqueous medium cross the membrane and accumulate in the sampler. The estimated freely dissolved water concentrations for $\sum SCCP$ were 0.0036ng/L in Lake Victoria and 0.113ng/L in the Three Gorges Reservoir, with $C_{10}H_{16}C_{l6}$, $C_{10}H_{15}C_{l7}$, and $C_{11}H_{16}Cl_6$ being the most abundant compounds. Concerning $\sum MCCPs$, the observed water concentrations were 0.00045ng/L in Lake Victoria and 0.0008ng/L in the Three Gorges Reservoir, with $C_{14}H_{24}Cl_6$, $C_{14}H_{23}C_{l7}$, and $C_{14}H_{22}C_{l8}$ being the most abundant compounds (Omwoma et al., 2019).

The lack of data regarding CPs in the environments of tropical countries is possibly associated with the analytical difficulties in the determination of these substances in environmental matrices, and their more recent listing in the Stockholm Convention in comparison to the brominated flame retardants. However, some studies indicate environmental contamination by CPs in tropical countries. For instance, CPs were detected in indoor dust samples from South Africa at ΣCP concentrations ranging from 33 to 663μg/g (levels of MCCPs > SCCPs > LCCPs), indicating the wide use of these substances in this country (Brits et al., 2020). Another study evaluated the occurrence of SCCPs and MCCPs in salmon samples acquired from supermarkets in Germany, which revealed that Chilean farmed salmon samples presented higher CPs levels than samples from other European countries. The mean concentrations observed in the

Chilean farmed salmon samples was 47 ng/g ww for $\sum$SCCP and 39 ng/g ww for $\sum$MCCP, which were higher than the mean levels observed in farmed salmon samples from Norway, Scotland, and Denmark (mean $\sum$SCCP levels ranging from 7.9 to 13 ng/g ww; and mean $\sum$MCCP levels ranging from 14 to 21 ng/g ww), and wild salmon (mean $\sum$SCCP level: 5.3 ng/g ww; mean $\sum$MCCP level: 7.6 ng/g ww). These results indicate a possible higher contamination level of the feed used for Chilean farmed salmon, which could be a consequence of higher environmental contamination. The levels of CPs in all the fish samples were higher than the levels of HBCDDs and polychlorinated biphenyls, indicating that CPs are among the most abundant persistent organic pollutants in this matrix (Krätschmer et al., 2019).

16.4.4 Organophosphate esters (OPEs)

A few studies evaluated the occurrence of OPEs in the aquatic environment of tropical countries. Three studies reported the OPE levels in surface water, and contrarily to the results observed for PBDEs, to which most of the studies indicated the same predominant compounds (BDE-209, BDE-47, and BDE-99), the OPE profiles differed among the studies, indicating different use patterns.

A study evaluated the occurrence of OPEs (TCIPP, TCEP, TDCIPP, TDBPP, and TPHP) in WWTP effluents and surface water from the Vaal River catchment (South Africa). OPEs were detected in 100% of the samples, the $\sum$OPEs concentrations ranged from 90 to 1414 ng/L in surface water, and the most abundant compound was TDBPP (mean of 228 ng/L), followed by TCIPP (mean of 149 ng/g) and TDCIPP (mean of 116 ng/L). TPHP was not detected in any of the samples, which was attributed to its low water solubility. The higher concentrations were observed in industrial areas and sites located downstream from the discharges of WWTPs. Concerning WWTP effluents, the most abundant compound was TCIPP (mean of 364 ng/L) followed by TDBPP (221 ng/L), while lower levels were observed for TCEP (58 ng/L) and TDCIPP (20 ng/L). The TPHP was not detected in any of the effluent samples (Chokwe and Mporetji, 2019).

Another study evaluated the presence of OPEs in surface water from Lake Victoria (Uganda, Africa). Eight OPEs were included in the study (TEP, TNBP, TCEP, TCIPP, EHDPHP, TPHP, TEHP, and TMPP), and all presented high detection frequencies (>90%), except for TEP (63%). The most abundant compounds were TMPP (25–8100 ng/L), TCEP (24–6500 ng/L), TPHP (4–4300 ng/L), and TEHP (33–4300 ng/L). The effluents from industries, WWTPs, and municipal discharges were indicated as the main sources of these contaminants (Nantaba et al., 2021).

OPE concentrations were determined in surface water samples from the Piracicaba watershed (Brazil), and the study included the following 10 substances: TIBP, TNBP, TCEP, TCIPP, TDCIPP, TPHP, TBOEP, EHDPHP, TEHP, and TMPP. All the OPEs were detected except TMPP. The highest concentrations were observed for TBOEP (up to 5900 ng/L; median 180 ng/L), followed by TCIPP (up to 440 ng/L, median 89 ng/L), and TDCIPP (up to 480 ng/L, median 16 ng/L). The highest OPE concentrations was observed in urban and industrial areas, and an increase in the concentrations were observed at the downstream points of the discharge of municipal WWTPs and textile industries. The TEHP was only detected at the points under the influence of the textile industry, at concentrations up to 750 ng/L (Cristale et al., 2020).

16.5 Conclusions

Although some hazardous flame retardants have been prohibited in different countries and/or were included in the POPs List of Stockholm Convention (PBDEs, HBCDD, SCCPs), these substances are still released to the environment by the products containing them. In addition, the environmental levels of alternative substances (ex. OPEs) tend to be higher than the levels observed for brominated flame retardants. The aquatic compartment is particularly vulnerable to flame retardant pollution because these substances reach surface waters by different routes, being the discharges of domestic and industrial effluents important ones. Regarding tropical regions, different studies show evidence of environmental contamination by flame retardants. However, most the studies are concentrated in a few countries, and data on the occurrence of CPs and OPEs in the tropical aquatic environments are very limited. The analytical techniques needed for the determination of these substances in environmental matrices, their relatively high costs, and the necessity of qualified professionals are some of the reasons for the limited data available. Finally, different studies indicate the need for more attention to the management of solid waste containing flame retardants in tropical countries, as well as the establishment of environmental education programs regarding the correct disposal of the materials and consumer goods containing these substances to avoid flame retardants contamination of aquatic environments (Tavengwa et al., 2022, Chapter 20).

This chapter falls under the section on fate and occurrence of emerging pollutants within aquatic ecosystems with other chapters, e.g., Ajayi et al. (2022), Cristale (2022), Vizioli et al. (2022), Galhardi et al. (2022), Hashemi and Kaykhaii (2022), Madikizela et al. (2022), Mashile et al. (2022), Montagner et al. (2022), Moodley et al. (2022), Ntshani and Tavengwa (2022), Sanganyando and Kajau (2022), and Yardy et al. (2022) that aims to make an understanding of the different emerging pollutants within the aquatic environment.

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CHAPTER

17

Rare earth elements and radionuclides

Juliana A. Galhardi, Karen Luko-Sulato, Lauren N.M. Yabuki, Leandro M. Santos, Ygor J.A.B. da Silva, and Yuri J.A.B. da Silva

17.1 Introduction

Rare earth elements (REE) include all elements of the lanthanide series, ranging from atomic number 57 (La) to 71 (Lu), with the addition of Scandium (Sc) and Yttrium (Y). The REEs are relatively abundant in the Earth's crust and occur typically dispersed, being rarely found in concentrated fractions. Due to their unique physical and chemical characteristics, these elements present an essential role in a diverse array of modern technological applications, such as the production of electronics, petrochemical engineering, metallurgy, energy, agriculture, and medicine (Wang et al., 2017; Galhardi and Bonotto, 2017; Yuan et al., 2018; Deluca et al., 2020; Tavengwa and Dalu, 2022, Chapter 1). Nevertheless, the increasing demand for REE ores has been contributing to the increased anthropogenic discharges of REE into the environment, which can represent a threat to living organisms (Yuan et al., 2018).

Natural radionuclides are often associated with the REE in geologic deposits and comprise part of the chemistry of soils and waters (Galhardi and Bonotto, 2017). A radionuclide consists of an atom with an unstable nucleus (such as Uranium; U, Thorium; Th, Radium; Ra, and Radon; Rn, from the actinide series) that emit radiation in the form of alpha particles (α), beta particles (β), or gamma rays (γ), while undergoing radioactive decay. Different species with distinct physical and chemical properties are generated until a stable nucleus is achieved. The decay of the three isotopes that initiate the natural decay series (^{238}U, ^{235}U, and ^{232}Th; Fig. 17.1) gives rise to a wide variety of radioactive products, including ^{234}U, ^{222}Rn, and ^{226}Ra. Although radionuclides are naturally present in the environment, anthropogenic sources such as agriculture, mining, and industry can increase the radiation dose to the living organisms. Higher concentrations of radioactivity in the environment are associated with greater damage and risks to human health. For example, chronic exposure to Ra or U is related to intense radiation doses, leading to the development of cancer (Jia et al., 2009).

For many years, human activities have been a significant source of trace metallic elements eventually contaminating the Earth's surface. Such actions overburdened the regime of aquatic and terrestrial ecosystems by introducing large quantities of metallic pollutants and contaminants through mining, industrial activities, and the use of trace elements in high-value goods (Khan et al., 2017). Although it is documented those anthropogenic activities can lead to the contamination of aquatic and terrestrial environments by lanthanides and actinides (Galhardi and Bonotto, 2017), only a few investigations concerning their exposure doses and consequent risks to human health took place in developing and tropical zones, where the environmental, demographic, and economic characteristics differ considerably from those from developed countries (Galhardi and Bonotto, 2017). Moreover, REE and radionuclides have been considered as classes of emerging contaminants because (1) they are currently unregulated regarding humans and the environment, (2) they are not routinely monitored in environmental and public health programs, and (3) their mechanisms of ecological and human toxicity are still poorly understood (Gwenzi et al., 2018).

Understanding the speciation, fate, and transport of REE and radionuclides on terrestrial and aquatic ecosystems is of great importance for addressing health-related and environmental issues (e.g., water pollution and farmland degradation) (Liu et al., 2017; Sanganyado, 2022, Chapter 19). The literature about adverse effects of REE and radionuclides is scarce when compared to toxic metals such as Cd and Pb, although the available information on human exposures indicates many adverse effects, including bioaccumulation, respiratory diseases, and only partly known pathological outcomes (Pagano et al., 2019). Therefore, monitoring studies of REE and radionuclides in aquatic

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$$
\begin{aligned}
&{}^{238}\boldsymbol{U(\alpha)} \rightarrow {}^{234}Th(\beta) \rightarrow {}^{234}Pa(\alpha) \rightarrow {}^{234}U(\alpha) \rightarrow {}^{230}Th(\alpha) \rightarrow {}^{226}Ra(\alpha)\\
&\rightarrow {}^{222}Rn(\alpha) \rightarrow {}^{218}Po(\alpha) \rightarrow {}^{214}Pb(\beta) \rightarrow {}^{214}Bi(\beta) \rightarrow {}^{214}Po(\alpha)\\
&\rightarrow {}^{210}Pb(\beta) \rightarrow {}^{210}Bi(\alpha) \rightarrow {}^{210}Po(\alpha) \rightarrow {}^{206}Pb
\end{aligned}
$$

$$
\begin{aligned}
&{}^{235}\boldsymbol{U(\alpha)} \rightarrow {}^{231}Th(\beta) \rightarrow {}^{231}Pa(\alpha) \rightarrow {}^{227}Ac^{(\beta)\rightarrow {}^{227}Th(\alpha)}_{(\alpha)\rightarrow {}^{223}Fr(\beta)} \rightarrow {}^{223}Ra(\alpha)\\
&\rightarrow {}^{219}Rn(\alpha) \rightarrow {}^{215}Po^{(\alpha)\rightarrow {}^{211}Pb(\beta)}_{(\beta)\rightarrow {}^{215}At(\alpha)} \rightarrow {}^{211}Bi^{(\alpha)\rightarrow {}^{207}Tl(\beta)}_{(\beta)\rightarrow {}^{211}Po(\alpha)} \rightarrow {}^{207}Pb
\end{aligned}
$$

$$
\begin{aligned}
&{}^{232}\boldsymbol{Th(\alpha)} \rightarrow {}^{228}Ra(\beta) \rightarrow {}^{228}Ac(\beta) \rightarrow {}^{228}Th(\alpha) \rightarrow {}^{224}Ra(\alpha)\\
&\rightarrow {}^{220}Rn(\alpha) \rightarrow {}^{216}Po(\alpha) \rightarrow {}^{212}Pb(\beta) \rightarrow {}^{212}Bi^{(\beta)\rightarrow {}^{212}Po(\alpha)}_{(\alpha)\rightarrow {}^{208}Tl(\beta)} \rightarrow {}^{208}Pb
\end{aligned}
$$

FIG. 17.1 Natural decay series initiated by ^{238}U, ^{235}U, and ^{232}Th.

ecosystems are critical to elucidate their role as pollutants. This chapter summarizes the knowledge about REE and radionuclides in freshwaters, including their occurrence, geochemistry, effects on aquatic organisms, and technologies for removal from waters and wastewaters.

17.2 Overview of REE and radionuclides in freshwaters

Several studies have been published on the geochemistry of REE and radionuclides in natural waters (Galhardi et al., 2020; Deluca et al., 2020; Alakangas et al., 2020). REE and radionuclides concentrations are mainly influenced by water type, salinity, redox conditions, pH, and processes such as organic and inorganic complexation, adsorption, precipitation, and ion exchange (Fig. 17.2). For example, the REE and U mobility in waters increase with the decrease of the pH (Galhardi and Bonotto, 2017; Galhardi et al., 2020; Adeel et al., 2019).

Sources of REE and radionuclides to freshwaters include natural emissions, industrial activities, mining, agriculture, and runoff. Surface waters are important pathways for the transport and distribution of REE and radionuclides among different environmental compartments. Although it is known that REE and radionuclides are mainly transported by freshwaters from the continents to the oceans, their occurrence forms, main reactions, and interactions with other compounds in freshwaters remain poorly understood (MacMillan et al., 2019).

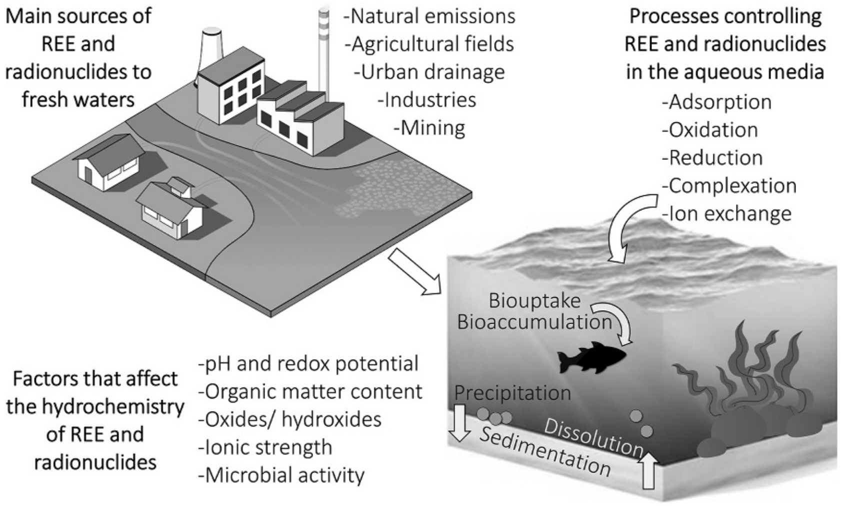

FIG. 17.2 Main sources of REE and radionuclides and factors that affect their geochemistry in freshwaters.

17.2.1 Geochemistry of REE in freshwaters

REEs are usually poorly soluble in natural ecosystems and present low contents in uncontaminated freshwaters (Gonzalez et al., 2014). Individually, their abundance in the Earth's crust ranges from 0.14 ppm (Eu) to 70 ppm (Ce and Y) (Ganguli and Cook, 2018). The distribution of REE follows the Oddo-Harkins rule, which states that elements with even atomic numbers are more abundant in the Earth's crust than those adjacent odd-numbered ones (Nikanorov, 2016). For comparative analysis, the measured REE concentrations can be normalized to some REE reference values, such as the Post-Archean Australian Shale (PAAS) (De Campos and Enzweiler, 2016). In rock-forming minerals, REE occurs as trivalent cations in carbonates, oxides, phosphates, and silicates (Battsengel et al., 2018). Nearly 200 minerals containing REE are presently known. However, only a few minerals are economically viable for mining, including bastnaesite ($(Ce,La)(CO_3)F$), monazite ($(Ce,La)PO_4$), xenotime (YPO_4), and rare earth bearing clay minerals (Haque et al., 2014; Battsengel et al., 2018).

The REE is generally subdivided into light rare earth elements (LREE) and heavy rare earth elements (HREE), although their definition might differ from author to author. IUPAC (2005) states that LREE is the lanthanides that have unpaired electrons ranging from 0 to 7 in the 4f orbital (from La to Gd), whereas the HREE have paired electrons in the 4f orbital (from Tb to Lu). Yttrium is included as HREE due to its chemical similarities, while Sc is not included in either category due to its chemical differences from the other REE (especially its small ionic radius). Consequently, one might not consider Sc as a valid member of the REE group (e.g., Ganguli and Cook, 2018; Mehmood, 2018).

Except for the acidic waters, most lakes and river waters exhibit levels of REE in the $ng\,L^{-1}$ occasionally $\mu g\,L^{-1}$ ranges (Migaszewski and Gałuszka, 2015). In general, REE concentrations in surface waters are higher than those in groundwaters (Adeel et al., 2019). Aside from anthropogenic inputs, the ultimate source of REE in natural waters comprises the weathering of bedrocks. In systems with low water/rock ratios, such as soils and groundwaters, the extent of water-rock interaction profoundly impacts the geochemistry of the REE in both solution and the solid phases (Welch et al., 2009). In addition to the geochemical signatures of the parent material, REE is mostly affected by the pH, redox potential, sorption, and complexation phenomena (Iwatsuki et al., 2017; Deluca et al., 2020).

REE occurs predominantly associated with the suspended load, which comprehends a complex mixture of clay and other mineral particles, amorphous SiO_2, Fe-Mn oxyhydroxides, and many different types of biogenic material (De Campos and Enzweiler, 2016). In surface waters, REE concentration can be divided into three pools: (i) dissolved fraction; (ii) REE linked to colloids and nanoparticles; (iii) REE particulate linked to solid particles (Elderfield et al., 1990). Furthermore, because the REE's ionic radii decrease following the increasing atomic number (from La to Lu), slight differences in the geochemical behavior between LREE and HREE have been observed in freshwaters (Munemoto et al., 2015; Merschel et al., 2017). Overall, LREE has higher particle affinities, whereas HREE is more easily complexed by dissolved ligands (Osborne et al., 2014; Deng et al., 2017).

REE is influenced by the formation of complexes with carbonate, sulfate, and phosphate. For instance, phosphate complexation can decrease REE mobility, whereas carbonate complexation increases their solubility (Johannesson et al., 1995, 2017). Organic complexation also plays an essential role in increasing the transport of REE in freshwaters (Merschel et al., 2017). REE-organic complexes with humic and fulvic substances are predominantly controlled by pH, ionic strength, competitive cations, and availability of dissolved organic matter (Tang and Johannesson, 2003; Pourret et al., 2007; Marsac et al., 2013). Increasing ionic strength can impact the concentration of competitive cations (e.g., Fe^{3+} and Al^{3+}) and the organic matter-REE interactions, leading to a low amount of REE bound to dissolved organic matter. In alkaline waters, carbonate complexes ($REECO_3^+$ and $REE[CO_3]_2^-$) outcompete organic substances for dissolved REE, whereas for acidic waters, sulfate complexes ($REEO_4^+$) and free REE^{3+} dominate (Tang and Johannesson, 2003).

Increasing pH leads to more sorption of REE by Fe-oxyhydroxides (Verplanck et al., 2004). Below pH 5, REE behaves conservatively even when Fe-oxyhydroxides are present. Furthermore, between a pH of 5.1 and 6.6, the REE are partially removed from the solution, which can lead to fractionation across the REE group (Verplanck et al., 2004). For groundwaters, in circumneutral pH ($7 < pH < 9$), REE-carbonate complexes are the major dominant forms of dissolved REE, followed by the free elements, sulfide or hydroxyl, fluoride, and phosphate complexes (Johannesson et al., 1996). Moreover, carbonate complex ($REECO_3^+$) has more affinity for the LREE, whereas bicarbonate ($REE[CO_3]_2^-$) dominates the complexation of the HREE in groundwaters (Johannesson et al., 1996; Sholkovitz, 1995).

Many relevant questions about the geochemical behavior of REE in groundwaters and surface waters have been answered in recent decades, such as the influence of organic ligands on REE speciation (Deluca et al., 2020), the water-rock interaction processes (Munemoto et al., 2015), the physical and chemical processes in aqueous systems (Desbarats et al., 2016), the fractionation patterns (Kumar et al., 2019; Alakangas et al., 2020), the role of manganese oxyhydroxides on REE transport (Liu et al., 2019), and the mechanisms that affect the Ce anomalies (Pédrot et al., 2015). Understanding the dynamics of REE in freshwaters at the local and regional scales is fundamental for improving the knowledge about their geochemical behavior in aquifer systems and surface water bodies.

17.2.2 Geochemistry of radionuclides in freshwaters

The radionuclides that contribute most to the natural radioactivity in waters are U, Th, Ra, and Rn, belonging to the natural decay series. Uranium exists as three alpha-emitting isotopes: ^{238}U (half-life, $t_{1/2}$, 4.5×10^9 years), ^{235}U ($t_{1/2}$ of 7.1×10^8 years), and ^{234}U ($t_{1/2}$ of 2.5×10^5 years). More than 100 uranium-containing minerals are currently known and can be divided into oxides, hydroxides, silicates, carbonates, sulfates-carbonates, sulfates, phosphates, arsenates, among others (Bonotto, 2004). Thorium has three alpha-emitting isotopes (^{232}Th, with $t_{1/2}$ of 1.41×10^{10} years; ^{230}Th, with $t_{1/2}$ of 7.5×10^4 years; and ^{228}Th, with $t_{1/2}$ of 1.90 years) and two beta emitters (^{231}Th, $t_{1/2}$ of 25.6 h; ^{234}Th, $t_{1/2}$ of 24.1 days), being less mobile in the environment than U.

Radium has about 25 isotopes with mass numbers ranging between 206 and 230, but only four occur naturally in the radioactive decay series: ^{226}Ra ($t_{1/2}$ of 1622 years, belonging to the ^{238}U series), ^{223}Ra ($t_{1/2}$ of 11.2 days, belonging to the ^{235}U series), ^{228}Ra ($t_{1/2}$ of 5.75 years), and ^{224}Ra ($t_{1/2}$ of 3.6 days), both belonging to the ^{232}Th series. Radium is considered one of the most toxic radionuclides; therefore, ^{226}Ra activity concentration is widely evaluated in freshwaters (Stackelberg et al., 2018). Radon is a gaseous element the originated from Ra decay and can be found as ^{222}Rn ($t_{1/2}$ of 3.8 days) in the ^{238}U series, ^{220}Rn ($t_{1/2}$ of 55.6 s) in the ^{232}Th series, and as ^{219}Rn ($t_{1/2}$ of 4 s) in the ^{235}U series.

In natural waters, radionuclides are mainly controlled by their content and chemical occurrence forms in the rocks and sediments. The main anthropogenic sources of radionuclides are related to fuel fabrication, fuel reprocessing, mining, inappropriate waste disposal, nuclear weapons tests, nuclear accidents, and global fallout (Amyot et al., 2017; Gwenzi et al., 2018; Adeel et al., 2019). Uranium concentrations can reach high values in surface waters affected by U mining activities (8720 μg L^{-1} in a Brazilian U-mining ore site; Campos et al., 2011). In rivers, U concentration generally ranges from 0.1 to 100 μg L^{-1}, whereas in groundwaters it can vary widely, depending on the U content in the bedrocks. Although Th is more abundant in the continental crust than U (abundances of 8.6 mg k^{-1} and 1.7 mg kg^{-1} for Th and U, respectively; Wedepohl, 1995), its concentration in natural waters is generally lower (Ferronsky et al., 1982).

The main natural source of Rn in the environment comprises rocks and soils. After being generated between the mineral grains, Rn escapes into the porous space and reaches the atmosphere, being eventually solubilized into groundwaters or surface waters. Therefore, Rn decay products, such as polonium (Po) and lead (Pb) (Fig. 17.1), can also be transported through groundwaters and surface waters. In general, groundwater presents higher levels of Rn than surface waters, mainly due to the slow rate of the water circulation flow and the presence of dissolved and particulate Ra in the aquifer systems (Galhardi and Bonotto, 2017).

Several factors affect radionuclides solubility in freshwaters, such as the pH, redox potential, concentration of complexing anions, organic matter content, and processes such as adsorption, chemisorption, and ion exchange (Fig. 17.2). A slight change in the redox potential can alter the U valence and its equilibrium in solution, resulting in considerable changes among the insoluble form (U(IV)) and the soluble form (U(VI)). Under acidic ($pH < 5$) and oxidizing conditions, U exists predominantly as uranyl (UO_2^{2+}), and at higher pH conditions, carbonated complexes predominate (i.e., $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$). Under conditions close to neutrality, U is mainly found as soluble complexes, such as UO_2OH^+, $(UO_2)_2(OH_2)^{2+}$, and $UO_2(HPO_4)_2^{2-}$ (Langmuir, 1978). Because U(VI) is more soluble, it can migrate as an aqueous species throughout aquifer systems and surface water bodies (Arnold et al., 2011).

In aquifer systems, processes such as dissolution, precipitation, sorption, and desorption at the water-rock interface can also control the mobility and transport of radionuclides. Adsorption is an important removal mechanism that affects radionuclides concentration in groundwaters, being controlled by the pH, redox potential, ionic strength, and the presence of complexing agents in solution (Prikryl et al., 2001). For example, oxyhydroxides, mineral colloids, and organic complexes greatly influence the geochemistry of U in the aqueous media (Santos-Frances et al., 2018). Other common sorbents of radionuclides include clay minerals, such as montmorillonite and kaolinite, which have high absorption capacities due to the high surface area and porosity. Furthermore, U can precipitate at the surface of minerals such as feldspars and kaolinite (Kabata-Pendias, 2011).

It has become clear that it is essential to better understand the geochemistry of radionuclides and the associated risks to the environment and human health. Site-specific investigations are yet required to better understand the fate of radionuclides as well as of REE in freshwaters. Nevertheless, this topic has not yet been well elucidated in tropical and developing areas, where the climate conditions and environmental problems related to water supply and land use play important roles in the contamination of freshwaters.

17.2.3 Occurrence of REE and radionuclides in freshwaters

The environmental release of radionuclides and REE in freshwaters has been a worldwide concern (Pastorino et al., 2020). Understanding the occurrence and sources of these emerging pollutants is essential to better manage water resources in developing and developed countries. REE and radionuclides concentration in freshwaters from several countries, including surface waters and groundwaters, are summarized in Tables 17.1 and 17.2, respectively. As discussed above, industrial and mining activities are among the primary anthropogenic sources of REE in freshwaters, while the main anthropogenic sources for radionuclides include (but not exclusively) effluents from nuclear installation, accident-derived radionuclides, global fallout, and natural radionuclides released as mining by-product (Galhardi and Bonotto, 2017; Adeel et al., 2019).

TABLE 17.1 Concentration of REE in freshwaters.

Study area	**Water type**	**REE ($\mu g\,L^{-1}$)**	**References**
Northern Anhui Province, China	Groundwater	0.103[a]	Sun et al. (2011)
Hetao Basin of Inner Mongolia	Groundwater	0.009–0.017[b]	Guo et al. (2010)
Nickel sulfide mine in western Australia	Groundwater	515[a]	Lei et al. (2008)
Jaintia Hills coalfield, northeastern India	Groundwater	715[a]	Sahoo et al. (2012)
River island-Majuli, Brahmaputra River, India	Groundwater	3.8[a]	Kumar et al. (2019)
Mount Vulture, southern Italy	Groundwater	0.019–0.947[b]	Deluca et al. (2020)
Tono area, central Japan	Groundwater	0.023–0.533[b]	Munemoto et al. (2015)
33 major Eastern China rivers	River water	5188[a]	Adeel et al. (2019)
Kinta River in Perak state, Malaysia	River water	1580[a]	Ito et al. (2017)
Tinto and Odiel river, southwest Spain	River water	880.6[a]	Borrego et al. (2012)
Along Gaoping river, Taiwan	River water	0.0067–0.0154[b]	Chung et al. (2009)
Lake Tanganyika, East Africa	River water	129.72–423.81[b]	Sako (2007)
Nickel sulfide mine in western Australia	Surface water	0.477[a]	Lei et al. (2008)
Abandoned mines in SW Sardinia, Italy	Surface water	53[a]	Medas et al. (2013)
Sarcheshmeh mine area of Kerman, Iran	Stream water	934[a]	Sharifi et al. (2013)
Italy	Stream water	0.02–5.26[b]	Petrosino et al. (2013)
Sweden	Stream water	0.076–29.31[b]	Petrosino et al. (2013)
South-west Spain	Stream water	29.54[a]	Fernández-Caliani et al. (2009)
Throughout Japan	Stream water	0.002–0.047[b]	Uchida et al. (2006)
Paranoá lake, central Brazil	Lotic water	0.014–0.193[b]	Amorim et al. (2019)
Podwiśniówka Mt., Poland	Mine water	0.64–24.9[b]	Migaszewski et al. (2013)
Cotonou, Benin, West Africa	Wastewater	0.15–34.0[b]	Atinkpahoun et al. (2020)

[a] *Average value.*
[b] *Minimum value–maximum value.*

TABLE 17.2 Concentration of radionuclides in freshwaters.

Study area	Water type	Isotope (mBq L^{-1})	References
Phu Yen province, Vietnam	Well groundwater	1.7–159 (29.1)[a]—^{226}Ra	Nguyen et al. (2020)
São Paulo State, Brazil	Well groundwater	49.7[b]—^{226}Ra	Lucas and Ribeiro (2006)
Karnataka State, India	Dug well groundwater	14.26–81.06 (33.05)[a]—^{226}Ra	Shivakumara et al. (2014)
Fujian Province, China	Groundwater	7.12–19.8 (12.7)[a]—^{226}Ra	Weihai et al. (2011)
Juban, Yemen	Groundwater	2250–3450 (2950)[a]—^{226}Ra	Abdallah et al. (2013)
Syria	Groundwater	21[b]—^{226}Ra	Othman and Yassine (1996)
Karoo basin, South Africa	Groundwater	41,000 ± 5000[b]—^{222}Rn	Botha et al. (2019)
Figueira, Paraná, Brazil	Groundwater	10,040 ± 126[b]—^{222}Rn 350 ± 140[b]—^{226}Ra	Galhardi and Bonotto (2017)
Shallow Nubian aquifer, Egypt	Groundwater	16.0 ± 5–750.0 ± 23[a]—^{226}Ra 18.0 ± 2–1421 ± 16[a]—^{228}Ra	Sherif and Sturchio (2018)
SE Brazil, East Paraguay, NW Uruguay, NE Argentina	Groundwater	2500–86,500[a]—^{222}Rn 120–440[a]—^{226}Ra	Bonotto and Elliot (2017)
Guarany aquifer, cities of Mato Grosso do Sul, Brazil	Groundwater	0.26–1.0[a]—^{210}Po 0.37–1.47[a]—^{210}Pb	Bonotto et al. (2009)
Continental Intercalaire aquifer, Algeria, and Tunisia	Groundwater	16.28–98.05[a]—^{226}Ra[b] 3626–31,487[a]—^{222}Rn[b] 23.68–566.84[a]—^{226}Ra[a] 6105–13,912[a]—^{222}Rn[a]	Elliot et al. (2014)
Huelva, Spain	Drinking water	20 ± 7[b]—^{210}Pb 11 ± 5[b]—^{234}U; 7.5 ± 3.3—^{234}U	Pérez-Moreno et al. (2020)
Chitrapuzha river, Cochin, India	River water	12 ± 9[b]—^{226}Ra 2.0 ± 1.0[b]—^{210}Po	Haridasan et al. (2001)
Kłodzko Valley, Poland	Spa water	5000 ± 2000–171,000 ± 87,000[a]—^{222}Rn 11 ± 6–1060 ± 30[a]—^{226}Ra 40 ± 10–330 ± 50[a]—^{228}Ra	Walencik-Łata et al. (2016)
São Paulo and Minas Gerais, Brazil	Spa water	6.6[b]—^{210}Po 4.7[b]—^{210}Pb	Bonotto and de Oliveira (2017)

[a] *Minimum value–maximum value (average value).*

[b] *Average value.*

Groundwater is often considered a significant source of drinking water and agricultural water worldwide. Therefore, high REE and radionuclide concentrations in aquifers pose a risk to human health (Bhatti et al., 2012; IAEA, 2014). Because the activity concentration of natural radionuclides in groundwaters is strongly associated with the aquifer physicochemical properties and geological context, it is observed that a great range of variation on radionuclides concentrations in different regions. For example, a recent study described the behavior of long-lived natural radionuclides in Spanish groundwaters, pointing out that the highest activity concentrations of ^{210}Pb (20 ± 7 mBq L^{-1}) and Ra (35 ± 17 mBq L^{-1}) were associated with aquifers of granitic bedrock, while carbonate rocks played an essential role in supplying ^{234}U (average value of 9.9 ± 1.8 mBq L^{-1}) for the groundwaters, with both aquifers exceeding the ^{226}Ra and ^{210}Pb permissible doses for water ingestion (i.e., 730 L year^{-1} for adults) (Pérez-Moreno et al., 2020).

REE concentrations in freshwaters also exhibit significant variability mainly due to anthropogenic inputs of contaminants to aquatic systems. Information about site-specific background concentrations of REE in freshwaters is essential for more accurate human health and ecological risk assessments. Adeel et al. (2019) described the REE distribution in surface waters (urban water, lake water, and river water) and groundwaters worldwide, indicating that Asia presented the highest risk of REE pollution (mainly due to Cerium (Ce) and Lanthanum (La)), followed by Europe, Africa, United States, and Australia.

17.3 Effects of REE and radionuclides to aquatic organisms

Although the emission of REE and radionuclides to the environment is part of nowadays society (Dushyantha et al., 2020), little is known about the fate of these emerging contaminants on environmental systems and their effects on the aquatic biota. Over the past few years, it has become clear that it is essential to better understand the role of human activities on freshwater pollution and the associated risks to the environment and human health. Characterizing freshwater pollution by REE and radionuclides is therefore an essential task to be promoted by research scientists, environmental managers, and regulatory agencies to better assess future exposures after waste disposal (Kumblad et al., 2006).

17.3.1 Pollution of freshwaters by REE and radionuclides

Since REEs are required for nearly all electronic and clean energy technologies, REE contamination has been reported mostly in urban and highly industrialized areas (He et al., 2010; Sun et al., 2017). As these elements are mainly applied in high technology, pollution concern has mostly arisen in developed countries and fast-growing economies (Adeel et al., 2019).

Mining activities have been pointed out as the primary input sources of REE into anthropogenic and environmental systems (Galhardi et al., 2020). In mineral deposits, REE is quite often associated with radionuclides, such as Th and U, sometimes to an extent that allows their commercial exploitation, e.g., Th extracted from monazites (IAEA, 2011). After being released from mining tailings, radionuclides may be transported to surface waters through surface runoff or groundwaters, following percolation of mining effluents through aquifer systems (Galhardi and Bonotto, 2017).

Agricultural fields can be regarded as additional vulnerable areas for REE and radionuclide contamination due to the use of REE-rich phosphate fertilizers, which may also contain high amounts of U, Th, and potassium (K) and are associated with high potential risks for human health through food and water ingestion (Silva et al., 2019; Vranješ et al., 2020). Moreover, agricultural and mining activities can be concurrent sources of radionuclides and REE to the environment (Galhardi et al., 2020).

Although restricted to fewer locations, nuclear energy exploration poses great concern due to the magnitude of the freshwater contamination risks. Activities such as mining of nuclear fuels, leaks at nuclear power plants, and nuclear testing have been reported as sources of river contamination by radionuclides (Gorlachev et al., 2020). Furthermore, nonnuclear industries, such as the soil and gas sectors, can also contribute to radionuclides input into the environment (Skipperud and Salbu, 2017).

Climate has an important role in freshwater contamination by radionuclides and REE. For example, radioactivity in river waters has been reported to increase in the summer as a consequence of higher temperatures, intensified fertilization of agricultural soils, and alterations in the soil structures (Selçuk Zorer, 2019). As a consequence, higher proportions of contaminants can be transported to water bodies by surface runoff (Shajib et al., 2020). In tropical areas, radionuclide concentrations were reported to increase during the rainy season due to the increased leaching rates of minerals from soils, rocks, and sediments (Galhardi and Bonotto, 2017). Therefore, the transport of contaminants from the ground into the aqueous media might suffer seasonal variations in different scales, according to the climate regime.

To monitor and predict possible risks related to contaminants in the environment, the maximum permissible concentrations (MPCs) or maximum contaminant levels (MCLs) are established as reference values for the maximum allowable concentration of a contaminant in drinking water (USEPA, 2017). As early as 2000, MPCs were established for REE as an effort of the Directorate-General for Environmental Protection of the Netherlands. MPC was calculated as the sum of the maximum permissible addition, obtained from ecotoxicity tests data, and the background concentration for each element. The calculation was based on the added risk approach, as REEs occur in the environment due to both natural and anthropogenic sources (Sneller et al., 2000). The derived MPC in surface waters is expressed in Table 17.3. For radionuclides, two guidelines are available to support regional regulations (USEPA, 2012; WHO, 2011). After the Fukushima Daiichi Nuclear Power Accident, the Japanese government established provisional new radionuclides standard limits for food and drinking water to improve food safety and assure consumer confidence in food quality. Only radionuclides with half-lives over 1 year and presenting increased emissions after the nuclear accident had the limits reviewed (JAPAN, 2012).

In Sub-Saharan Africa, the many natural REE reservoirs may be potential sources of freshwater contamination (Gwenzi et al., 2018). In drinking water samples from the Ethiopian portion of the Rift Valley, high REE concentrations were reported for samples from superficial sources, in some cases above European guideline values (Reimann et al., 2003). In Ghana, a national program to establish baseline radioactivity concentration near mines reported 2.51, 1.71,

TABLE 17.3 Permissible levels of REE and radionuclides on drinking waters around the world.

Elements	Limits for human consumption	Reference
REE—La to Lu	- 6.4, 10.1, 22.1, 9.1, 1.8, 8.2, 7.1, 9.3 μg L^{-1} (Y, La, Ce, Pr, Nd, Sm, Gd, Dy, respectively)	Sneller et al. (2000)
Radionuclides—U, Th, Ra, and Po	- 0.1 Bq L^{-1} (^{210}Po, ^{228}Ra) - 1 Bq L^{-1} (^{232}Th, ^{235}U, ^{226}Ra) - 10 Bq L^{-1} (^{238}U, ^{137}Cs)	WHO (2011)
Radionuclides—Th, Ra, Rn, and Po	- 5 pCi L^{-1} (Combined ^{226}Ra and ^{228}Ra) - 4000 pCi L^{-1} (Rn) - 30 μg L^{-1} (U)	USEPA (2012)
Radionuclides—Cs, Sr, Pu, and Ru	- 10 Bq kg^{-1}	JAPAN (2012)

and 41.43 Bq L^{-1} for ^{238}U, ^{232}Th, and ^{40}K, respectively, in river waters from the Central and Western regions of the country (Adukpo et al., 2015). Radionuclide's concentrations exceeding the guidelines published by the World Health Organization (WHO) were found in Nkalagu river dam (120.45 ± 6.51 Bq L^{-1} of ^{40}K, 5.49 ± 0.70 Bq L^{-1} of ^{238}U, and 0.14 ± 0.01 Bq L^{-1} of ^{232}Th), southeastern Nigeria, known for its limestone deposit (Ugbede et al., 2020).

In Malaysia, water samples from the surroundings of Lynas Advanced Material Plant (LAMP), the world largest rare earth refinery plant, showed background activities of 0.33 ± 0.05 Bq L^{-1}, 0.18 ± 0.04 Bq L^{-1}, and 4.72 ± 0.29 Bq L^{-1} for ^{226}Ra, ^{232}Th, and ^{40}K, respectively, which were reported as potential risks to residential areas surrounding the plant (Kolo et al., 2015). In a U ore extraction and processing mine in Taboshar, Tajikistan, a U concentration of 2.0 mg L^{-1} was found in waters from the pit lake, while ^{238}U concentrations of 6 kBq kg^{-1} (dw) was found in the sediments, which showed a low transfer rate of radionuclides to the waters (Skipperud et al., 2013).

Tritium, a radioactive isotope of hydrogen, was lower than the minimum detectable activity (0.6 Bq L^{-1}) in the river, rain, mineral bottled, and tap waters samples from different areas of Catalonia, Spain. Only samples from the Ebro River presented high activity (3.6–0.6 Bq L^{-1}), which may be related to the proximity to the nuclear power station of Asco (Palomo et al., 2007).

For two decades, Gadolinium (Gd) anomalies have been found in surface and groundwaters in Europe, Australia, Brazil, and the United States. Used as a contrasting agent in magnetic resonance imaging, Gd has a short residence time in the human body and tends not to be removed by conventional wastewater treatment systems, being discharged mostly unaltered into rivers (UNEP, 2016). Anomalies have been observed in countries that bear highly developed health care systems (Adeel et al., 2019; Balaram, 2019). However, the increased Gd pollution seemly will not take long to be spread out in developing nations, such as in Cotonou, Democratic Republic of Congo, where Gd anomalies have been reported even through magnetic resonance imaging was implemented in the city shortly before the water monitoring (Atinkpahoun et al., 2020).

Water pollution by emerging contaminants is of huge concern in developing countries, where the inadequate disposal of wastes is recurrent (Atinkpahoun et al., 2020; Lange et al., 2017). In addition, environmental monitoring programs in developing countries seem ineffective given the magnitude of environmental impacts (Gwenzi et al., 2018). Other factors corroborate this scenario, such as the broad use of products for crop protection (e.g., fertilizers, fungicides, pesticides), availability of techniques to efficiently remove radionuclides and REE from waters, analytical challenges related to the proper quantification of contaminants under relevant environmental concentrations, and the effects of regional climate change on the fate of the contaminants in the environment. Careful monitoring of emerging contaminants in freshwaters from developing countries is required upon selecting the appropriate mitigation strategies.

17.3.2 Toxicity of REE and radionuclides to aquatic organisms

Some REE chemical attributes have been successfully related to their toxicity. For example, LREE concentrations are frequently reported to be higher and more toxic than HREE to aquatic organisms (Pastorino et al., 2020; Yang et al., 2016). The high electronegativity of the REE was shown to pose significant risks to trout juveniles (Dubé et al., 2019). Toxicity tests performed with *Hydra attenuata* exposed to REE at concentrations likely to occur in the environment indicated that atomic number and ionic radius influenced the REE toxicity. The lethal and sublethal doses of REE to *H. attenuata* ranged from 0.21 to 0.77 mg L^{-1} (LC50), and from 0.02 to 0.27 mg L^{-1} (EC50) (Blaise et al., 2018).

Low trophic level organisms tend to present higher bioaccumulation of REE (Blaise et al., 2018; MacMillan et al., 2017). Higher REE concentrations were found in benthic species when compared to pelagic ones, probably as a consequence of higher exposure of benthic organisms to contaminants in sediments (Mayfield and Fairbrother, 2015; Pastorino et al., 2020). Bioaccumulation of REE was reported in carps (*Cyprinus carpio* L.) for La, Ce, Praseodymium (Pr), Neodymium (Nd), and Samarium (Sm) (Hao et al., 1996); in aquatic plants and crustaceans for Ce, Gd, La, Strontium (Sr) and Pr (Blinova et al., 2018); as well as in fish, phytoplankton, crustacean (*Daphnia* sp.), and several arctic animals (Yang et al., 1999; MacMillan et al., 2017).

Considering the many pathways for the release of radionuclides into the environment, they are often released along with co-contaminants, such as REE, metals, pesticides, and fertilizers, showing additive, synergistic, or antagonistic effects to aquatic organisms (Skipperud and Salbu, 2017). The synergetic or antagonistic effects depend largely on the exposed organism (Romero-Freire et al., 2019) and the contaminant properties. For example, ^{90}Sr and ^{137}Cs have long half-lives and high radiation dosages, making their effects persistent and severe to living organisms. At the body tissues, calcium (Ca) can be replaced by radioactive iodine (I) and Sr, whereas K can be replaced by Cs (Echols et al., 2009). Furthermore, Ca replacement by REE was reported in zebrafish embryos (Cui et al., 2012). In some cases, ion competition may be beneficial, as Ca^{2+} and Mg^{2+} competing with UO_2^{2+} for sites at the cell surface (Markich, 2013), and Fe and Cu competing with U for biomolecules (Frelon et al., 2013), resulting in reduced bioaccumulation of U species and lower ecotoxicity. Competition effects can also occur among elements from the same chemical group, as reported for the REE (Tan et al., 2017).

Radionuclide transfer from water to organisms in aquatic systems can be quantified through the concentration factor (CF), which is defined as the ratio between the radionuclide concentration in a biologic tissue and the surrounding water (IAEA, 2010). An online international wildlife radionuclide transfer database is available (Copplestone et al., 2013), highlighting the importance of monitoring the bioaccumulation of these contaminants in the aquatic ecosystems. Other databases have been compilated with CF values and concentrations of radionuclides in aquatic organisms (e.g., International Atomic Energy Agency, 2004; Beresford et al., 2015; Howard et al., 2013; Howard and Larsson, 2008; IAEA, 2010). The ERICA Project was created to estimate the level of wildlife exposure to ionizing radiation and to be a tool for the environmental management of terrestrial and aquatic ecosystems. The project is divided into ERICA Integrated Approach, which compilates scientific data of exposure, effect, and risk assessment, and ERICA Tool, which comprises a software designed to facilitated ERICA Integrated Approach access (Howard and Larsson, 2008).

Cesium bioaccumulation has been reported to a large number of aquatic organisms and is detailly reviewed elsewhere (Metian et al., 2019). Based on the gut content, stable nitrogen, and carbon isotopes, food web-related U bioaccumulation was reported in fish (*Micropterus dolomieu*, *Perca flavescens*, *Lepomis macrochirus*) and invertebrates (bivalves and zooplankton) species in a lake historically impacted by mining activities in northeastern Ontario, Canada, 30 years after the mine inactivation (Kraemer and Evans, 2012). For 2 years, Ishii et al. (2020) studied aquatic organisms, among them 30 fish species, from three lakes and five rivers in Fukushima after the Fukushima Dai-ichi Nuclear Power Plant accident, reporting the occurrence of ^{137}Cs biomagnification for piscivore fishes from the lakes, which did not happen with the riverine fishes.

Uranium showed a low feeding-dependent trophic transfer and accumulation in the digestive gland (the main target), gills, muscle, and molt of *Orconectes limosus* (Simon and Garnier-Laplace, 2005). Although absorbed U has been reported to be primarily retained in hard tissues of aquatic organisms from fresh and seawater systems (Cooley, 2000; Edwards, 2003), it may be assimilated by the digestive gland and translocated along with Ca from the gland to the mineralized compartments during the ecdysis process (Simon and Garnier-Laplace, 2005).

17.3.3 Field and lab exposure of aquatic organisms to REE and radionuclides

The extrapolation of the (i) in laboratory (in lab) data obtained for adult individuals to all the other stages found within a species lifespan, (ii) exposure of the model to a single stressor or a stressor group, and the (iii) lack of long-term chronic exposure to a contaminant pose significant uncertainties regarding the effects of stressors on aquatic organisms at a transgenerational level (Skipperud and Salbu, 2017). Nevertheless, in lab tests have been shown to successfully explain processes involved in field observations (Metian et al., 2019).

Higher REE concentrations in organisms from lower trophic levels and the role of sediments as a source of REE have been corroborated by microcosm experiments (Yang et al., 1999) and field studies (Pastorino et al., 2020; Weltje et al., 2002). In addition, field studies indicate that bioaccumulation occurs for both REE and radionuclides, but only radionuclides present biomagnification at significant trophic transfer rates (Cardon et al., 2020; MacMillan et al., 2017). From laboratory studies, element fractionation at a subcellular level has been pointed out as a possible explanation for low REE trophic transfer (Cardon et al., 2020).

Ecotoxicity of REE and radionuclides from leachates of a niobium (Nb) mine in Canada was assessed to phytoplankton (*Raphidocelis subcapitata*), duckweed (*Lemna minor*), and water flea (*Daphnia magna*). Toxicity was observed only in the less diluted concentrations (75% and 100% v/v), but higher than those likely to be found in real environmental conditions due to leachate dilution by groundwater and rainwater (Paquet et al., 2019).

Knowing the ligands present in the aqueous solution is essential for an accurate risk prediction. For example, high levels of carbonates and phosphates ligands could reduce REE bioavailability in mining tailings, resulting in an underestimation of toxic effects (Gonzalez et al., 2014; Sneller et al., 2000). Co-precipitation of REE with phosphate and carbonates in lab experiments has been indicated as a major reason for diverging results about REE toxicity in the literature. In the absence of phosphate and carbonates ligands, a pattern of higher ecotoxicity for REE with higher atomic numbers can be identified. However, because precipitation is stronger for REE with higher atomic numbers, no ecotoxicity pattern can be observed when such ligands are in the media (Gonzalez et al., 2014). Additionally, REE may be complexed with natural organic matter ligands, showing increased bioavailability in natural waters (Yang and Wilkinson, 2018).

As emerging contaminants, the biological effects of REE and radionuclides are still not well understood, especially in the case of REE-engineered nanoparticles (ENPs). Because some REE by-products involve the development of innovative nanotechnology, there is an increasing concern about the ecotoxicity of these novel contaminants. For example, Ce ENPs have been shown to influence the gene transcription in *Chlamydomonas reinhardtii*, whereas the transcriptomic activity was affected by the ENPs coating composition (Morel et al., 2020). For Ce, Gd, La, Sr, and Pr ceramic oxides, low acute toxicity (EC50 N 100 mg L^{-1}) was observed in crustaceans and duckweeds, although the accumulation of the oxides was observed (Blinova et al., 2018).

17.4 Removal of REE and radionuclides from freshwaters

Removal of emerging contaminants from freshwaters is a worldwide concern, which still lacks regulation for some classes of contaminants to protect the environment and human health. It is extensively known that inorganic contaminants adversely affect freshwaters, causing environmental damages and numerous human health problems. Although there is a huge diversity of technologies with wide applications for the removal of inorganic contaminants from aqueous media, in many cases, combinations of different techniques are required for the effective and proper elimination of the contaminants. Below, a general view of the main technologies for the removal of REE and radionuclides from waters and wastewaters is described.

17.4.1 Technologies for removing and recycling REE and radionuclides from the aqueous media

The most used physical, chemical, and biological methods for the removal of REE and radionuclides from aqueous solution are presented in Table 17.4. Processes such as aeration, coagulation, flocculation, chemical precipitation, solvent extraction, ion exchange, biosorption, the use of membranes, electrochemical reactions, and nanomaterial are described.

17.4.1.1 Aeration

Aeration is generally the first major process taking place in wastewater treatment plants. It uses microorganisms from the wastewaters to remove contaminants such as dissolved metals and radionuclides (WHO, 1996). For example, the highest removal efficiency for Ra was reported to be reached after optimization of the aeration process using diverse aerators, packed tower, and gas-degas technology followed by the stages of oxidation and filtration/catalytic filtration (Lumiste et al., 2012).

17.4.1.2 Coagulation/flocculation

Flocculation is typically applied before sedimentation and rapid sand filtration, in which charges are neutralized by adding coagulants (e.g., iron, titanium, and zirconium salts) following the combination of small particles into larger aggregates (flocs) (MRWA, 2003). This process is also applied in combination with metal precipitation, which forms low-solubility metal compounds bound to carbonates, sulfides, and hydroxides. Kim et al. (2019) reported coprecipitation of radionuclides with hydrous ferric oxide (HFO) followed by a coagulation-flocculation system using HFO-anionic polyacrylamide (PAM) composite floc, which successfully removed radionuclides from radioactive wastewaters (removal of 99% for Mn-54, Co-60, Sb-125, and Ru-106).

TABLE 17.4 Main techniques for the removal of REE and radionuclides from waters and wastewaters.

Technique	Description	Elements to be removed	References
Aeration	Process of adding air into wastewater to allow aerobic biodegradation of the pollutant components	Ra	Lumiste et al. (2012)
Coagulation/ Flocculation	Addition of compounds that promote the clumping of the fine into larger flocs, thus being more easily separated from the water	Mn, Co, Ru, Sb	Kim et al. (2019)
Chemical precipitation	Dissolved metals (in basic conditions) are converted into an insoluble metal hydroxide via chemical reaction by a precipitant agent	Am, I, Ra, Sr, U	Munter (2013), Zhang et al. (2019)
Solvent extraction	Separation technique using solvents which separates complexes based on their solubility	Cs, Er, Ho, Lu, Tm, Y, Yb	Hidayah and Abidin (2018), Bengiat et al. (2018), Silva et al. (2019)
Adsorption and ion exchange extraction	Purification of aqueous solutions using natural or synthetic ion exchange resins	Ce, La, Yb Co, Cs, I, Sr, Th, U	Alshameri et al. (2019), Zhang et al. (2019), Felipe et al. (2020)
Biosorption	Process-based on the removal of metal ions, radionuclides, and REE by biological material such as active biomass that presents a complex diversity of chemical mechanisms	Dy, Er, Eu, La, Lu, Nd, Sc, Sm, Tb, Y, Yb; Am, Cs, U	Gupta et al. (2018), Costa et al. (2020), Giese (2020), Ferreira et al. (2020), Lapo et al. (2020)
Membrane technologies	The Method that combines adsorption of target contaminants and filtration based on the size exclusion mechanism of membranes	Gd, Nd, Sm, Tb; Co, Cs, I, Mn, Sb, Te, U	Rana et al. (2013), Pereao et al. (2018), Zhang et al. (2019)
Electrochemical treatment	The electrochemical technologies consist in the use of electrolysis which breaks down substances using the electricity generated between two electrodes	Co, Cs, Graphite radioactive, U	Bespala et al. (2019), Alkhadra et al. (2020)
Nanomaterials	Nanoparticles with small sizes and a high surface area used as potential adsorbents for pollutants	Co, Cs, La, Nd, Sc, Y, Yb	Galhoum et al. (2016), Yang et al. (2017), Attallah et al. (2018), Ramasamy et al. (2019)
Integrated technologies	Combination of two or more treatment technologies to improve the removal of radionuclides and REE	Co, Sr	Ortiz-Oliveros et al. (2012), Wu et al. (2014), Arnal et al. (2017)

17.4.1.3 Chemical precipitation

Chemical precipitation is widely used for the removal of trace metals, radionuclides, and REE from aqueous solutions. The process is simple and requires inexpensive equipment (Kurniawan et al., 2006). The pH is adjusted to basic conditions (pH 10–11), which allows dissolved metals to be converted into insoluble metal hydroxides via a chemical reaction with a precipitant agent (e.g., lime, alum, iron, and magnesium salts). Precipitates can then be separated from water by sedimentation or filtration. The conceptual chemical reaction of precipitation is shown in Eq. (17.1) (Wang et al., 2004):

$$M^{2+} + 2(OH)^- \leftrightarrow M(OH)_2 \downarrow \tag{17.1}$$

where M^{2+} and OH^- denote the dissolved metal ion and the precipitant, respectively, while $M(OH)_2$ is the insoluble metal hydroxide.

Despite its advantages, chemical precipitation requires a large number of chemicals for proper metal removal. Therefore, it produces a huge amount of sludge that requires further treatment, resulting in a long-term environmental impact due to sludge disposal (Wang et al., 2004). According to Munter (2013), precipitation with lime can remove 85%–95% of U, whereas the posterior co-precipitation with barium (Ba) sulfate or chloride, followed by sedimentation and filtration, removes 50%–95% of Ra. Other salts have been discussed in a review of Zhang et al. (2019), in which cuprous chloride, sodium permanganate, and strontium nitrate have been reported to precipitate radioactive I^-, americium (Am), and Sr.

17.4.1.4 Solvent extraction

Solvent extraction refers to separation techniques based on the solubility of solvents and complexes. This technique is time-consuming and requires large volumes of solvent, which generates large amounts of toxic waste (Pereao et al., 2018). Selective precipitation and co-precipitation combined with solvent extraction have been developed for more effective removal of highly soluble ions, such as Cs and rare earth oxalates/rare earth carbonates. Effluents are initially purified with sulfuric acid and then treated with oxalic acid and sodium carbonate or with a solution containing synthetic water-soluble organic ligands (Bengiat et al., 2018; Silva et al., 2019). Liquid-liquid extraction (LLE) techniques have been developed due to the convenient arrangement for aqueous solutions, while ionic liquid (IL)-based processes have been applied to the extraction of holmium (Ho), yttrium (Y), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu) (Hidayah and Abidin, 2018).

17.4.1.5 *Adsorption and ion exchange*

At the moment, adsorption may be the best and most efficient technique for water and wastewater treatment, based upon the choice of the most cost-effective adsorbent. The main chemical characteristics of radionuclides and REE (positive charge and ionic potential) make them powerfully adsorbed by ionic resins (especially the cationic resins). Compared to conventional methods, such as precipitation and solvent extraction, the ion exchange technology presents a better performance to treat large volumes of even trace levels of metallic ions. Moreover, natural material used for the sorption of contaminants can be regenerated and reused for many decontamination cycles, thus representing a green process for water treatment. Therefore, by using natural and synthetic materials as ionic resins, the ion exchange process can be applied for the removal of REE from contaminated waters (Kołodyńska and Hubicki, 2012).

Countless natural materials exhibit ion exchange properties for the removal of many radionuclides and REE. For example, clay minerals (kaolinite (Kao), montmorillonite (Mt), muscovite (Ms), and illite (Il)) removed above 80% of La and Yb from waters, following the order Kao > Ilt > Mt > Ms (Alshameri et al., 2019). Among the synthetic materials applied for the removal of REE, the resins Dowex 50WX8 and Lewatit MDS 200H showed effective removal of Y, La, Ce, Nd, Gd, and dysprosium (Dy) from acid mine drainages (pH 1.4–3.4) (Felipe et al., 2020). To purify the radioactive wastewaters generated by the Fukushima Daiichi plant, Japan, four ion exchangers (zeolite, silicotitanate, hexacyanoferrate, and sodium titanate) were tested. While zeolite and silicotitanate were used to remove radiocesium and radiostrontium from the cooling waters recirculated in the reactors, hexacyanoferrate, and sodium titanate were applied to purify the radionuclides after a primary separation (Lehto et al., 2019).

With the advances in polymer technology, synthetic polymers have been prepared based on molecular imprinting with the same shape as the target contaminant. These ion-imprinted polymers can recognize the target analyte selectively, even in the presence of other ions (Pereao et al., 2018). For example, chitosan has been modified through the ion-imprinted technique for application in the nuclear industry, showing selective sorption of Co(II) over Fe(II), contrarily to the selectivity of Fe(II) over Co(II) by the raw chitosan (Nishad et al., 2012).

17.4.1.6 *Bioremediation*

Physicochemical techniques for radionuclides and REE removal from large volumes of water can be costly. Therefore, there is an increasing interest in the development of more sustainable and economical alternatives for the decontamination of impacted waters. In this scenario, biosorption has been pointed out as a greener technology for the removal of metal ions, radionuclides, and REE from contaminated waters. Biological materials, such as microbial, plant, and animal biomass, are applied for the removal of contaminants based on mechanisms including absorption, ion exchange, surface complexation, and precipitation (Gadd and Biosorption, 2008).

Activated carbon materials have been widely used to remediate effluents due to their porous structure, which improves the adsorption efficiency of metal ions (Radovic et al., 2001). Costa et al. (2020) discussed several carbon materials (biochar from bamboo, cactus fibers, rice husks) for the removal of REE. In addition, some plant biomasses (dandelion root, chitosan) were applied as adsorbents to remove Am, Eu, Sr, and U from aqueous solutions, with higher removal rates for Sr and Am (80% and 90%, respectively) (Fuks et al., 2016; Wang et al., 2020).

For nuclear waste management, several microorganisms were reported as sustainable bio-sorbents (Gupta et al., 2018). Pinto et al. (2020) obtained efficiency rates ranging from 60 to 90% for REE removal from waters using a living macroalgae *Ulva lactuca*. Biomass produced from fermentation, food, brewing, and distilling industries can also be applied as bio-sorbents. Ferreira et al. (2020) examined raw coffee husks as potential biosorption materials to remove U, americium (Am), and Cs, with adsorption of 1.96, 39.4×10^{-6}, and $46.6 \times 10^{-9}\,\mathrm{mg\,g^{-1}}$, respectively, as their maximum capacity. Lapo et al. (2020) applied banana waste as sustainable adsorbent materials for the REE recovery (Nd^{3+}, Eu^{3+}, Y^{3+}, Dy^{3+}, Tb^{3+}), showing that banana rachis presented an adsorption capacity of $\sim 100\,\mathrm{mg\,g^{-1}}$ for most of the REE.

In addition to biological technologies, anaerobic digestion has been extensively proposed for metal recovery. For example, Nogueira et al. (2019) developed a biological reactor for treating acid mine drainage containing a high concentration of sulfate ($\sim 1000\,\mathrm{mg\,L^{-1}}$), dissolved metals, U, and REE. The higher removal efficiencies of La, Ce, Pr, Nd, Sm, and Y (more than 70%) emphasize the potential use of anaerobic bio-digestion for the treatment of mining wastewater, providing possibilities for REE and metal recovery.

The most appealing biosorption technique feature is its low cost (using even residual biomass), in addition to the minimum generation of sludge, high removal efficiency, the regeneration capacity of the bio-sorbents, and great recovery potential of the elements bound to the bio-sorbents. In some cases, the recovered metals can be used as input materials for several industries. On the other hand, the efficiency of contaminant removal by the bio-sorbents should be tested on batch experiments considering factors such as pH, temperature, bio-sorbent dosage, the concentration of pollutants, agitation rate, and period of contact (Gadd and Biosorption, 2008).

17.4.1.7 Membrane technologies

Membrane technology combines the adsorption of target contaminants and filtration based on membrane size exclusion. The contaminant removal is thus controlled by the membrane pore size and the adsorption capacity of target pollutants (Abdullah et al., 2019).

The microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) membranes present pore size ranges of 100–1000 nm, 10–100 nm, 1–10 nm, and 0.1–1 nm, respectively. Each membrane type requires a specific pressure level during the filtration process, which can be classified as low-pressure processes (microfiltration—MF and ultrafiltration—UF); high-pressure processes (nanofiltration—NF and reverse osmosis—RO); osmotic pressure process (forward osmosis—FO), and liquid membrane—LM (Carolin et al., 2017). The most used membranes for the removal of REE (e.g., Gd, Nd, Sm, Tb) and radionuclides (e.g., Cs, U) are the NF and RO membranes (Rana et al., 2013; Pereao et al., 2018).

Membranes can mainly be composed of ceramic and polymer materials. Polymeric materials such as polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), polyethylsulphone (PES), polysulphone (PS), polypropylene (PP), and polyethylene (PE) are commercially used as membranes mostly due to their chemical resistance. Nevertheless, biopolymeric materials such as chitosan and activated carbon have gained eco-friendly visibility in the past years, while ceramic membranes (e.g., oxides of titanium, zirconium, and silicon carbide) have been used in extreme conditions such as high temperatures and aggressive chemical solutions, as they are more robust compared to polymeric membranes (Pereao et al., 2018).

17.4.1.8 Electrochemical treatment

Electrochemical technologies, such as electrocoagulation and electrodialysis, are capable of removing suspended and dissolved solids, metals, REE, and radionuclides from water and wastewaters (Pereao et al., 2018). For example, U was efficiently removed (recovery of 89.7%) by electrocoagulation using an optimized Fe anode and Alizarin S chelate within 24 min under a current density of 2.4 mA cm^{-2} (Li et al., 2020). Recently, the electrodeionization/shock electrodialysis, which combines electrodialysis and an ion exchange resin, was capable of continuously removing Co and Cs from contaminated nuclear wastewater (Zhang et al., 2019; Alkhadra et al., 2020).

17.4.1.9 Nanomaterials

Among the emerging technologies, nanotechnology has been showing an increasing potential for contaminant removal from wastewaters. Nanoparticles are being developed as potential adsorbents of contaminants due to their small size and high surface area, which improves their adsorption capacity (Kyzas and Matis, 2015). Carbon nanotubes (CNTs) modified into single-walled carbon nanotubes (SWCNT) and multiwalled carbon nanotubes (MWCNT) presented great adsorption capacity for La^{3+}, Sc^{3+}, and Y^{3+} (Ramasamy et al., 2019). Silica (SiO_2)-derived nano adsorbents comprise another attractive tool for the removal of REE. For example, the Prussian blue functionalized SiO_2 (nanomaterial of SiO_2-Fe-CN) successfully removed 95.7% and 88.8% of $^{134}Cs^+$ and $^{60}Co^{2+}$, respectively, from effluents at pH 5.5 (Attallah et al., 2018).

Functionalized magnetic nanoparticles stand as a promising novel class of green material for water treatment due to their acid resistance and reuse capacity (Pereao et al., 2018). Galhoum et al. (2016) successfully applied chitosan-coated magnetic nano-based particles for the removal of Nd and Yb from solutions at pH close to 5. Yang et al. (2017) developed a sodium-copper hexacyanoferrate (NaCuHCF)-functionalized magnetic nano-adsorbents capable of removing radioactive Cs from seawater.

17.4.1.10 Combined technologies

Water treatment effectiveness can be improved based on an integration of two or more technologies for the removal/recovery of contaminants. For example, a combined coagulation-flocculation/dissolved air flotation column system was efficient to remove ^{60}Co from nuclear industry wastewaters (Ortiz-Oliveros et al., 2012). Wu et al. (2014)

developed a hydraulic pellet co-precipitation microfiltration process for the treatment of radioactive wastewater containing Sr. By combining a membrane with evaporation, it was possible to improve the contaminant removal rate, decrease energy consumption, and generate less volume of by-products. Similarly, Arnal et al. (2017) proposed treatment of the radioactive wastewater from an experimental pool reactor by using membranes and evaporation systems, reaching satisfactory decontamination of 98.5% of the radioactive water (681 m^3).

17.4.2 Economical and technical challenges for the removal and recycling of REE and radionuclides from waters

One of the greater limitations among all techniques for the removal of radionuclides and REE from aqueous media is based on the high cost to treat large volumes of effluents. Treatments based on ion exchange activated carbon, and membranes can be very expensive for large amounts of water (Dhir, 2014). The removal of complex analytes from waters remains a challenge across scales, but emerging technologies (e.g., reverse osmosis, nanofiltration, activated carbon) are showing high removal efficiency, although at high operational costs (see Tavengwa et al., 2022, Chapter 20).

While small-scale wastewater treatment plants might offer benefits such as the ability for onsite resource recovery, they are not effective to treat large quantities of wastewater (Diaz-Elsayed et al., 2019). Therefore, capital investment and operational costs should be considered within the prospectus of the life-cycle assessment of wastewater treatment plants (Pereao et al., 2018). Preliminary costs of different processes for REE and radionuclides removal from waters might differ according to the region. For example, in Italy, the operational costs of reverse osmosis are five times higher than aeration and adsorption by activated carbon. Compared to the US, the total costs of ion exchange, lime softening (chemical precipitation), and MnO_2-based methods (coagulation/flocculation followed by filtration) were in the same range of price, 0.07–0.19 eur m^{-3} (Munter, 2013).

Besides lowering the costs, efforts are being made to reduce the production of by-products and to recover metals and other products from the wastes. For example, the transition from the conventional land application of biosolids to a process that enables waste volume reduction (incineration, pyrolysis/gasification) could minimize the mass of solid residue to be discarded in the environment (Diaz-Elsayed et al., 2019).

The feasible advantage resulting from recycling REE from wastes (mainly fluorescent powders, fluid catalytic cracking catalysts, and permanent magnets) is based on attractive cost-effectiveness and environmental prospects. As an example, the production of a high-value product using recycled material has a cost around 70 times lower than the production using a primary supply (Amato et al., 2019). On the other hand, the recovery of REE from lamp waste by hydrometallurgical processes might result in further environmental impacts (Liu and Keoleian, 2020).

Although the recycling of REE and radionuclides from waste is not yet significant (e.g., up to 2011, the REE recycling rate was lower than 1%), mostly due to technological limitations and shortage of economic incentive, studies focusing on the development of effective recycling routes for REE have been increasing (Binemans et al., 2013). For example, bioleaching as an alternative for the recovery and recycling of REE from a variety of primary and secondary sources has been increasingly explored (Rasoulnia et al., 2020). Korkmaz et al. (2018) developed a sustainable hydrometallurgical process for the recovery of some REE (Ce, La, Nd, Pr, Y) from nickel-metal-hydride (NiMH) batteries of hybrid electric vehicles. The electrodes were leached with sulfuric acid (anode) and hydrochloric acid (cathode) and the REE separation was performed by precipitation. Nanofiltration was applied to recover the hydrochloric acid for reuse in further leaching cycles.

Several authors explored the possibilities to recycle REE from solid wastes. For example, Binemans et al. (2013) presented the main advantages and disadvantages of different recycling methods for products containing REE, such as REE magnets, NiMH batteries, and lamp phosphors. Ambaye et al. (2020) described emerging technologies for the recovery of REE from end-of-life electronic wastes, such as bioleaching, biosorption, cryo-milling, electrochemical processes, the use of nanomaterials, siderophores, hydrometallurgy, pyrometallurgy, and supercritical CO_2. Furthermore, Dutta et al. (2016) highlighted the economic and engineering aspects of the life-cycle assessment of REE by multinationals such as Mitsubishi Electric, Honda, Solvay Rhodia, and Veolia. Environmental benefits associated with the recycling of REE include the reduction of environmental impacts originated from REE mining and mineral processing. In addition, the development of technologies for greener mining and recycling of electronic waste have also been proposed as solutions toward effective protection of freshwater resources and sustainable development.

This chapter falls under the section on fate and occurrence of emerging pollutants within aquatic ecosystems with other chapters, e.g., Ajayi et al. (2022), Cristale (2022), Vizioli et al. (2022), Galhardi et al. (2022), Hashemi and Kaykhaii (2022), Madikizela et al. (2022), Mashile et al. (2022), Montagner et al. (2022), Moodley et al. (2022), Ntshani and

Tavengwa (2022), Sanganyando and Kajau (2022), and Yardy et al. (2022) that aims to make an understanding of the different emerging pollutants within the aquatic environment.

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CHAPTER

18

Nanoparticles in biosensor development for the detection of pathogenic bacteria in water

R. Fanelwa Ajayi, Simone Barry, Mulisa Nkuna, Nzumbululo Ndou, Tessia Rakgotho, Sphamandla Nqunqa, Nokwanda Ngema, Velaphi Thipe, and Takalani Muluadzi

18.1 Introduction

Water covers about 71% of the earth's floor, making planet earth our solar gadget with the maximum available handy water (How Much Water is there on Earth? 2020). Of this water, approximately 3% of this water comes from freshwater assets and around 0.0001% of the available fresh water can be found without difficulty abstracted by human beings, e.g., from rivers, lakes (Where is All of the Earth's Water? 2020). Some apparent modern-day uses of freshwater include cooking, drinking, washing, irrigation, heating/cooling, removal of waste, transportation, and manufacturing (EEA, 2020; Tavengwa and Dalu, 2022, Chapter 1). Freshwater is likewise vital for public regeneration and arguably is important for intellectual well-being and as 'blue spaces' to humans throughout the advanced and growing global (de Bell et al., 2017) The current water disaster sees 783 million human beings worldwide without safe water, with 84% of those living within rural areas of developing countries (WHO, 2020). About 1 in 5 instances of deaths globally involving adolescents below the age of five are associated with some form of water-associated sickness because of poor quality water or lack of sanitation (UNICEF, 2020).

Therefore, water must be one of the most incredibly prioritized natural sources located on (and under) the surface of the ground. Additionally, aquatic illnesses caused by microbial pathogens can also typically spread through infected waster assets, such as lakes, reservoirs, and lakes. The outcomes of illnesses resulting from pathogen infections can be seen within wastewaters flowing downstream of rural and urban human settlements. Waterborne pathogens which include *Salmonella typhi*, *Escherichia coli*, *Shigella dysenteriae*, *Pseudomonas aeruginosa*, *Campylobacter jejuni*, *Vibrio cholerae*, and *Legionella* spp. are commonly found in both wastewater and freshwater resources.

In terms of wastewater remedies, studies have concluded that, with the rapidly expanded population in rural and city habitations (Ashipala and Armitage, 2011; Chirisa et al., 2017), humans in low and middle countries often live with poorly evolved infrastructures, challenged with low-quality wastewater treatments systems and sewage insurance (Palanca-Tan, 2017; Karpouzoglou and Zimmer, 2016). These challenges result in greywater and excreta being disposed into flood canals and drainage systems eventually being discharged into lakes and rivers with no treatment at all. In the end, untreated wastewater is reused for irrigation (Raschid-Sally, 2010; see Mashile et al., 2022, Chapter 8) which has a terrible effect on both farming communities and the customers of farmed products (World Health Organization, 2006). In some instances, unmaintained freshwater supply pipes with leakages can also be at risk of being infected as a result of neighboring drainages. Untreated wastewater imposes severe problems for the environment and climate, in addition to public health. Due to the absence of correct protocols, microorganisms, heavy metals, and organic chemical substances, originating from industry and domestic households or industry are launched into the environment as pollutants, also imparting waterborne ailment-related pathogens with a thriving environment (Ejeian et al., 2018).

As reported by the World Health Organisation, waterborne illnesses caused by pathogenic infections lead to about 600,000 fatalities a year in middle-income countries with 1.5 million fatalities globally. In developing countries,

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waterborne sicknesses are the second maximum cause of mortality after respiration infections (Water, Sanitation and Hygiene: Fact Sheet, 2016). Incidences of waterborne illness-related mortality are concentrated in remote parts off of the world, especially in areas of Asia, South America, and Africa (World Health Organization and United Nations Children's Fund UNICEF, 2014; Osiemo et al., 2019). The common fact about these areas apart from the prevalence of illnesses is the excessive levels of poverty which halts the development of freshwater shipping resources, wastewater infrastructure, and affordable water monitoring systems (Van Derslice, 2011). Further exacerbating the situation is the apparent shortage of sanitation and reduced knowledge in the locals regarding sanitation, hygiene, and water pollution. This makes it challenging to provide the evidence required by governmental bodies and policymakers to implement regulations and strict rules regarding water research, infrastructure improvement, and hygiene systems. Industrialization and rapid urbanization in developing countries is also contributing factors to the deterioration of ground aquatic resources. The cause is large affluent masses from growing businesses and home establishments sporting excessive nutrient masses and microbial species from floor runoff (Qin et al., 2014; Cabral, 2010). This runoff similarly contributes to the improvement of pathogenic microbial groups with the capacity for causing diseases (Pandey et al., 2014).

When water resources which include rivers, reservoirs, and lakes become unsafe for water intake due to microbial contamination, the responses by high-income nations versus middle to low-income nations are broadly distinct. High-income countries believe that it is the responsibility of water carrier vendors to ensure that water excellence strives and have the mandate to report to regulatory inspectorates, their governments, and their customers (Ellis et al., 2017). It is up to water service carriers to locate water contamination hotspots and to enforce mitigation techniques. In middle to low-income nations, this is not often the case. Water carrier providers are not held to the same level of law due to much less strict degrees of law concerning the protection and maintenance of water resources. Due to this decreased level of the law, 785 million people lack essential water services, with approximately an additional 2 million people predicted globally to be using water supply with fecal contamination. In low-income countries, 22% have a deficit in wastewater control, 22% of healthcare facilities and providers lack water provisions, and 21% have no access to proper sanitation (WHO, 2019).

It is therefore very important to develop tools that are capable of monitoring and measuring water contaminants at low concentrations. It is very important to develop rapid, accurate, and sensitive monitoring and detecting techniques to ensure a safe and clean water supply (Berneschi et al., 2019). Currently, conventional methods such as spectrometry (Faraji et al., 2010), chromatography, ultraviolet (UV) and fluorescence (FL), culture and colony counting (Chen et al., 2003), and immunological methods (Li et al., 2009) are the most commonly used methods for detecting and monitoring water contaminants. Although these methods are sensitive, selective, and quantitative, they do also suffer some disadvantages like the use of expensive instruments, the requirement of trained personal to operate the instruments, complicated sample preparation, are time-consuming and due to their big size, it's impossible to perform on-site detection (Jin and Maduraiveeran, 2017; Waheed et al., 2018). Therefore, it is very important to develop very sensitive, selective, cheaper, and portable biosensors for monitoring and detecting water contaminants. In contrast to conventional methods, biosensors are fast, very sensitive, cheaper, accurate, portable, and can detect environmental contaminants at very low concentrations.

18.2 Concepts of biosensors

Biosensors are devices capable of detecting organic compounds by measuring the signals given from biological recognition events to ascertain goal concentrations. Biosensors are now ubiquitous in modern-day to day lifestyles and can be seen available on the market, e.g., glucose, and lactate sensors. Some assessments may even be received in supermarkets, such as pregnancy checks exploiting paper-based lateral flow assays and ELISA checks with electrical sign outputs (Sharma et al., 2015; Despande and Rocco, 1994; Mishra et al., 2012; Echeverry et al., 2010; Yoo and Lee, 2010; Valentini et al., 2013). Biosensors may be used for a large number of applications; examples encompass drug detection, food protection, disorder diagnostics, environmental monitoring, as well as the detection of pathogenic microorganisms. The overall workflow of any biosensing device starts with the goal of analyte binding to the probe (bioreceptor) on the platform of a transducer. The transducer then interprets the physical signal, e.g., light, mass, heat, and so forth into an electrical signal that can be analyzed and displayed to the consumer through an interface (Fig. 18.1) (Sharma et al., 2015; Despande and Rocco, 1994; Mishra et al., 2012; Echeverry et al., 2010; Yoo and Lee, 2010; Valentini et al., 2013). There are four main categories of biosensors presently described in the literature: acoustic, optical, thermal, and electrochemical. This chapter will only explore the development of electrochemical biosensors and their application to the detection of waterborne pathogens.

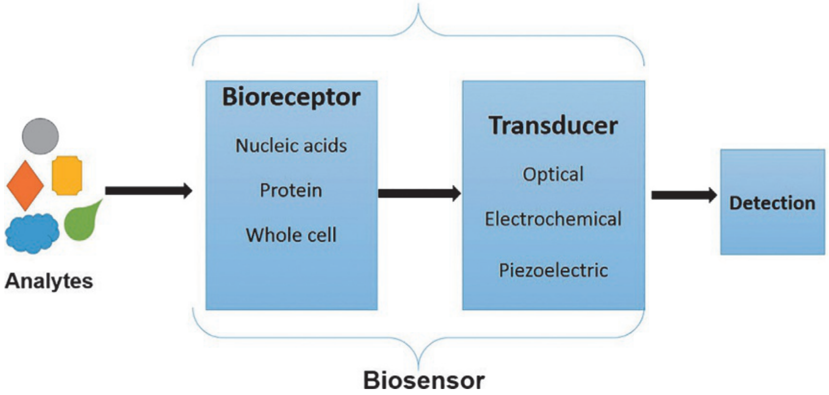

FIG. 18.1 Components of a biosensor.

18.2.1 Electrochemical biosensors

Electrochemical biosensors, products developed from the field of electrochemistry, were studied notably due to their simplistic design, their versatility, and their prompt response times. The role of electrochemical biosensors is the transduction of organic recognition activities at the interface at the working electrode, into a processable electrical response. In turn, the electrical signal proportionally displays the attention of the analyte that has been added to the tool (Bohunicky and Mousa, 2010; Van Dorst et al., 2020; Echeverry et al., 2010; Paddle, 1996). Four main varieties of electrochemical biosensors are seen in the literature concerning binding affinity research, namely; potentiometric, amperometric, conductimetric, and impedimetric. Potentiometric techniques examine the ability variation between the reference electrodes and the working electrode, which must be appropriately managed to envision the interaction of ions in solution while affected by biological molecules at the surface of the transducer. Amperometric strategies involve measuring the current regarding the oxidation and reduction ability of species that possess redox-capable ions. Impedimetric sensors allow for the analyses of complicated capacitance and resistance parameters regarding the reduction and oxidation of molecular species. Conductimetric techniques involve the measurement of the alternate of conductance for a solution following recognition of charged analytes when the biorecognition reaction occurs (Bohunicky and Mousa, 2010; Van Dorst et al., 2020; Echeverry et al., 2010; Paddle, 1996).

Electrochemical biosensors have been seen to hold several advantages as opposed to their counterparts. The benefits of electrochemical biosensing consist of a complete linear reaction; they have a variety of target compounds, are high reproducibility, have superior self-assembled monolayers, and possess low limits of detections (Faridbod et al., 2011). In broad terms, these sensors are widely applied in the analyses of environmental waters. Included herein is also the use of high-performance liquid chromatography (HPLC) (amperometric), hand-held pH meters (potentiometric), or reliable sensing structures for commonplace chemical pollutant monitoring, such as illicit drugs (Yang et al., 2016), endocrine disruptive compounds (Mayedwa et al., 2019), pesticides (Abdalla et al., 2019), and heavy metal ions (Ding and Lisak, 2019). There is absolute confidence that such chemical sensors are of significant importance in high-quality water tracking, populace sizes, and community lifestyle estimations (Senta et al., 2015).

As analytical tools, biosensors quantify and provide means of identifying analytes. The selectivity in biosensors is enabled through the use of functionalization of the biosensor interfaces using biological recognition entities such as aptamers, oligonucleotides, antibodies, enzymes, antibodies, oligonucleotides, and aptamers. Although great success has been observed in biomarker detections using electrochemical interfaces and their use widely suggested for various complicated samples, extensive dilutions discharged to drainage systems, and sewers result in tremendous challenges towards biomarker detection in real samples (Gracia-Lor et al., 2017; Khalil et al., 2018; Tran et al., 2016; Li et al., 2019). In systems as complex as aquatic environments, knowledge regarding the troubleshooting of various types of biosensors can provide a complete view of the operational principles while selecting and designing a good enough analytical interface. Furthermore, enzyme interactions are prone to pH challenges and may be compromised if operated in heavily contaminated water samples. Additionally, biofouling is another challenge because nonspecific bindings not only intrude on the sample diffusion in the vicinity of the working electrode, but also compromises the selectivity in affinity-based sensors. Natural solvents or other contaminants found in the water pattern may additionally denature the used proteins and interfere in the interaction of specific nucleic acid systems (Gracia-Lor et al., 2017; Khalil et al., 2018; Tran et al., 2016; Li et al., 2019).

It is clear that during the construction of biosensors great care should be taken to ensure that the overall designs of the biosensors are capable of conducting their desired applications. Although the use of biological compounds proves to be most effective in the development of electrochemical biosensors; they have also proven to be challenging. The major challenge is ensuring that these biological compounds are handled at the correct temperature to ensure their optimal and effective use especially during the detection or monitoring stage of the biosensor operations. With a rapidly growing interest among scientists towards the detection of water pathogens; biosensor designs have become highly innovative and highly sensitive since the topic surrounding the preservation of water reservoirs continues to one of great concern. With new water pathogens changing their mutations regularly ever so often with the underprivileged population most at risk; some scientists have suggested additional measures to the development of biosensors to mitigate this issue. One such suggestion involves the use of nanoparticles to purify contaminated water. As much as this is a promising solution that has also been explored in some sectors; there is also the concern of the adverse effects of these nanoparticles if they are not removed correctly after the purification process. As such, pathogen detection and water quality monitoring and management are seen as the immediate solution to preserve the remaining water supply, we currently have on the globe.

18.2.2 Conventional methods for water quality monitoring

Numerous traditional protocols exist which allow for the straight determination of waterborne pathogens. These include Fluorescence in Situ Hybridization (FISH), DNA microarrays, MALDI-MS, microscopy, PCR, pyrosequencing, microbiological techniques, and immunology methods. Although these strategies can serve their purpose, they also come with their benefits and disadvantages. Regrettably, there is no standardized procedure that involves the evaluation and collection of water samples to analyze waterborne pathogen of interest. Conventional detection strategies are highly challenged since it is incredibly hard to measure individual pathogens simultaneously. Differences in physiologies, decreased pathogen concentrations in large sample volumes, and challenges regarding sample collections, among pathogen groups, pose more challenges in water-based detections. Also, there is a continuous development of molecular assays for single pathogens in each of the significant pathogenic groups such as protozoa, viruses, and bacteria. This section will explore some conventional methods for water monitoring.

18.2.2.1 Immunological-based methods

Immunological-based strategies usually are primarily based on a specific and selective interaction between an antigen and antibody. This method is typically carried to detect specific proteins, whole-cellular microorganisms, and harmful toxins. The standard methods for the detection of specific microorganisms are the enzyme-linked immunosorbent assay (ELISA), serum neutralization assessments (SNT), and immunofluorescence. The serotyping of viruses uses SNT where the sample is blended then extracted from a plaque assay using an antiserum followed by the assessment of the possible lowered infectivity (Jain et al., 2012; Almeida et al., 2010).

18.2.2.2 DNA microarrays

DNA microarrays are beneficial quantitative and qualitative strategies that are commonly used for tracking the entire genome, particularly for gene expression in varied growing conditions. This technique is capable of in situ monitoring and can detect specific mutations in DNA sequences. Alternatively, hybridization can be reversed through the process of reverse hybridization. It involves the use of unlabeled probes attached to reliable support modified with fluorescently labeled nucleic acid. Microchip devices are examples of this type of hybridization where some microarrays can contain 10 to 10,000 ssDNA fragments per glass chip. As a result, several hybridizations may be completed concurrently (Shen and Qin, 2012). After hybridization, a confocal laser scanner bound to a computer allows for fluorescence detection. The fluorescent signal is dependent on the amount of nucleic acid; consequently, it is feasible to qualitatively and quantitatively quantify specific regions of targeted molecules in one reaction. Upon covering with the test pattern, the DNA probe and fluorophore labeled target DNA bind on the occasion of a positive reaction. Since the fluorophore is capable of emitting light, consequently, binding of the target DNA to the probe effects fluorescence. While there are benefits of excessive throughputs with the use of this method, the production on the other hand is rather steep. Microarrays also have application in the evaluation of genes of closely related microbes, in studying gene expression and antimicrobial resistance genes, and identifying pathogenic microorganisms such as bacteria in particular. Moreover, DNA/RNA chips may also be used in the detection of viruses (Lee et al., 2010; Zhou et al., 2011).

18.2.2.3 *Mass spectroscopy*

One other technique for the direct and fast evaluation of bacterial species, mainly in clinical microbiology laboratories includes the use of matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS). A few advantages are associated with the use of this approach which includes fast analyses, it can be operated cheaply, it has high reproducibility, is capable of analyzing small samples, and it is capable of analyzing a wide variety of isolates at the same time (Hurst et al., 1996; He et al., 2011; Donohue et al., 2006; Erler et al., 2015). Cellular proteins unique to each microorganism allow this technique to generate particular m/z signatures aided by expressed by microbiological species in these proteins. However, a prohibiting issue of this technique is the identification of microorganism species not included within the known database. To rectify this, the mass spectra of the novel microbial lines are continually being added to the database. Further added negative aspects of this technique are the steeply-priced instrumentation it uses and the complex identity of some blended cultures and phylogenetically related bacterial species (Hurst et al., 1996; He et al., 2011; Donohue et al., 2006; Erler et al., 2015).

18.2.2.4 *Microbiological laboratory methods*

The cultivation of microbiological processes which include the culturing of target microorganisms upon or within nutrient agar or broth mediums has been used in applied microbiology since the dawn of the 19th century. The aim of these strategies is the determination of the level of water contamination, especially drinking water used by humans and animals (Shannon et al., 2007). These strategies certainly have a place in water microbiology even though they are not widely used in standard water testing. Justifying their use is attributed to specific incidences, inclusive of in-area analysis measurements, floods, or injuries. There are some benefits ascribed to the use of cultivation techniques such as specificity, sensitivity, simplicity, and minimal false positive and negative findings (Saxena et al., 2014; Bhagwat, 2003). The foremost drawback of using this approach is the time required for acquiring significant outcomes, frequently requiring samples to be left for prolonged periods to allow substantial colony growth for analysis. Skilled technicians are still required even though false-positive data readings are rare with the use of these techniques.

18.2.2.5 *Polymerase chain reaction (PCR)*

The Polymerase Chain reaction (PCR) is an easy method primarily based on the amplification of a particular DNA collection. This method offers selective and rapid amplification of nucleotide sequences within in vitro conditions. In prognosis, this assay includes several essential steps, such as PCR amplification, DNA extraction from selected samples, and the detection of amplicons. When a few colonies are present in a clinical sample, each experimental design should be cautiously designed and carried out. The principal benefits of PCR are reliable evaluations as opposed to classical cultivation strategies, are rapid, can be tailored according to the evaluation requirements of several types of nucleic acids, and has high sensitivity (Kong et al., 2002).

Despite their high sensitivities, PCR has limitations with the appearance of false-positive in some infected samples, while false-negative results are also presented when analyses are conducted in samples that inhibit PCR. Often, quantification of the sample is usually challenging and thus requires a professional technician for analysis (Toze, 1999). On the other hand, the simultaneous detection of genes is also possible through the use of Multiplex PCR (mPCR). The nature of upscaling allows for some benefits with the use of this technique since it is affordable and allows for shorter evaluation times. Regrettably, the primary downside of this method is the optimization, which is extra complicated when compared to one set of primers as in the original PCR method. At most, four distinct target sequences are amplified to ensure sufficient specificity, understandable data interpretation, and sensitivity. mPCR is often used to identify antimicrobial, simultaneously identify numerous bacterial species, or to identify genes encoding staphylococcal enterotoxins (Marangi et al., 2015; Parshionikar et al., 2004).

18.2.2.6 *Microscopy techniques*

Microscopic assessment is one of the fundamental tactics for the evaluation of microbial populations, and it performs a crucial function in water analysis. This approach permits rapid detection and may assist in the quantification of microorganisms in water. The evaluation of water samples can also be analyzed through the modification of microscopy in forms such as electron microscopy, fluorescence, light, and flow cytometry. The oldest form of microscopy is light microscopy which can be utilized in laboratories as quantitative techniques or microorganism identifying for the estimation of microbial populations (Walker and Keevil, 1994). In fluorescence microscopy, the excited fluorochrome is exposed by light at shorter wavelengths and then emitted at extended wavelengths from the fluorochrome. Since there is a loss of energy during the fluorescence process, emission spectra are transferred to higher wavelengths. This is followed by emitted and excited wavelengths being observed and divided through appropriate filters within the microscope. Other microscopy-based techniques such as electron microscopy, consists of two versions, namely scanning and transmission microscopy. Scanning electron microscopy involves coating the sample with a thin metallic film and scanning using an electron beam while transmission electron microscope permits designated imaging of characteristic intracellular systems of microorganisms' magnification and resolution capable of nanometer range analyses (Mazumder et al., 2010). Additionally, flow cytometry involves the analyses of bacteria, nuclei, and cell mobile in a liquid stream intersecting a high-intensity, stable and focused beam of light, commonly created by a laser. Characteristics of each carried cell are recorded by the current, and it is capable of analyzing numerous cells contained in samples in a second. The advantage of this method is its ability to collect data regarding individual cells in samples. Furthermore, this method is highly specific if the correct and required fluorescent dyes for labeling selected microorganism species are available. The downside of this technique is the financial burden of investing in a flow cytometer instrument, together with the need for skilled personnel to operate the instrument. Another drawback is that solid samples must undergo a treatment process to separate cells from one another and that samples cannot be stored for prolonged periods. An added challenge is the lack of differentiation between dead and viable cells and not to mention interference with matrix measurements (Turle, 2008).

The analysis of the above-mentioned conventional methods demonstrates the combined challenges of these methods. These challenges are a combination of the need for skilled labor to conduct the required measurements, the high cost of instruments, the generation of false positive or false negative data, and complex identification of some water pathogens. In general, the use of electrochemical biosensors for the monitoring and the detection of water pathogens out ways the use of conventional methods by far especially in terms of cost to develop the biosensors and the need for skilled labor. The ability to construct and operate a biosensor is easily transferable skills among scientists with similar skill sets. Although biological compounds and electrodes have to be purchased to ensure the optimal operation of the biosensors; these costs are still less as opposed to the use of any of the conventional methods. Furthermore, since the biosensor construction is based on the binding of the desired water pathogen with an antigen attached on a modified electrode surface; false-negative data are rare since the chosen antigen is always specifically selected for the pathogen in question. Furthermore, the chosen electrode surface is also selected based on the transduction electroactive material onto which the antibody is attached allowing for a rapid and highly selective, and sensitive detection and monitoring process.

18.2.3 The importance of water treatment and water management

In 2012, the world population reached over 7 billion people, equating to double the world population in less than 50 years. Approximately more than 55% of the world's population inhabit cities, where the population in 394 cities across the world exceeds more than 1 million people. By 2030, it is estimated that 53% of developing countries and 83% of developed countries will live in urban areas. Urban areas continue to expand with the rapid growth in the world population, posing a significant threat to the availability of resources, the dynamics of nature, and the quality of the environment; thus, the advancement of our knowledge and understanding of urban hydrological processes remains a priority (McGrane, 2016). Water is a vital component of the earth's ecosystem and plays a vital role in the functioning of flora and fauna (Ali et al., 2018a, b). It is essential for human life; an indispensable resource for the economy, and fundamental in the climate regulation cycle. However, less than 3% of the globe's water consists of freshwater, and 2.5% of that percentage is frozen. Humanity is, therefore, dependent on the remaining 0.5% to meet and fulfill its freshwater requirements (Rajini, 2015). Water resources are continuously being contaminated by point and nonpoint sources. This is due to the overgrowing human population and the uncontrolled development of industries. Other activities such as agriculture and domestic activities as well as environmental and geological activities are also responsible for the low quality of water, globally (Ejeian et al., 2018). The maintenance of high-quality natural aquatic systems is imperative, as contaminated water poses a source of disease in humans and other organisms (Kuklina et al., 2013).

Microbial contamination of drinking water by waterborne pathogens and related diseases is a significant source of public health concern globally, not only by the morbidity and mortality that they cause but due to the high cost of their prevention and treatment (Ejeian et al., 2018). These diseases are directly related to environmental deterioration and pollution. Despite the continued efforts to maintain water safety, waterborne outbreaks are still being reported globally. Proper assessment and detection of pathogens in water and water quality monitoring are critical factors for decision-making regarding water distribution systems' infrastructure; the choice of best water treatment and prevention of waterborne outbreaks (Ramírez-Castillo et al., 2015). To prevent the risk of future outbreaks of microbial infection and protect the integrity of the water supply, the development and implementation of water management programs are necessary. In July 2010, it was recognized by the General Assembly of the United Nations, that water and sanitation is a human right, and that safe and clean water is essential for the realization of all human rights (Durán-Sánchez et al., 2018) thus it is imperative that water management and water preservation strategies are developed and adopted.

18.2.3.1 Water management

Water management is a process that involves the planning, monitoring, and controlling the quality of water and the use of a water facility to obtain an optimum and sustainable use from available water (Rajini, 2015). A water management program will address the gaps in the water system by identifying control points; conduct routine monitoring of control measures, and when necessary, taking corrective actions (Ahmed et al., 2019). In a facility water management plan, facility surveys will be conducted; the use of water will be monitored, and saving options will be identified by engaging building users and allocating water resources (Rajini, 2015). The sustainable management of water resources is of utmost importance to meet the growing water demand and to achieve a safe and environmentally sustainable future supply.

Recent studies have suggested that at least 71% of the global population is confronted with some degree of water scarcity during certain months of the year (Ejeian et al., 2018). In a few decades, the world may be faced with a great scarcity of water (Ali et al., 2018a, b) and the supply of clean water is an essential requirement for the establishment and maintenance of diverse human activities (Dhote and Ingole, 2012). Effective water quality monitoring has become critical for water quality management programs. Without the intensive, accurate, and long-term acquisition of data, the condition of the world's water resources cannot be assessed adequately, practical preservation and remediation programs cannot be carried out, and program success cannot be evaluated appropriately (Glasgow et al., 2004).

Society today is faced with the challenge to develop sustainable management that ensures an adequate supply of quality water and at the same time prevents the overexploitation and degradation of associated aquatic ecosystems (Durán-Sánchez et al., 2018). Water management is a continuous process that aims at creating a closer link and a better understanding of human and natural needs, as well as interactions between both. Water safety management demands a quantitative understanding of how processes and actions affect water quality, which in turn requires an understanding of risk assessment. This volume is intended to guide on using risk assessment when selecting appropriate treatment processes, to ensure the production of high-quality drinking water (LeChevallier, 2013).

18.2.3.2 Water quality monitoring

Water quality is a measure of the critical water quality parameters: biological, chemical, microbiological, and physical characteristics of water (Myers, 2014). Water-quality monitoring provides an understanding of the conditions of the quality of water in national groundwater, rivers, streams, and aquatic systems and how these conditions vary on a local, regional, and national scale. Commonly, the primary purpose of monitoring the quality of water has been to establish whether observed water quality is agreeable for intended uses (World Meteorological Organization, 2013). The source and the suitability of water should be regularly examined and monitored before usage as water is required for various purposes and needs to be safe for usage (Roy, 2018).

With the occurrence of water pollution, reliable data is required for early warning detection of potential microbial contaminants in the water distribution system (Nurani et al., 2020). Low water conditions are not only indicative of environmental degradation but also pose a threat to the ecosystem. Therefore, the quality of water is essential in both environmental and economic aspects (Roy, 2018). With continual water quality monitoring, information is collected at regular intervals at set locations to define the current conditions and determine whether conditions are changing over time by identifying irregularities in the water quality parameters (Nurani et al., 2020) and how natural features and human activities affect these conditions and where these effects are most prominent (Geetha and Gouthami, 2016). Estimations of pollutant fluxes discharged by lakes, rivers, and oceans can be determined and as well as treatment options for undrinkable or contaminated water. Monitoring allows for the determination of ecological flows and establishes a baseline to assess the effectiveness of water management programs or remedial measures. The extent and nature of pollutant controls can be assessed in various water bodies and the effectiveness of existing pollution-control measures; (World Meteorological Organization, 2013). As a result of years of research, water quality analysis has implemented standard protocols that involve the sampling, preservation, and analysis of water samples. These standards are put in place through water management programs to protect the integrity of the water supply (Masaaki, 2014). The aim is to ensure the suitability of efficient water use for a designated purpose and reducing the burden of waterborne diseases (Roy, 2018; Ahmed et al., 2019). Also, the monitoring system provides real-time analysis of data collected and suggests suitable remedial measures (Geetha and Gouthami, 2016).

18.2.3.3 *Water treatment*

Water treatment involves using various functions (biological, chemical, physical, and physicochemical) to reduce and or to eliminate toxins and contamination in water. The objective of water treatment is to acquire water with the right properties for its intended uses. It is for this reason that the process of water treatment varies as a function of the properties of the water being supplied. The recovery of water and the reuse of water from different sources such as stormwater, greywater, and wastewater can assist through increasing the efficiency of water and diminish impacts of water scarcity. This, however, poses a threat to human health and the environment, significantly when the water source is contaminated (Nguyen et al., 2017).

To date, much research has been conducted focusing on the elimination of waterborne pathogens from drinking water (Chandra Bhomick, 2017). Significant pollution of freshwater ecosystems has varying effects on the quality of water sources (Ejeian et al., 2018) and many improvised techniques and treatment processes have been developed to combat this problem. Waterborne pathogens in water are mainly released into water bodies from runoff of animal husbandry facilities and human sewerage and are the cause of approximately 1.3 billion deaths of children each year globally. The outbreak of diseases such as cholera, diarrhea, shigellosis, cryptosporidiosis, giardiasis, gastroenteritis, typhoid fever, and salmonellosis, is typical in rural areas of developing countries as a result of the consumption of water that is infested with pathogens. Water treatment helps in reducing the rate of mortality as a result of waterborne diseases (Chandra Bhomick, 2017). Water treatment has become increasingly imperative as a result of the shortage of drinking and the growing requirements of the global population. Assessing the quality of water by determining the various properties of water, such as the physicochemical properties or pollutants (biological or chemical) is an essential part of operating a water treatment. It allows for the provision of essential data for the evaluation of the degree of treatment of freshwater sources required to ensure human health and ecological safety and prevent the outbreak of waterborne diseases (Hossain and Mansour, 2019; Do et al., 2020).

Wastewater is made up of various harmful materials and elements that have been adversely generated and released from commercial, domestic, agricultural, or industrial activities. The concentration of constituents in wastewater is essential in determining the type, the design, and the functioning of treatment processes, as well as for the reuse of waste (Ejeian et al., 2018). Wastewater can be reclaimed as a supplemental source for nonpotable uses in a distributed water scheme onsite, or it can be further treated according to the standards of potable water, by eliminating consumer and industry-derived synthetic contaminants and pollutants (Hodges et al., 2018). When used with caution, nanoparticles have shown to contribute positive effects towards water treatments and pathogenic microbe detection in water.

18.3 Nanoparticles for the development of biosensors

Nanoparticles (NPs) are referred to as materials with structural components which are sized (in at slightest one measurement) between 1 and 100 nm. These materials possess the characteristics of adsorption, catalysis, and high reactivity. Nanoparticles are produced through size reduction using top-down methods such as milling, high-pressure homogenization, and sonication or through bottom-up processes such as reactive precipitation and solvent displacement (Divya and Jisha, 2018). Nanoparticles have been studied in numerous areas of research and development and have been successfully applied in different fields, such as catalysis (Parmon, 2008) medicine (Kusior et al., 2013), sensing (Bujoli et al., 2006), and biology (Khin et al., 2012). Since they are small in size, this means they consist of a large specific surface area; therefore, their mobility in solution is high (Tang et al., 2014). Heavy metals (Yan et al., 2015), organic pollutants (Liu et al., 2014), inorganic anions (Kalhapure et al., 2015), and bacteria have been reported to be successfully removed by various kinds of nanoparticles.

Therefore, the study of nanoparticles in biosensors is proving to be an advantage particularly, for water applications. Metal nanoparticles like gold nanoparticles (AuNPs), silver nanoparticles (AgNPs) (Teodoro et al., 2019), platinum nanoparticles (PdNPs), magnetic nanoparticles, carbon nanotube (Ahmed et al., 2019), and graphene are the most commonly used nanoparticles for sensing applications. These nanoparticles have been used in detecting heavy metal gases (Compagnone et al., 2013), chemicals (Shrivas et al., 2015), pharmaceuticals (Jouyban and Rahimpour, 2020), and bacteria (Wang et al., 2019) the water and in the environment.

Water-quality monitoring, both at large and small scale, poses a challenge due to the variability and complexity of the matrix and the low concentrations of pollutants that ought to be detected. With these issues in mind, nanoparticles-based sensor platforms are expanding levels of attention from the research community. The selection of the best method and material for the treatment could be a highly complex task with several factors to be considered such as, the quality measures that need to be met, the proficiency, and the cost (Huang et al., 2008; Oller et al., 2011).

Therefore, the following conditions need to be considered within the decision on water treatment technologies; treatment adaptability and final efficiency, re-use of treatment agents, environmentally friendliness, and low cost. Due to their properties, nanoparticles-based sensor platforms for water quality, promise ultralow multiplex detection and quick and shorter analysis time (Muqsit and Zeynep, 2019).

The performance of biosensors is featured by their reaction time, the limit of detection, dynamic range, and specificity (Hoa et al., 2007). The nanoparticles are therefore applied to biosensors to improve and progress their performance and offer excellent prospects by enhancing sensitivity and by providing simultaneous detection of their targets. The presence of nanoparticles enhances biomolecular recognition events because of their sizeable surface-area ratio, the number of biomolecules immobilized onto the surface is increased, in turn, the number of binding events becomes maximized (Samphao et al., 2015). Nanoparticles can be implemented in optical, magnetic, or electrochemical biosensors for pathogenic bacteria detection. Optical biosensors are based on surface plasmon resonance (SPR). This type of biosensor allows label-free qualitative and quantitative measurements of biomolecular interactions between a biomolecule immobilized on a metal surface and the analyte in solution (Cho et al., 2020). Magnetic biosensors use magnetic nanoparticles to utilize the magnetic field created by magnetic particles that attract molecules in a biological assay, while in the absence of these magnetic materials within biological samples, this may result in lower background signals (Joung et al., 2008). In electrochemical biosensors nanoparticles assists in the movement of the electrons between the analyte and any attached biological entity (Koets et al., 2009). There is a need for the development of more versatile, adaptable, reliable, and sensitive targeting of pathogens and an investigation on the nanoparticles capability and their incorporation into biosensor systems. Table 18.1 shows some of the research that has been completed regarding different types of nanoparticle-based biosensors for the detection of pathogenic bacteria.

The common feature in all the research studies depicted in Table 18.1 is not only the use of nanoparticles in each study but also the positive outputs which include amplified signals, improved sensitivity, decreased LOD, and minimal noise interferences. These properties all signify the successful construction of the created biosensors in each study. As mentioned previously, these are all the attributes required to ensure the success of a chosen biosensor application. In the below section, a few more comparative studies are discussed to illustrate some of these attributes.

A study by Joung et al. (2008) using an SPR biosensor system and gold nanoparticles (Au-NPs) to detect *Escherichia coli* (*E. coli*) 16s rRNA using peptide nucleic acid probes, illustrated the potential of the biosensor to amplify SPR detection employing Au-NPs. The signal was amplified, and the sensitivity of the biosensor was improved in the presence of the nanoparticles (Joung et al., 2008). This kind of biosensor illustrated an example of the use of an optical biosensor towards the detection of a water pathogen. The results showed that the substitution of the conductive metal surface of an SPR sensor by noble-metal NPs, the interaction of the NPs with the light results in smaller dimensions compared to the incident wavelength which leads to the local oscillation of the plasmon around the NPs with a frequency known as the localized SPR (LSPR). The LSPR spectrum of metal NPs is characterized by the presence of intense adsorption and scattering peaks, which significantly improves the sensitivity of the sensors. Zhu and co-workers also developed an LSPR biosensor with Au-Ag NPs for the detection of *Staphylococcus aureus* enterotoxin B. The results showed that the presence of the nanoparticles improved the sensitivity of the sensor (Zhu et al., 2009). Koets et al. (2009) developed a magneto-resistant sensor using superparamagnetic particles for detecting labels of *E. coli* and *Salmonella*. The presence of the magnetic particles improved the speed of the assay by reducing diffusion limitations. Wang and colleagues presented a sensitive magnetic nanoparticles (MNPs) biosensor based on immobilized Fe_3O_4/Ag MNPs and Au/Ag-NPs to capture and separate bacteria. The Fe_3O_4/Ag MNPs were used as platforms for capturing bacteria, as well as biosensor substrates to improve the signals of captured bacteria. An additional amount of the Au/Ag-NPs was also introduced to improve the detection sensitivity further (Wang et al., 2018). The MNPs based biosensor could detect and

TABLE 18.1 Nanoparticle-based biosensors for the detection of pathogenic bacteria.

Nanoparticles	Pathogen detected	Output	Reference
Au-NPs	*E. coli*	LOD decreased	Koets et al. (2009)
Fe_3O_4	*Salmonella*	Immuno-magnetic separation, high sensitivity	Liu et al. (2007)
CdSe/ZnS core/shell dendron nanocrystals	*E. coli* O157:H7	Improved sensitivity	Lee et al. (2008)
Superparamagnetic NPs	*E. coli* O157:H7	Minimized noise and interferences	Lin et al. (2008)
Fe_3O_4	*S. aureus*	Signal amplification	Yeung et al. (2006)
Au-NPs	*E. coli*	Signal amplification and improved properties	Zhu et al. (2009)

quantify small magnetic field variations caused by the presence of superparamagnetic beads bound to the antigens immobilized onto the sensor surface through an antibody-antigen reaction.

Nanoparticles are categorized based on their physical and surface properties such as carbon nano-adsorbents (CNTs), metal oxide nanoparticles, aluminum oxide nanoparticles (Al_2O_3-NPs), iron oxide nanoparticles (FeO-NPs), zinc oxide nanoparticles (ZnO-NPs), titanium dioxide nanoparticles (TiO_2-NPs), and cerium dioxide nanoparticles (CeO_2-NPS). Metallic nanoparticles such as gold nanoparticles (Au-NPs) and silver nanoparticles (Ag-NPs), mixed oxide nanoparticles like iron titanium nanoparticles (Fe/Ti-NPs), polymer nano-adsorbents, nanofibers, and nano-clays are also included (Lu et al., 2016). Additionally, metallic/metal oxide nanoparticles such as titanium oxide nanoparticles and palladium nanoparticles are used as nano-sensors for the detection of organic and inorganic pollutants in the water systems (Abdel-Karim et al., 2020; Khan et al., 2019a, b).

It is imperative to further understand the unique properties of the different types of nanoparticles and to also know how they differ particularly for their respective potential applications in sensor development. Several nanoparticles will be discussed below to showcase their unique properties in either water purification or sensor construction.

18.3.1.1 Gold nanoparticles

Gold nanoparticles (Au-NPs) have been used to develop sensors for the detection of various environmental contaminants because of their unique properties such as adjustable optical properties, strong adsorption, stability, catalytic properties, high surface area, and high capacity (Ahmed, 2019). Gold nanoparticles have been used in colorimetric sensors (Chang et al., 2019), fluorimetric sensors (Du et al., 2019), and electrochemical sensors (Bui et al., 2016) for water contaminant detection. They have been widely used to improve the selectivity and sensitivity of colorimetric sensors due to their unique optical properties like localized surface plasmon resonance (LSPR) effect, and surface-enhanced Raman scattering (SERS) properties (Upadhyayula, 2012). Au-NPs have unique (LSPR) properties that have high molar extinction coefficients, with size-dependent, and different color changes that help in the detection of analytes (Chang et al., 2019). Moreover, Au-NPs have been used to improve (SPR)-based sensors by increasing their stability, sensitivity, and selectivity (Fathi et al., 2019). Singh et al. (2015) have developed a lateral flow immunoassay incorporated with Au-NPs for the detection of pathogens in water and food. In another study, a colorimetric paper-based sensor with incorporated Au-NPs was developed for the detection of mercury (Hg) ion in water. The developed sensor was based on color changes that were observed in the presence of mercury ions in water. The results obtained were recorded and analyzed using a smartphone (Chen et al., 2014).

Furthermore, Au-NPs have been used to improve the performance of electrochemical and fluorimetric sensors. In electrochemical sensors, Au-NPs play an essential role in improving the electron transfer and immobilizing biomolecules to electrode surfaces and increasing the electrochemical transduction ability (Upadhyayula, 2012). Bui et al. (2016) developed the first electrochemical paper-based sensor for nitrate and mercury ions detection in agricultural water runoff. The developed electrochemical sensor contains disposable carbon paper electrodes that were fabricated with selenium particles (Se-NPs) and gold nanoparticles (Au-NPs) to enhance the sensitivity and selectivity of the sensor. Additionally, Au-NP-based colorimetric sensors for detecting sulfite ions in water were also developed (Du et al., 2019). Most sensor devices with incorporated functionalized Au-NPs have been developed for the detection of heavy metals and chemicals in water. Furthermore, they have shown rapid detection, low limit detection, high selectivity, and sensitivity when compared to their counterparts. This is an indication that Au-NPs can be used in the future for the design of more portable biosensors for the detection of water contaminants, especially bacteria and emerging contaminants like personal care and pharmaceuticals products.

18.3.1.2 Platinum nanoparticles

Platinum nanoparticles (Pt-NPs) have gained much interest in designing electrochemical sensors for various environmental applications. As a noble metal, Pt possesses a high electrocatalytic activity which has allowed extensive research on it. Numerous studies have reported on the ability of Pt-NPs to facilitate electron transfer to increase the surface areas coupled to enhanced mass transport characteristics (Zhao et al., 2007).

One such example is the development of electrochemical sensors with Pt-NPs chemically modified on glassy carbon electrodes (PtNP/GCE) for the detection of *E. coli*. The sensors were based on the determination of p-aminophenol that was produced by an enzymatic reaction in a solution of *E. coli*. The sensitivity of the sensor was improved by the Pt-NPs modified electrodes (Cheng et al., 2020). Furthermore, a molecularly imprinted electrochemical sensor was developed in another study by incorporating gold electrode decorated with chitosan-platinum nanoparticles (CS-PtNPs) and graphene-gold nanoparticles (GR-AuNPs) nanocomposites for the detection of erythromycin in water (Lian et al., 2012). The sensor displayed excellent stability, good reproducibility, and high selectivity towards the detection of erythromycin in real spiked samples.

The success of Pt-NPs in the area of sensors and electrocatalysis is attributed to their capability to be tailor-made to ensure specific reaction pathways while providing a high surface area to volume ratios. Furthermore, their superior optical and electronic properties can influence their functionality in sensor applications while their crystallographic axis orientation, chemical composition, crystal structure quality, and surface condition are additional attributes that influence their electron transport mechanisms (Chen et al., 2014; Rick et al., 2016; Leus et al., 2016).

18.3.1.3 *Silver nanoparticles*

Over the years, through the development of nanotechnology, silver nanoparticles (Ag-NPs) have been investigated in water treatment (Lu et al., 2016). They have been reported to be used in the removal of fungi, viruses, and bacteria from water due to their high toxicity to these pathogenic microorganisms which makes them good antimicrobial agents to clean water (Deshmukh et al., 2019). Direct application of Ag-NPs is dangerous and causes problems such as aggregating in aqueous media that gradually reduces efficiency during long-term use (Li et al., 2011). However, attaching Ag-NPs to filter materials is considered more effective for water disinfection due to their high antimicrobial activity and low cost (Lu et al., 2016). Furthermore, Dhanalekshmi and Meena (2016) added that the DNA molecule of microbes contain elevated sulfur and phosphorus elements, which Ag-NPs can bind and destroy. Furthermore, Ag-NPs dissolution will release silver ions, which have antimicrobial properties, and interact with thiol groups of necessary enzymes to inactivate them and interfere with the functioning of microbe cells (Prabhu and Poulose, 2012).

Ag-NPs have also gained much interest in developing sensors for various applications because of their unique properties such as size distribution; excellent surface-enhanced Raman scattering (SERS), low cost, simplicity, stability, catalytic activity, and excellent biocompatibility properties. They have been used to detect metals contaminants such as copper, lead, and nickel (Teodoro et al., 2019), hydrogen peroxide, cyanide (Carbone et al., 2019), bacteria (Cheng et al., 2020) and pharmaceuticals (Jouyban and Rahimpour, 2020) in water. In electrochemical sensing, Ag-NPs play an essential role in improving the electron transfer on the electrode surfaces for the electrochemical sensors (Sebastian et al., 2018). An example is an electrochemical sensor that incorporated Ag-NPs and was designed for the detection of *E. coli* bacteria in water (Sepunaru et al., 2015). Additionally, a study by Fiorati et al., 2020 also reports on the incorporation of Ag-NPs towards the fabrication of plasmonic sensors for the detection of water contaminants like heavy metals and organic compounds (Fiorati et al., 2020). Ag-NPs with oxacalix-arene templates were also fabricated into electrochemical sensors for the detection of methyl-mercury in water. A plasmonic colorimetric sensor with polyvinyl alcohol (PVA) was also incorporated with Ag-NPs and developed for detecting lead (Pb) ions in water in which the sensor was developed using paper-based analytical devices. It was used to monitor the color change when the lead ion is present in water, and the redshift absorption band of Ag-NPs/PVA in the visible region was observed. After the addition of Pb (II) and the color intensity of the paper-based device was recorded using smartphones, and the data was processed using the ImageJ software (Shrivas et al., 2019).

The above-mentioned studies are an indication of the multifaceted nature of Ag-NPs allowing these nanomaterials to be among the easiest to work with it particularly towards sensor fabrication.

18.3.1.4 *Iron nanoparticles (Fe-NPs)*

Iron, the most ubiquitous metal and the fourth most dominant element in the earth's crust is the structural support of our modern infrastructures. Iron reactivity is much crucial in microscopic applications. Iron nanoparticles (Fe-NPs) have been used in water treatment since the 1990s because of their high surface area, different adsorption phenomenon, and broad distributions of reactive surface sites (Devatha et al., 2016). Iron nanoparticles have proved to be effective in the removal of different chemical pollutants such as lactam and nitroimidazole-based antibiotics, azo dyes, chlorinated solvents, chlorinated solvents, chlorinated pesticides, among others. Based on several trials and chemistry of contaminates, different pathways of contaminants removal have been documented including, sorption, complexation, precipitation, and surface-mediated chemical reduction (Sushma and Richa, 2015). Li and Zhang (2007) documented that the removal of ions (Cd^{2+} and Zn^{2+}) from water samples through the application of Fe-NPs takes place through sorption or surface complexation. However, with other ions with high standard electrode potentials than that of iron, their removal occurs through surface-mediated reductive precipitation (Sushma and Richa, 2015). Most completed studies report on the use of iron oxide nanoparticles in water treatment as opposed to the use of iron nanoparticles. Thus, there is a need to document the application of iron nanoparticles in water purification processes since such knowledge is still elusive. Furthermore, there is no documented information regarding the removal of biological water contaminants such as bacteria, viruses, and fungi from drinking water through the application of iron nanoparticles (Prathna et al., 2017) let alone there in-sensor fabrication.

18.3.1.5 Zinc nanoparticles (Zn-NPs) and zinc oxide nanoparticle (ZnO-NPs)

Zinc is regarded as an addition or alternative for iron and silver nano-zerovalent particles for the elimination of water pollutants (Bokare et al., 2013). Nano-zerovalent particles have substantial reduction as compared to nano-zerovalent particles. Therefore, it was found that the degradation of contaminates ability of nano-zerovalent zinc particles is slower than that of zinc nanoparticles (Zn-NPs) (Madhura et al., 2019). Much of the dehalogenation in wastewater have been focused on the nano-zerovalent zinc particles and their application. There are not enough findings documented regarding the application of zinc nanoparticles in water treatment. In 2010, Tratnyek et al. (2010) evaluated the reactivity of various types of nano-zerovalent iron and zinc and found that nano-zerovalent zinc could degrade carbon tetrachloride much faster than through the application of nano-zerovalent iron on maximum experimental conditions. Fig. 18.2 is an illustration of how nanoparticles disrupt the growth of bacteria.

On the other hand, zinc oxide nanoparticles are regarded as environmentally friendly since they are compatible with organisms, and they are useful in water treatment (Dimapilis et al., 2018). The ZnO-NPs photocatalytic capacity is similar to that of TiO_2-NPs due to similarity in their bandgaps even though ZnO-NPs have low cost as compared to TiO_2-NPs (Lu et al., 2016). Furthermore, ZnO-NPs can adsorb many different solar spectra and more light pockets than other semi-conducting metals. The big band gap between ZnO-NPs makes the absorption of light to be more difficult in ultraviolet light (Assi et al., 2017). The zinc oxide splits water into OH and H^+, which allows the interaction between produced electrons from the photoactivation of ZnO with the oxygen molecule from superoxide anions (Khan et al., 2019a, b).

According to Khan et al. (2019a, b), other radicals such as hydrogen peroxide are formed through the interaction of radicals with both organic and inorganic molecules. The ZnO-NPs have been reported to be active against waterborne pathogens. ZnO nanoparticles have shown antimicrobial activity against pathogens in the gut of mice through oral uptake. Furthermore, ZnO nanoparticles also interact with and inhibit the enzyme activity of adenyl cyclase, which plays a vital role in the pathogenicity of bacteria. The mechanism of antimicrobial activity of ZnO-NPs has been documented over the past years, zinc ions released from nanoparticles have been found to exhibit antimicrobial activity (Fukui et al., 2012). Others found that the direct interaction of nanoparticles damages the cell wall and cell membranes, which leads to intracellular leakage (Dimapilis et al., 2018). Application of ZnO-NPs can also degrade organic pollutants such as dyes (fast green), methylene blue, and aniline (Kumar et al., 2016).

It is the demonstrated versatility of ZnO-NPs as opposed to Zn-NPs that makes them superior choices in most water-related applications. Their application in sensor development is not fully explored in particular for microbial detection. However, their capabilities of disrupting the cell walls and cell membranes in antimicrobial studies provide a great premise to explore ZnO-NPs at length for sensor application.

18.3.1.6 Titanium dioxide nanoparticles (TiO_2-NPs)

TiO_2 nanoparticles are one of the most used photocatalyst nanoparticles, mostly in water treatment since they have high stability, affordability, photocatalytic production of reactive oxygen species (ROS) as well as low toxicity to human health (Qu et al., 2013a, b). Recently, photocatalytic degradation technology has been applied in the decontamination of water sources. In light of the catalyst-dependent processes, contaminates can be oxidized into low molecular

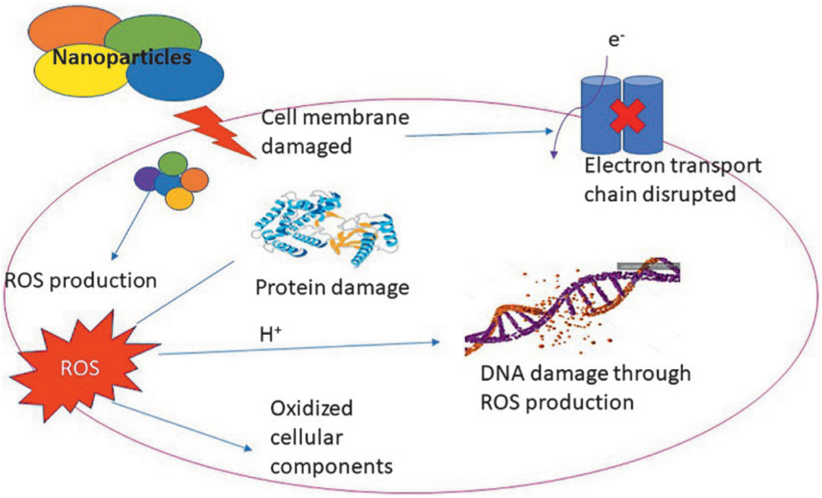

FIG. 18.2 Mechanisms of nanoparticles action in bacteria cells.

weight and synthesized into carbon dioxide, water, and ions (NO_3^-, PO_4^{3-}, and Cl^-) (Lu et al., 2016). They have been applied and researched as catalysts in the ozonation process, which provides complete mineralization of organic contaminants. Most known photocatalysts are metal oxide or sulfide semiconductors, which TiO_2 has been thoroughly studied in the last decades due to its high photocatalytic activity, affordability, photostability, and chemical and biological stability (Guesh et al., 2016; Rawal et al., 2013).

According to Lu et al. (2016) in the presence of UV irradiation, TiO_2 produces ROS, which is less time to degrade contaminants completely. UV light is the source that plays a significant role in the activation of TiO_2. TiO_2 takes in the UV light, which leads to the production and the movement of electrons to the conduction band (CB) and the abundance of positive holes in the valence band (VB). The electrons facilitate the reduction of the preadsorbed oxygen into ROS. Simultaneously, the holes are injected into the photosensitizer (PS), blocking electron-ion recombination and forming a water oxidative site which produces reactive hydroxide (HO^-). All the elaborated ROS degrade and mineralize the adsorbed pollutants (Nour et al., 2018). Furthermore, these nanoparticles have less selectivity which makes them more useful in the degradation of different kinds of contaminants such as chlorinated organic compounds, polycyclic aromatic hydrocarbons, dyes, phenols, pesticides, arsenic, cyanide, and heavy metals) (Lu et al., 2016).

Hydroxyl radicals produced in the presence of UV irradiation make TiO_2 nanoparticles destroy the structure and functionality of different cells. Titanium dioxide nanoparticles' photocatalytic properties have been reported to kill a wide range of microorganisms, including Gram-negative and Gram-positive bacteria, fungi, algae, protozoa, and viruses (Foster et al., 2011). Over the years, TiO_2 nanoparticles have also been found to be antiviral agents against *Herpes simplex* (Hajkova et al., 2007), *hepatitis B* (Zan et al., 2007), MS-2 bacteriophage (Cho et al., 2011), and poliovirus 1 (Liga et al., 2011).

With this in mind, it is evident that the properties of TiO_2 nanoparticles illustrated above particularly towards their interaction with various microbes are a good indication of the possibility of using these nanoparticles in sensor construction for the detection of pathogenic microbes. A dual application of these nanoparticles is envisaged, one being the detection of the microbes of interest while the other would be the eradication of pathogenic microbes at identified water polluted sources.

18.3.1.7 *Iron oxide nanoparticles (FeO-NPs)*

Over the years, there has been an increase in the investigation on the use of iron oxide nanoparticles (FeO-NPs) for the removal of heavy metals because of their simplicity and availability. Commonly used nano-adsorbents are magnetic magnetite (Fe_3O_4), magnetic maghemite (γ-Fe_2O_4), and nonmagnetic hematite (α-Fe_2O_3). Generally, because nano-adsorbents are small, it becomes a challenge for their separation and recovery for water treatment. However, the separation and recovery for magnetic magnetite and magnetic maghemite can easily take place through the use of an external magnetic field (Lu et al., 2016). Due to these, they have been applied as adsorbents in the removal of heavy metals from water sources (Fig. 18.3). To enhance the adsorbent activity and to prevent iron oxide nanoparticles disturbance by other metals ligands (ethylenediamine tetra-acetic acid (EDTA), L-glutathione (GSH), mercaptobutyric acid (MBAS), and meso-2,3-dimercaptosuccinic acid (DMSA)) (Warner et al., 2010) and polymers (copolymers of acrylic acid and crotonic acid) (Ge et al., 2012) are added to tune their adsorption properties. Both the ligand shell and polymer shell have a vital role in the stability of nanostructures. Ligand shells have been found to facilitate the

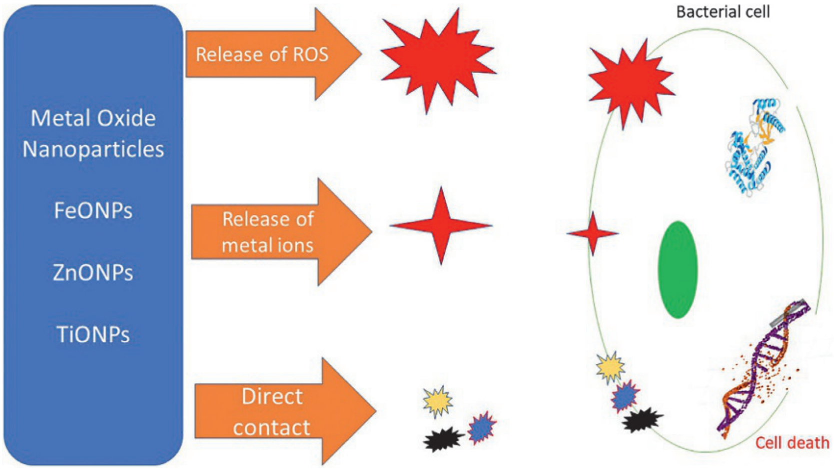

FIG. 18.3 Antimicrobial activity of metal oxide nanoparticles.

incorporation of different functional groups into the shell and intact the magnetic magnetite nanoparticles whereas the polymer shell prevents cluster of particles and improve stability of the structures, hence metal ions can bind and carry-on polymer molecules from cleaned water (Khaydarov et al., 2010; Ge et al., 2012).

Once more, the use of these nanoparticles in sensor development particularly for the detection of microbes is elusive. Their magnetic properties could be used as a unique tool to trap microbes in polluted water while quantifying the microbes.

18.3.1.8 Carbon nanotubes

Carbon nanotubes (CNT) are a group of fascinating materials because of their structures and electronic properties, which makes them receive much attention mostly in sorption processes. CNTs are nanomaterials made of graphite sheets that are popularly known as graphene sheets where the carbon atoms are arranged in sp^2 hybridization at the corners of hexagons. Carbon nanotubes are an exciting group of nanoparticles, which have been widely investigated for their mechanical strength and electrical conductivity which are classified into two groups namely, single-walled carbon nanotubes (SWCNTs) and multiple-walled carbon nanotubes (MWCNTs) (Table 18.2). SWCNTs have a single layer of sp^2 carbon sheet rolled into a tube, and MWCNTs have multiple layers of the same sp^2 carbon (Pokhrel et al., 2018; Sarkar et al., 2018). The advantage of CNTs in water treatment includes; great capacity to adsorb different contaminants, fast kinetics, large specific area, and selective towards aromatics (Khin et al., 2012). Furthermore, they have been used for various applications because of their unique physical and chemical properties such as optical, thermal, electrical, and mechanical properties. CNTs have been used for the detection of heavy metals like lead (Pb) (Xu et al., 2019), mercury (Hg) (Hassan et al., 2015), and cadmium (Cd) (Pokhrel et al., 2018).

According to Chatterjee and Deopura (2002), CNTs cannot be applied alone without supporting medium or matrix to form structural components. Hence, for the removal of fluoride, CNTs have been used in combination with another nanomaterial whereas for the removal of chromium CNTs were used in combination with iron oxide (Gupta et al., 2011). In recent years, there has been an increase in the use of modified multi-walled CNTs for the elimination of heavy metals from water sources. According to Zhao et al. (2011) Pb ions were removed from water through the application of graphene-based nanoparticles.

Because of their properties such as high surface area, rapid charge transfers, and compatibility, CNTs have been used to develop environmental sensors (Jin and Maduraiveeran, 2017). In electrochemical sensor designs, CNTs have been used to promote electron transfer and electrode-analyte interactions to improve the detection rates, selectivity, and sensitivity (Qu et al., 2013a, b). An electrochemical sensor was developed by using zinc oxide (ZnO)/CNT nanocomposite as a probe for the detection of hydrazine in wastewater in the presence of phenol. The developed electrochemical sensor with ZnO/CNT nanocomposite was able to detect both the hydrazine and phenol in wastewater at low concentrations (Karimi-Maleh et al., 2020). Additionally, CNT-based voltammetry sensors were developed to detect the presence of anthraquinone hair dyes in wastewater. The sensor was designed by modifying the glassy carbon electrodes with MWCNTs, and the anthraquinone was detected in water samples at low concentrations. Another study reports an electrochemical sensor fabricated with polyaniline/sulfated zirconium dioxide/MWCNTs nanocomposite and designed for the detection of hexavalent chromium Cr (VI). The sensor showed a low detection limit with stable and good reproducibility for hexavalent chromium Cr (VI)) in wastewater (Zhao et al., 2018). A cheaper electrochemical sensor fabricated with chemically modified (MWCNTs) containing β-cyclodextrin (βCD) was developed as well for the detection and monitoring of low levels of bisphenol A (BPA) in water. The developed sensor has shown good sensitivity and selectivity results.

TABLE 18.2 Differences between classes of carbon nanotubes.

Single-walled carbon nanotubes (SWCNTs)	Multiple-walled carbon nanotubes (MWCNTs)
• Single layered graphene	• Multiple layered graphene
• Dependent on the catalyst for the synthesis	• Can be synthesized without a catalyst
• Difficult bulk synthesis	• Easy bulk synthesis
• Easily twisted and more pliable	• It cannot be easily twisted
• Simple characterization and evaluation	• It is a very complex structure
• Not fully dispersed and form bundled structure	• Homogeneously dispersed without apparent bundled formation

18.3.1.9 Graphene

Graphene is defined as a two-dimensional (2-D) nanomaterial with sp^2 hybridized carbon sheet arranged in a honeycomb lattice. Graphene has been widely used in electrochemical sensors because of its good electrical and thermal conductivity, flexibility, large surface area, and high electron mobility (Yeu et al., 2020). Graphene has been fabricated and applied on electrochemical sensor electrodes because of its excellent physical, chemical, and electrical properties to improve the sensitivity, selectivity, and detection time of sensors (Jin and Maduraiveeran, 2017). The main advantage of graphene in the design of electrochemical sensors is its large surface area and the presence of oxygen-containing groups on their surface which helps in the detection of analytes (Chang et al., 2014). Heakal et al. (2020) developed a sensor that contained a modified graphene/graphite paste electrode with diphenylcarbasone ionophores to detect and monitor the presence of Al (III) ions in water samples. The electrochemical sensor incorporated with graphene (GR) and ZnO nanorods (GR-ZnO/GCE) was designed for the detection of sulfamethoxazole (SMX) and trimethoprim (TMP) simultaneously in water. The developed sensor had good stability, selectivity, and it was reproducibility (Yeu et al., 2020).

The possibility of using nanomaterials for the detection of pathogens in water should be encouraged. The studies listed above reflect the possibility of their use towards the development of electrochemical biosensors which capability of detection of harmful microbes in water. Respectively, their properties reflect the advantages of these nanomaterials, which will aid sensor development for both bacteria and virus detection in water.

18.4 Use of bimetallic or trimetallic nanoparticles in water purification

Bimetallic nanoparticles have gained much attention in the past 10 years because of their different optical, electronic, magnetic, and catalytic properties. Bimetallic nanoparticles are produced through the combination of two different metal nanoparticles which have a different composition and makeup (Belenov et al., 2017; Arora et al., 2020). The same applies to trimetallic nanoparticles being produced in three different metal nanoparticles. Bimetallic or trimetallic nanoparticles are more effective than monometallic nanoparticles due to their synergistic traits (Huynh et al., 2020). Bimetallic NPs show improved activities as compared to their corresponding monometallic NPs. They are two classes of bimetallic nanomaterials which are mixed and segregated, within the segregated class there are also subclasses based on their atom's configuration namely, alloy, intermetallic, subclusters, and core-shell (Srinoi et al., 2018).

Bimetallic nanoparticles have been applied in water treatment due to their activity in different fields, including the antimicrobial potential they possess (Arora et al., 2020). Other than antimicrobial activity bimetallic nanoparticles have been used in the removal of nitrate (NO^{3-}) in water sources. Li et al. (2017), Kang et al. (2012), and He et al. (2011) investigated the effectiveness of Fe/Ni nanoparticles in the removal of nitrate and found that application of 0.2 g/L nanomaterials managed to remove 99% of nitrate within 15 min from water samples. According to Muradova et al. (2016), the effectiveness of reduction of NO_3^- depends on different factors such as contact time, reductive agent concentration, and properties, and surrounding medium composition. Furthermore, in their study, they found that Fe/Cu bimetallic nanoparticles removed nitrate from water samples. There is little information regarding the application of both bimetallic and trimetallic in the water treatment processes.

Through the successful application of monometallic nanoparticles in water treatment, it opens the possibility of using bi/trimetallic nanoparticles in water purification processes, and the synergistic characteristics of bimetallic and trimetallic nanoparticles will contribute to useful methods. Additionally, the use of these types of nanoparticles towards the construction of sensors would further add an interesting factor to existing knowledge on water purification. The detection and quantifying of microbes could significantly increase and the sensitivity of the sensors would be superior due to the presence of multiple nanoparticles in the design of the sensors.

18.5 Application of chitosan nanoparticles in water treatment

In the past, the use of natural additives with low toxicity, high biodegradability, and biocompatibility has gained much attention for water and wastewater treatment (Nechita, 2017). Chitosan has been investigated for its applicability as a bio-sorbent and composites for the pollutants from wastewaters such as heavy metal ions, organochloride pesticides, suspended solids, turbidity, organic oxidized substances, fatty and oil impurities, or dyes (Nechita, 2017). Chitosan is a natural biopolymer derived from the deacetylation of chitin (CT) (Krupa-Małkiewicz and Fornal, 2018), has a great capacity in reticulation and cation exchange in acid solutions, and has a great affinity with metallic ions. CT is a linear, natural, biodegradable, and nontoxic polymer that does not dissolves in most solvents. Chitosan is safe for the environment, and it is characterized by biodegradability, bioactivity, and biopolymers (Vahedikia et al., 2019). Chitosan is applicable in different fields as agriculture, waste treatment, food, textile, and pharmaceutical sector, cosmetics development, and biomaterials such as gels, films, polymer membranes, and nanofibers (Rufato et al., 2018). They are used as flocculating agents for polluted water (Ali et al., 2013), in heavy metal or metalloid adsorption (Cu(II), Cd(II), Pd(III), Fe(III), Zn(II), Cr(III) among others) (Nechita, 2017).

Chitosan nanoparticles have been used as a disinfecting agent of drinking water as it shows high antimicrobial activity in membranes, sponges, or outside coating of water storage tanks. It has excellent results compared to other antimicrobial agents due to its high antimicrobial activity against bacteria, viruses, and fungi, and has less or no toxicity on animals and humans (Rabea et al., 2003). Chitosan nanofibers are reported to be applied in adsorption of Pb_2^+ and Cu^{2+} with adsorption capacities of 263.2 and 485.4 mg^{-1}, respectively (Haider and Park, 2009). According to Olivera et al. (2016), the application of chitosan nanoparticles is expected to be the most effective way for adsorption of toxic dye because of their higher surface area, and chitosan nanoparticles have been investigated for the adsorption of Acid Red 73 (AR73), Acid Orange 10 (AO10), Acid Orange 12 (AO12) and Acid Red 18 (AR18). Moreover, based on the review conducted by Olivera et al. (2016), nano chitosan has been applied most in the adsorption of dyes and metals during water processes. On the other hand, Liu et al. (2015) investigated the application of magnetic chitosan nanoparticles (MCNP) in the removal of arsenic from water, and it was found that MCNP managed to remove As (V) and As (III) and managed to adsorbed 95% arsenic in 15 min. The mechanism of action of the antimicrobial activity is still inclusive; hence there is a need to document such information mostly on the water contaminant pathogens. Furthermore, their use in sensor construction is imperative and begs for an interesting run in the sensor research areas. Their ability to adsorb would be of benefit definitely when constructing the sensors which would then allow for the detection and quantification of microbes of interest.

18.6 Properties and types of bacteria found in water

Water-associated health problems are the most causes of morbidity and mortality all over the world (Ishii and Sadowsky, 2008). Among these, diarrheal diseases are estimated to cause around 1.8 million deaths each year, more especially in developing countries. However, food and water-borne diseases still occur in developed countries. In the United States of America (USA), about 76 million cases of foodborne diseases occur each year, contributing to about 325,000 hospitalizations (CDCP, 2005). Pathogenic agents causing these diseases include enteric bacteria such as *Escherichia coli*, Shigella, Salmonella, and *Campylobacter Jejuni.* Seawater is the habitat of most microorganisms, including several bacteria such as *E. coli, Salmonella* spp., *Proteus* spp., *Pseudomonas aeruginosa, Aeromonas hydrophila*, and *Staphylococcus aureus* (Baker-Austin et al., 2018). This section will discuss the characteristics of a few selected bacterial species that are of importance in water.

18.6.1 *Escherichia coli* (*E. coli*)

E. coli are facultative anaerobes, nonsporulation, gram-negative rods, and gamma proteobacterium. They fall under the family Enterobacteriaceae and are also a member of the fecal coliform bacteria. Their primary habitat is the lower intestines of warm-blooded animals, including human beings. In every 1 g of colon material, there are about one million *E. coli* cells and are often released into the environment through fecal excretion (Ishii and Sadowsky, 2008). Winfield and Groisman (2003) believed that *E. coli* could not survive in their secondary habitat (water, sediments, and soil), since it encounters many stresses in these environments such as different temperatures, moisture content, different soil texture, low organic matter, salinity, solar radiation, and predation (Ishii and Sadowsky, 2008). However, some studies showed that *E. coli* can survive for some time in the environment and also be able to replicate in water, on algae, and in soils in the tropical, subtropical, and temperate environment (Ishii et al., 2006; Beversdorf et al., 2007).

Escherichia coli are generally found to inhabit the human large intestine, and most strains are harmless (Ishii and Sadowsky, 2008), whereas, some strains acquire bacteriophage or plasmid DNA-encoding enterotoxins or invasion factors and become pathogenic or harmful. There are six groups of *E. coli* strains isolated from intestinal diseases, based on epidemiological evidence, phenotypic characteristics, clinical features of the disease, and specific virulence factors. From these, enterotoxigenic *E. coli* (ETEC. 0148), enterohemorrhagic *E. coli* (EHEC. 0157), and enteroinvasive *E. coli*

(EIEC, 0124) serotypes are of outstanding importance and are water-borne pathogens (Cabral, 2010). Each group of *E. coli* serotypes has unique somatic (O) and flagellar (H) antigens and specific virulence traits.

Shiga toxin-producing *E. coli* (STEC) such as the EHEC, are known for causing bloody diarrhea as well as fatal human diseases, such as hemolytic uremic syndrome (HUS) and hemorrhagic colitis (HC) (Brooks et al., 2005). *E. coli* 0157:H7 is among the most recognized serotypes of the EHEC strains, and is associated with most food and water-borne diseases. ETEC is the primary cause of traveler's diarrhea, while other additional serotypes include the enteropathogenic *E. coli* (EPEC) and the enteroaggregative *E. coli* (EAEC). EPEC is responsible for watery diarrhea in children, whereas the latter can cause persistent diarrhea which can go for more than 14 days (Ishii and Sadowsky, 2008).

18.6.2 Salmonella

Salmonella are small gram-negative, nonspore-forming rod-shaped facultative anaerobes that belong to the *Enterobacteriaceae* family. *Salmonella* cells are unable to ferment lactose, sucrose, or salicin, but they can produce gas from glucose fermentation while using citrate as the sole carbon source. They are parasites that affect the human's intestines, cattle, avian, insects, and reptiles. These are foodborne and water-borne that have been found in water, food products (meats, milk, and egg products), and shellfish (Meena et al., 2020). All salmonella is grouped into two main species; namely, *Salmonella bongori* (*S. bongori*) and *Salmonella enterica* (*S. enterica*). *S. bongori* has one subspecies (V), and *S. enterica* has seven subspecies including group II (*S. enterica* subsp. *salamae*); group IIIa (*S. enterica* subsp. *arizonae*); group IIIb (*S. enterica* subsp.*diarizonae*); group IV (*S. enterica* subsp. *houtenae*); and group VI (*S. enterica* subsp. *indica*). Furthermore, *S. enterica* is differentiated into more than 2500 serovars based on their various biochemical characteristic like surface antigens, the composition of their carbohydrate, flagellar, and lipopolysaccharide structure (Pradhan and Negi, 2019).

S. enterica species are the most common *Salmonella* strains that cause infection in humans and other mammals. There are three major diseases caused by salmonella in humans; these include the noninvasive nontyphoidal salmonella, invasive nontyphoidal salmonella, and typhoid fever (Kurtz et al., 2017). Nontyphoidal salmonellosis (NTS) refers to many diseases caused by all serotypes of *salmonella* except for the typhoidal serotypes in humans. Invasive nontyphoidal salmonella (iNTS) is an emerging *Salmonella* strain that is mostly found in sub-Saharan Africa. Like noninvasive NTS, the *Salmonella* serotypes that are associated with iNTS are *S. typhimurium* and *S. enteritidis* (Kurtz et al., 2017; Kehl et al., 2020; Al-Rifai et al., 2020).

Salmonellosis is known as acute, gastroenteritis, acquired orally through contaminated water or comestibles. It is among the most commonly isolated foodborne pathogens associated with fresh fruits and vegetables. Salmonellosis is characterized by acute enterocolitis, which is accompanied by inflammatory diarrhea, a symptom rarely observed in individuals infected with invasive serovars. The infection occurs after ingestion of the bacteria in contaminated food products and water, with symptoms showing as early as 6–72 h after consumption. The onset of symptoms is marked by abdominal pain and diarrhea with or without blood, while nausea and vomiting are also common. Typically, the gastroenteritis will resolve itself in 5–7 days without a need for treatment, although symptoms are usually more severe and longer-lasting in children (Kurtz et al., 2017).

Typhoid fever is caused by infection with Salmonella Typhi. S. Typhi differs from iNTS strains due to the presence of the polysaccharide capsular antigen, VI which is a virulence factor of S. Typhi, that allows it to survive in acidic environments after infection since acapsular S. Typhi is less virulent. Unlike NTS broad host specificity, S. Typhi is restricted to humans only. S. Typhi can survive and replicate within host cells, particularly phagocytes (i.e., macrophages, dendritic cells, neutrophils, etc.), and the bacteria uses these cells to translocate to systemic sites of the body, such as the liver, spleen, and bone marrow (Kurtz et al., 2017).

Salmonella are primarily found in the intestinal tract of animals, mainly humans, birds, reptiles, and sometimes in insects. They are also found to contaminate water sources when they are excreted in feces, and their transmission is facilitated by insects and other animals. Salmonella can be found in other parts of the body as well.

18.6.3 Shigella

The genus *Shigella* is gram-negative bacilli, nonspore-forming, nonmotile, ranging from 0.5–0.7 μm in size, and are facultative anaerobic pathogen belonging to the *Enterobacteriaceae* family. They are also very closely related to *E. coli* (Saima et al., 2018). Shigella and *E. coli* are differentiated based on serology, pathogenesis, and physiology. While *Shigella* species are urease and oxidase negative, they usually ferment sugars without producing gas and lactose (Ud-Din and Wahid, 2015). There are four species of *Shigella* namely, *Shigella dysenteriae*, *Shigella flexneri, Shigella boydii*, and *Shigella sonnei*. These species are divided into serotypes, and Shigella *dysenteriae* have 14 serotypes and subserotypes, *Shigella boydii* have 20 serotypes, whereas and *Shigella sonnei* has a single serotype (Livio et al., 2014).

Shigella species are the leading cause of the gastrointestinal disease known as shigellosis or bacillary dysentery, still a significant health challenge all over the world. It is most common in developing countries as a result of improper waste management, poor hygienic conditions, and consumption of polluted water (Saima et al., 2018). Symptoms range from minor diarrhea to severe inflammatory dysentery with the passage of mucoid and bloody stools. Other symptoms include abnormal cramping, fever, nausea, malaise, vomiting, and convulsions (Marteyn et al., 2012). All over the world, shigellosis is the leading cause of mortality and morbidity in children under the age of 5 years (Wen et al., 2012). Statistics show that high cases of Shigella infections are high in Asia with 91 million cases and 414,000 deaths every year, followed by Africa with over 8 million reported cases annually and the USA with 500,000 cases each year (World Health Organization, 2005; Saima et al., 2018). Shigella can be transmitted through the fecal-oral route and direct contact with the infected individual. These species are highly infectious, as only about 10–100 organisms are enough to cause health problems and the bacteria is resistant to the stomach environment and can easily bypass the gastric acid barrier. According to Saima et al. (2018), the disease can be controlled by oral rehydration combined with antibiotics. Currently, there is no protective vaccine targeting Shigella, but there are undergoing researches to develop an active vaccine against Shigella.

18.6.4 Campylobacter jejuni

*Campylobacter jejun*i (*C. jejuni*) is one of the major bacterial species that is the cause of foodborne and water-borne infection in developing countries (Rodrigues et al., 2018; Meurer et al., 2020). *Campylobacter jejuni* is S-shaped, gram-negative rod, nonsaccharolytic, nonspore-forming, catalase, oxidase, and Hippurate hydrolysis positive bacterial species (Igwaran and Okoh, 2019). *Campylobacter* is mostly found in contaminated food (mostly poultry), water, produce, and unpasteurized dairy products (Rodrigues et al., 2018). *C. jejuni* is the major enteric pathogen that shows significant strain-to-strain differences in their pathogenicity patterns and is also the notable species that caused infections than other pathogenic Campylobacter species (Igwaran and Okoh, 2019; Norren et al., 2019).

There are two subspecies of *C. jejuni*, including *C. jejuni* subsp. *jejuni (Cjj)* and *C. jejuni* subsp. *doyley (Cjd).* The main phenotypic feature that is used to differentiate Cjj from Cjd strains is the inability of Cjd to reduce nitrate and its high susceptibility to cephalothin. Cjd strain causes both enteritis and gastritis, whereas Cjj is the leading bacterial cause of entering invasive diarrhea (Igwaran and Okoh, 2019).

Humans can be infected by *C. jejuni* through various routes such as direct contact with a companion, farm animals, and through consumption of contaminated food and water. Infections caused by *C. jejuni* symptoms are characterized by severe enteritis, abdominal cramps, fever, and bloody diarrhea with mucus. Secondary complications such as autoimmune neuropathy and inflammatory bowel disease (IBD) and immunoreactive complications like Miller-Fisher syndromes may also occur following infection by *C. jejuni* (Igwaran and Okoh, 2019; Divsalar et al., 2019; Sylte et al., 2020). There are several treatments for *C. jejuni* infections; however, macrolide (azithromycin and E) and fluoroquinolones (CIP) are the most recommended antibiotics (Norren et al., 2019).

18.6.5 Vibrio

Vibrio is a genus of ubiquitous bacteria that are found in different aquatic and marine environments (Baker-Austin et al., 2018). Vibrio are small, gram-negative rods, with a single polar flagellum. Vibrios are facultative anaerobes, and they are both fermentative and respiratory metabolism (Cabral, 2010). Most vibrios are halophilic, meaning their growth is influenced by sodium, except for V. cholera. Furthermore, most species are oxidase-positive and can reduce nitrate to nitrite. The genus consists of 28 species, and V. cholerae, *V. parahaemolyticus*, *V. alginolyticus* and *V. vulnificus* are the most significant human pathogens found in aquatic environments and seafood (Baker-Austin et al., 2018). Most vibrios have pili in their cells, and their structures are made of TcpA protein (Cabral, 2010).

Vibrio sp. are among the majority of water and foodborne pathogens, causing severe health problems in the human population (Thompson et al., 2006). Most vibrio cases are reported during warmer seasons. Moreover, most infections are a result of consumption of contaminated water and undercooked contaminated seafood, resulting in different symptoms in humans (Altekruse et al., 2000). In humans, Vibrio causes two different groups of infections, namely, cholera and noncholera syndrome, where V. cholerae is the etiological agent of cholera. A severe diarrheal illness usually results from the consumption of contaminated food and water (Baker-Austin et al., 2018).

Treatment is essential since it reduces the mortality rate by more than 50%. Standard treatment includes replacement of both water and salts lost during diarrhea syndrome, especially potassium through oral administration in light dehydration. Nevertheless, in severe cases, rapid and intravenous-administration is mandatory. Doxycyclin is by far the only antibiotic that is used, whereas water and salt replacement is the primary treatment method. However, according to Wong et al. (2015), treatment of *V. vulnificus* and *V. cholerae* infections requires adjuvant antibiotic therapy whereas, for *V. vulnificus* which has a high mortality rate treatment should include either quinolone alone or tetracycline. Furthermore, penicillin alone is not useful; hence it is recommended that patients with *V. vulnificus* syndrome should be given treatment synergistically with quinolone.

18.6.6 *Legionella pneumophila*

Legionella pneumophila (*L. pneumophila*) is a thin, aerobic, pleomorphic, flagellated, nonspore-forming, gram-negative bacterium of the genus Legionella. *L. pneumophila* is the primary human pathogenic bacterium in this family and is the causative agent of legionnaires disease, also known as legionellosis. *L. pneumophila* was first recognized in 1976 after an outbreak at a convention of the American Legion in Philadelphia, Pennsylvania thus, the name legionnaires' disease (Mekkour et al., 2013). This disease is the pneumonic form of an infection usually caused by *L. pneumophila* serogroup.

Legionella species, more especially *L. pneumophila*, are responsible for more drinking water and nonrecreational water-borne disease outbreaks in the US than other microorganisms (Whiley and Bentham, 2011). Moreover, the cases of legionellosis are consistently increasing significantly (Whiley and Bentham, 2011), mostly, which are due to exposure through the respiratory route. However, other forms of the disease have been reported. *L. pneumophila* causes two forms of illness, including Pontiac fever, which is responsible for flu-like symptoms, and the potentially deadly pneumonia (Schwake et al., 2015).

The infection occurs from inhalation of airborne water droplets or mist contaminated with viable *L. pneumophila*, which are transported to the alveoli in the lungs (Reinhart, 2019). However, the bacterial load of *L. pneumophila*, which is required to cause an infection, is not yet known (Mekkour et al., 2013). According to Diederen (2008), sporadic cases are reported throughout the year; hence the epidemic cases are reported during summer and autumn due to warmer weather which encourages the proliferation of bacteria in water. Most cases of legionnaires disease (LD) are reported in individuals of age between 40 and 70 years old. However, even healthy people can become surfer from LD, but most people at high risk are smokers, patients with cancer, chronic respiratory diseases, kidney problems, those who are immune-compromised (Mekkour et al., 2013; Reinhart, 2019).

Legionella infection is one of the most misdiagnosed infections; as a result, some studies proved it to be underdiagnosed and undertreated (Chahin and Opal, 2017). Nevertheless, if Legionella is diagnosed, there are several treatments to be administered. Mekkour et al. (2013) reviewed the LD treatment. They documented that the adult patients with LD should be given Macrolides (500 mg Azithromycin) every day or clarithromycin (500 mg) every 12 h. Additionally, Fluoroquinolones (500 mg) or 400 mg moxifloxacin every 24 h, Rifampin (300–600 mg) every 12 h, Doxycycline (200 mg) followed by 100 mg every 12 h as well as a combination of Levofloxacin (500 mg) + other fluoroquinolone and Azithromycin every day.

18.7 Advantages and disadvantages of nanoparticles in water treatment

Years ago, nanoparticles were successfully applied in various fields such as biology, sensing, medicine, and catalysis. Recently several studies have shown that nanoparticles are useful for water treatment in the removal of pollutants, and it has drawn wide attention. Literature report different kinds of nanoparticles to be effective against water pollutants such as organic pollutants, heavy metals, bacteria, and inorganic anions. Nanoparticles have different classes such as metal nanoparticles, nanocomposite, metal oxides, and carbon nanotubes. Just like everything in life, they too have pros and cons. Most of these classes share common drawbacks (Lu et al., 2016; Zhong et al., 2006).

Metal nanoparticles are also known as zero-valent nanoparticles. As mentioned previously, various metal nanoparticles have been reported in water treatment; for example, silver nanoparticles have been used for the disinfection of water since they are highly toxic to microorganisms. However, silver nanoparticles are reported to have some drawbacks when directly applied to water. When silver nanoparticles are directly applied in aqueous media, they tend to aggregate, which slowly reduces the effectiveness of the nanoparticles for long-term use (Li et al., 2012). Literature also reports the use of other metal nanoparticles such as iron, zinc, aluminum, and nickel in water treatment, and among these nanoparticles, iron nanoparticles (Fe-NPs) are reported to be widely studied due to their properties such as adsorption properties, low cost, as well as oxidation and precipitation (Rivero-Huguet and Marshall, 2009). The disadvantage of iron nanoparticles, when used in water treatment, is that they generate iron sludge, which becomes another problem after the degradation of pollutants. Zinc nanoparticles are reported as an alternative to iron nanoparticles; since it is a more potent reductant compared to iron. Hence the rate of degradation of contaminants may be faster than that of an iron. Zinc nanoparticles are mostly reported to participate in dehalogenation reactions, and these studies indicate that the CCl_4 reduction is more effective on zinc nanoparticles compared to iron nanoparticles. Although these studies show successful reductions of contaminants using zinc nanoparticles, they are limited in the degradation of halogenated organic compounds. Metal nanoparticles have strong reducing abilities and good adsorption properties due to their unique size and large surface area, which makes them have excellent performance in water treatment. Studies also show that metal nanoparticles are also successfully applied in the removal of heavy metals, phenols, organic dyes, nitroaromatic compounds, halogenated organic compounds, and other large contaminants. Although metal nanoparticles have several advantages, they also have disadvantages with the major one being their inability to separate from the degraded species (Wen et al., 2016; Bokare et al., 2013; Tratnyek et al., 2010).

Metal Oxide nanoparticles are mostly used as photocatalysts; currently, in water treatment, particularly in photocatalytic degradation methods for the degradation of contaminants. TiO_2 nanoparticles are reported to be the most widely studied metal oxide nanoparticles in the last decade since they have high photocatalytic, photostability and are reasonably priced. In the presence of catalysts and light, TiO_2 nanoparticles can successfully degrade water pollutants by oxidizing them into low molecular weight intermediates while requiring ultraviolet excitation for charge separation within the particles to occur due to larger bang gaps of the nanoparticles (Guesh et al., 2016; Yan et al., 2015). The ultraviolet radiation under 400 nm will form hydroxyl radicals allowing TiO_2 nanoparticles to disrupt the function and damage the cell. The result is reactive oxygen species (ROS) that will ultimately degrade the pollutants in a short reaction time. However, TiO_2 NPs are reported to have little selectivity, therefore, are useful in the degradation of various pollutants such as cyanide, arsenic pesticides, phenols, dyes, polycyclic aromatic carbon hydrocarbons, and chlorinated organic compounds. The drawbacks of TiO_2 nanoparticles include the large bandgaps of 3.2 eV that make the nanoparticles require the excitation of ultraviolet. Another main drawback about TiO_2 nanoparticles is that they are not easily removed from the treated water (Belver et al., 2019; Bera et al., 2019).

Carbon nanotubes have also gained much attention in research applications due to their electrical properties and unique structure. Their advantages in water treatment include selectivity towards aromatics; they have large surface areas, have fast kinetics, and have a great capacity to adsorb a wide range of contaminants (Khin et al., 2012). Their main drawback is the high cost and low volume of production. Moreover, carbon nanotubes alone, without the matrix or medium to provide structural support, are not significant (Chatterjee and Deopura, 2002).

As previously mentioned, the use of nanoparticles alone has its disadvantages, for example, metal nanoparticles are difficult to remove from the treated wastewater, and they undergo oxidation as well as aggregation, whereas metal oxides are restricted in the ultraviolet region because of their band gaps. Moreover, carbon nanotubes are restricted by their high cost, low volume of production, and also, they require a supporting matrix or medium. Nanocomposite materials for water treatments are promising for the significant degradation of water pollutants. For example, composites of metal nanoparticles and ceramic filters are reported to be fully effective and improve the removal efficiency of microorganisms in wastewater. Metal oxides nanoparticles studies show that doping them with other metals such as silver improves their visible light absorbance leading to an increase in photocatalytic activity under ultraviolet radiation (Mikelonis et al., 2016). Other studies report that doping metal oxides with nonmetals such as C. S, F and N narrows the bandgap in the ultraviolet region and can help in the degradation of dyes (Liu et al., 2006; Adamek et al., 2013).

The advantages of using nanoparticles out ways the disadvantages by a huge margin. These advantages have been successfully observed in water purification as well as in the detection of harmful chemicals and pathogenic microbes in water. The question scientists should be asking themselves is whether or not there are alternative methods to ensure the safe synthesis of these nanoparticles. An alternative would be the use of green method nanoparticles which would allow the synthesis of less toxic nanoparticles using single-step synthesis methods. It should be noted that these nanoparticles should be disposed of safely. Since the field of nanotechnology is expanding at a rapid rate, cleaner and sustainable methods are imperative during the synthesis processes to preserve human and animal life while protecting the environment.

This chapter falls under the section on fate and occurrence of emerging pollutants within aquatic ecosystems with other chapters, e.g., Cristale (2022), Vizioli et al. (2022), Galhardi et al. (2022), Hashemi and Kaykhaii (2022), Madikizela et al. (2022), Mashile et al. (2022), Montagner et al. (2022), Moodley et al. (2022), Ntshani and Tavengwa (2022), Sanganyando and Kajau (2022) and Yardy et al. (2022) that aims to make an understanding of the different emerging pollutants within the aquatic environment.

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PART 3

Management policies and legislations on emerging pollutants

C H A P T E R

19

Policies and regulations for the emerging pollutants in freshwater ecosystems: Challenges and opportunities

Edmond Sanganyado

19.1 Introduction

Advances in the production of synthetic substances have contributed significantly to an improvement in the quality of life and life expectancy worldwide (Johnson et al., 2020). For example, agrochemicals play a significant role in increasing crop yields to ensure that they meet the growing global food demand, while pesticides are essential in public health for protecting humans from vector-borne diseases such as malaria, chikungunya, Lyme disease, West Nile virus, trypanosomiasis, dengue fever, and the plague (Nicolopoulou-Stamati et al., 2016; van den Berg et al., 2020). Pharmaceuticals and personal care products (PPCPs) directly improve quality of life by preventing or treating human diseases and improving daily personal hygiene and beauty, respectively (Boxall et al., 2012; Ebele et al., 2017; Liu and Wong, 2013). Synthetic substances are widely used in various industries such as petroleum, mining, textile, fine chemicals, and electronic industries to improve product quality and process efficiency as well as raw materials. Hence, synthetic substances are a ubiquitous component of our daily lives (Table 19.1).

The presence of emerging pollutants in freshwater ecosystems is an issue of global concern (see Tavengwa and Dalu, 2021, Chapter 1). Emerging pollutants enter freshwater ecosystems at various stages of the product life cycle, such as production, distribution, use, and disposal. For example, during textile production, azo dyes are discharged into rivers and lakes as part of industrial effluent (Cao et al., 2019; Hashemi and Kaykhaii, 2022, Chapter 15), use of pharmaceuticals and personal care products result in their discharge into wastewater and subsequently, the environment (Sanganyado et al., 2017; Mashile et al., 2022, Chapter 8; Madikizela et al., 2022, Chapter 10), and phthalates, polybrominated flame retardants, and rare earth elements often enter groundwater following the disposal of electronic and plastic products on landfills (Gwenzi et al., 2018; Cristale, 2022, Chapter 16; Galhardi et al., 2022, Chapter 17). Although often present in freshwater ecosystems at low concentrations, emerging pollutants are biologically active compounds or particles with the potential of eliciting an adverse biological effect in aquatic organisms at low concentrations (Dey et al., 2019; Inam et al., 2015). In 2016, 12.6 million premature deaths worldwide were linked to environmental degradation (Neira and Prüss-Ustün, 2016). The Global Burden of Disease estimated that 1.3 million deaths in 2016 were causally linked to 12 synthetic substances (GBD, 2017). For that reason, environmental pollution was recently ranked together with biodiversity loss and climate challenge as priority global challenges at the 5th United Nations Environment Assembly meeting (UNEA5) (United Nations Environment Assembly, 2021).

19.1.1 Scope of the chapter

Most synthetic substances are considered emerging contaminants because they are not regularly monitored or 'carefully' regulated despite having the potential to elicit adverse ecological and human health effects when they are

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TABLE 19.1 Examples of emerging contaminants frequently detected in freshwater.

Class	Examples
Pharmaceuticals	Fluoxetine
	Propranolol
	Tetracycline
Flame retardants	Polybrominated diphenyl ethers
	Organophosphate flame retardants
	Hexabromocyclododecanes
Personal care products	UV filters
	Synthetic musk
	Disinfectants
Pesticides	Neonicotinoids
	Pyrethroids
	Azole fungicides
Industrial chemicals	Phthalates
	Per- and polyfluoroalkyl substances
	Polychlorinated biphenyls

discharged into the environment (Rosenfeld and Feng, 2011). This is probably because of a lack of data on their chemodynamics, ecotoxicology, and toxicology, which hinders an accurate assessment of their potential human and ecological risk (Sauvé and Desrosiers, 2014). However, several studies have detected emerging contaminants in various environmental compartments such as rivers, lakes, glaciers, groundwater, soil, sediments, seawater, and biota (Dulio et al., 2018; Gavrilescu et al., 2015; Müller et al., 2020).

Prevention, control, and management of emerging pollutants are critical for protecting life below water (Sustainable Development Goal (SDG) 14), life on land (SDG 15), and water quality (SDG6), as well as promote responsible consumption and sustainable production (SDG 12) (Sanganyado, 2022). Environmental policies and regulations often seek to minimize the unintentional entry of chemicals, particles, and biological matter into the environment during the product life cycle (Sanganyado, 2020). Hence, this chapter discusses challenges in the regulations of emerging contaminants in freshwater ecosystems, focusing on synthetic chemicals and microplastics (see Yardy et al., 2022, Chapter 9). In addition, this chapter explores the recent innovations that could improve the environmental regulation of emerging contaminants.

19.2 Challenges in regulating the emerging contaminants in freshwater systems

The synthetic substance industry, particularly the chemical industry, is the most regulated. However, most national, international, or regional regulatory agencies focus on only two types of policies for protecting humans and the environment (Creton et al., 2010; Dulio et al., 2018; United Nations Environment Programme, 2019). The most common policies focus on controlling emissions and wastes during production, storage, and distribution. Examples of such policies include collecting emissions data, monitoring data, setting emissions limits, issuing permits, and establishing safety and accident procedures. The second type of policy focus on protecting users and the environment from synthetic substances. Such policies cover data collection, exposure and hazard assessment, maintenance of chemical inventories, and product use and marketing restrictions. However, most production and product policies overlook the environmental behavior and ecotoxicology of synthetic substances, and this has contributed to the lack of data on most emerging contaminants.

19.2.1 Limitations of international conventions on synthetic substance management

Environmental policies are often supported by international agreements on the management of synthetic substances and waste. For example, following the Basel Convention, many countries established national legislation on exporting and importing hazardous waste (United Nations Environment Programme, 2019). Amendments to the Basel Convention have added new synthetic substance classes as evidence of their potential adverse human and ecological effects mounted. For example, as of January 2021, exporting scrap plastic is only permitted with the prior written consent of the importing country and the transit countries. However, the United States of America, a major producer and exporter of hazardous waste, remains not party or signatory to any major conventions such as Basel Convention, Stockholm Convention, Rotterdam Convention, and Minamata Convention as of 2019 (United Nations Environment Programme, 2019). The US has not ratified any of these conventions since it has failed to pass federal laws that comply with conventions. However, many developing nations continue to export hazardous materials such as e-waste, plastics, and textile materials despite being parties to numerous international conventions. This is because international conventions lack enforceable regulatory authority.

The export and import of e-waste are an excellent example of the limitations of international conventions in controlling the discharge of emerging contaminants in freshwater systems. For example, the US generated approximately 6.9 million tons of e-waste in 2016 while exporting 50%–80% to developing nations in 2011 (Bhutta et al., 2011; Wang et al., 2020a). Developing nations that export e-waste often lack effective, sustainable, and regulated recycling capacity. Hence, most exported e-waste is disposed on landfills, where it ends up leaching into the groundwater (Gwenzi et al., 2018). Sadly, disposal of e-waste in landfills and its recycling is a major source of emerging contaminants (e.g., rare earth elements, polychlorinated biphenyls, polychlorinated dibenzo-*p*-dioxins and dibenzofurans, brominated flame retardants, and plasticizers) in freshwater systems (Gwenzi et al., 2018; Shi et al., 2019). For that reason, China, India, and other Asian nations introduced laws that limit or prohibit the import of e-waste (Fu et al., 2018; Zhang et al., 2012). For example, China amended several legislations on e-waste management such as The Law on the Prevention of Environmental Pollution from Solid Waste, Ordinance on the Management of Waste Household Electrical and Electronic Products Recycling and Disposal, and Management Measure for the Prevention of Pollution from Electronic Products, Notification on the Import of the Seventh Category of Wastes, and Notice on Strengthening the Environmental Management of Wasted Electrical and Electronic Equipment, as discussed by Zhang et al. (2012). However, the ban on e-waste has not resulted in any marked decrease in the discharge of e-waste associated emerging contaminants in China's freshwater systems. This is probably because the domestic generation of e-waste in China is increasing exponentially with only 25% recycled in formal e-waste recycling centers (Fu et al., 2018). Around 6 million tons were generated domestically in 2014 while an increase to 28.4 million is estimated by 2030 (Fu et al., 2018). Hence, restriction on the importation of e-waste might protect aquatic systems in developing countries but not rapidly growing economies with extensive electronic and electrical industries such as China and India.

19.2.2 Poor synthetic substance regulatory infrastructure

Many countries and regional bodies have established regulatory frameworks for assessing and managing the safety of synthetic substances throughout their lifecycle. These regulatory frameworks contain a register of the chemicals manufactured, imported, or used in the country. Most countries have different national agencies tasked with evaluating requests for registration and approval of some synthetic substance (Wang et al., 2020b). Frequently, there are separate inventories for different classes (e.g., cosmetics, pesticides, pharmaceuticals, food additives, and industrial chemicals) which are sometimes managed by different regulatory agencies. For example, the Tobacco Research Board and Medicines Control Authority are responsible for registering and issue certificates for commercial use of pesticides and pharmaceuticals in Zimbabwe. In South Africa, the Directorate of Agricultural Inputs Control in the Department of Agriculture, Forestry and Fisheries, and the South African Health Products Authority is responsible for keeping the pesticide and pharmaceuticals inventory. However, thousands of synthetic substances pass through regulatory cracks due to illegal activities, manufacturer confidentiality practices, and inadequate regulatory infrastructure (Kosamu et al., 2020). These "ghost" synthetic substances inadvertently enter the aquatic environment during use and disposal.

19.2.2.1 Lack of environmental behavior and ecotoxicology data

Manufacturer confidentiality practices are a significant cause of the lack of data on synthetic substances that enter the freshwater environment. A recent study found that they are 350,000 chemicals in national and international inventories. However, the identities of 50,000 and 70,000 chemicals remain publicly unknown or are poorly described as they are considered confidential by the manufacturers, respectively (Wang et al., 2020b). For example, chloroperfluoropolyether carboxylates were unregulated alternatives of per- and poly-fluoroalkyl substances in New Jersey soils and rivers (Valsecchi et al., 2017; Washington et al., 2020). The lack of regulation on chloroperfluoropolyether carboxylates despite their widespread occurrence in the environment was attributed to: (i) a lack of regulatory attention on synthetic substance alternatives; (ii) absence of mandatory reporting or review of new chemicals premanufacture to the Environment Protection Agency under the US Toxic Substances Control Act; (iii) classification of chloroperfluoropolyether carboxylates data as confidential business information; (iv) or EPA passed chloroperfluoropolyether carboxylates into the market without requiring health and safety data considering that 85% of new substances authorized without health and safety testing (Gold and Wagner, 2020).

The scarcity of environmental behavior and ecotoxicology has contributed to the increase in the use of more toxic alternatives than restricted or banned synthetic substances. A recent study found that although the total amount of pesticides used in the US between 1992 and 2016 decreased drastically, the total toxicity to insects and aquatic invertebrates increased significantly (Schulz et al., 2021). Global mapping of the environmental risk posed by current use pesticides found that South African, Chinese, Indian, Australian, and Argentine watersheds were regions of great concern since they had a significantly high risk of pesticide pollution, high biodiversity, high prevalence of water scarcity (Tang et al., 2021). A recent systematic review found that organophosphate ester flame retardants had similar persistence and aquatic toxicity as polybrominated diphenyl ethers, which they replace (Blum et al., 2019). Hence, proactive legislation that emphasizes the generation and public sharing of data on physicochemical properties, environmental fate and transport, bioaccumulation potential, and ecotoxicity of alternative synthetic substances should remain a priority among regulatory agencies (Sharkey et al., 2020; Sweetman, 2020).

19.2.2.2 *Illegal trading of illicit drugs*

Illegal activities such as the trade and use of illicit drugs have contributed to the occurrence of illicit drugs in freshwater systems (Fontes et al., 2020; Pal et al., 2013; Petrie et al., 2017). The United Nations Office on Drugs and Crime estimated that 250 million people used illicit drugs at least once in 2015 alone (Fontes et al., 2020). Previous studies in Henares River, Spain, found amphetamine concentrations of up to 309 $\mathrm{ng\,L^{-1}}$ (Martínez Bueno et al., 2011). Novel psychoactive substances are a growing class of illicit drugs that take advantage of the advances in information technology and the lax nature of chemical regulations. Buying and selling novel psychoactive substances has proliferated since sellers use misleading labels on the use, routes of administration, purity, and chemical identity to hide from regulatory agencies (Hägele et al., 2020). It is estimated that there are 730 novel psychoactive substance derivatives on the black market, with most of them being simple modifications of prohibited illicit drugs (Hägele et al., 2020). However, out of the 237 known opioids (a class of psychoactive substances), only 22 parent compounds and 22 transformation products have been detected in wastewater and surface water globally (Campos-Mañas et al., 2018). Hence, the occurrence of many more scheduled illicit drugs and their derivatives continue to be discharged into the environment due to lax regulations.

19.2.2.3 *Inadequate technical capacity to assess, monitor, and register synthetic substances*

Regulatory agencies often lack the technical infrastructure to monitor and maintain synthetic substance inventories. Like most regulatory agencies in developing countries, the Pesticide Control Board could not conduct pesticide residue analysis in the environment and controlling illegal importation (Kosamu et al., 2020). A 2014 survey by the World Health Organization found that 50% of African countries had limited or no laboratory capacity to assess, monitor, or detect emerging contaminants in environmental matrices (WHO Regional Office for Africa, 2014). Of the 40 countries surveyed, 18 did not have a national reference laboratory, and only 10 countries had laboratories affiliated with regional or international laboratories. Environmental monitoring and characterization of emerging contaminants are often conducted using gas or liquid chromatography, yet less than 42.5% of surveyed countries had such equipment in their national laboratories. A study in Malawi found that the Pesticides Control Board, which is mandated with the authorization of pesticides, lacked essential facilities for assessing the environmental risk of pesticide use or certifying the quality of pesticide formulations preregistration (Kosamu et al., 2020). A recent global survey found that there were disparities in pesticide regulations between high-income and low-income countries. Low-income countries had lacked pesticide legislation, capacity for registering pesticides, and environmental protection policies on pesticide contamination (van den Berg et al., 2020). Hence, strengthening the capacity to conduct chemical and biological analysis is imperative for improving emissions monitoring and product registry in developing countries.

19.2.2.4 *Imperfect science and policy interactions*

The development of effective environmental policies for protecting freshwater systems from emerging contaminants relies heavily on relevant, reliable, and competent scientific evidence. Hence, there is a need for efficient and effective crosstalk between policymakers, scientists, and the public. In Europe, working groups from the EFSA continually provide regulators with a synthesis of scientific evidence on the environmental behavior and ecotoxicology of pesticides. Through such evidence, synthesis reports led to the protection of bees by restricting the use of neonicotinoids in agriculture and incorporating stereochemistry when testing premanufacture the environmental behavior of pesticides (Sanganyado, 2020; Sanganyado et al., 2020). Wang et al. (2021) recently identified four major challenges in science and policy interaction on synthetic substances, namely: (i) current intergovernmental organization on the management of synthetic substances focus on few classes of emerging contaminants (e.g., antibiotics, lead, pesticides, and persistent organic pollutants; see Montagner et al., 2022, Chapter 12; Ntshani and Tavengwa, 2022, Chapter 11) or emerging contaminant containing waste (e.g., mine tailings, plastics, and e-waste); (ii) science-policy interface forums are mostly ad hoc in response to a disaster which makes it hard to have sustainable early warning and horizon scanning infrastructure; (iii) great effort is placed on offering science advice to legislators based on complex evidence, yet little or no attention is given on turning complex regulatory challenges to scientific questions, and (iv) lack of participation of scientists in science-policy interface forums. However, a recent survey of scientists worldwide found that the state of scientific evidence for legislative science advice was poor, particularly in low to low-middle income countries (Akerlof et al., 2019). Poor science and policy interaction could be due to mistrust between scientists and policymakers. Akerlof et al. (2019) found that scientists generally were unsure if proper communication of scientific evidence to legislators could improve the implementation of policies.

The International Panel on Chemical Pollution identified several factors that hinder the participation of scientists in policymaking, and these included intrinsic factors such as different goals on science, different approaches to pertinent questions, different perceptions on timeframes and different languages, and extrinsic factors such as lack of training, poor access to pertinent information, lack of communication platforms, and different value perceptions (IPCP, 2018). The lobbying activities of chemical manufacturers often exacerbate mistrust of evidence generated by scientists. For example, a recent study found that industry lobbying and lack of local scientific evidence, and poor public awareness were the major contributors to the lack of national regulations on nanoparticles (Andresen et al., 2018). In the US, an analysis of the demise of a climate policy that sought to regulate greenhouse gases found that political lobbying against the policy by industries that expected to lose contributed significantly to the bill's demise (Meng and Rode, 2019). Cai and Li (2020) found that the lobbying process was asymmetric and favored polluting companies rather than clean companies. A small, highly polluting company can weaken environmental regulations, while only a clean company with a big budget can positively influence the enaction of environmentally friendly regulations (Cai and Li, 2020). This asymmetry in the lobbying process could be attributed to the lack of adequate science-policy interface forums.

19.3 Current advances in emerging contaminant assessment

19.3.1 Advances in suspect and nontarget screening

Technical advances in exposure and effects assessment have contributed significantly to improving the accuracy and relevancy of ecological risk assessment of emerging contaminants in freshwater systems. Development of high-resolution mass spectrometry, multi-dimensional chromatography, and integration with high-performance computing has made it possible to detect emerging contaminants at pg L^{-1} surface water as well as determining unknown-known (suspect screening) and unknown-unknown (nontarget screening) chemicals in the environment (Hollender et al., 2017). A study at Puget Sound in Washington, USA, found 87 nonpolymeric emerging contaminants in the surface water, of which 45 were later confirmed and quantified (Tian et al., 2020).

Suspect and nontarget screening has immense potential for supporting emerging pollutant regulations due to its ability to determine contaminant sources and to detect 'ghost' compounds (e.g., transformation products, unregulated replacement synthetic chemicals, and potentially toxic natural products). Combining time-series analysis and cluster analysis is a powerful tool for identifying the sources of complex and dynamic mixtures of emerging contaminants when monitoring freshwater systems (Beckers et al., 2020). Source analysis revealed emerging contaminants in Puget Sound came from stormwater, local urban and industrial emissions, and wastewater effluent (Tian et al., 2020). Beckers et al. (2020) identified wastewater treatment plants, Bode River discharge, and diffuse, groundwater discharge, and minor point sources as the primary contaminant sources along the 47-km Holtemme River in Germany. Analysis of surface water and sediments from the Tennessee River in the US revealed that some replacement fluorinated compounds were based on perfluorobutane sulfonate and had shorter chains. In contrast, others were polyfluorinated compounds with some fluorine atoms substituted with a hydrogen atom or CH_2CF_2 units alternating (Newton et al., 2017). Nontarget screening of water samples in New Jersey found novel chloro-perfluoro-polyether carboxylates at abundance levels similar to those of the regulated compounds they were replacing (McCord et al., 2020). Interestingly, chloro-perfluoro-polyether carboxylates do not have any publicly available data on their health and safety evaluation (McCord et al., 2020). Hence, regular monitoring of rivers impacted by stormwater, industrial effluent, and domestic wastewater using nontarget screening can be a robust early warning tool for identifying unregulated or weakly regulated replacement products and transformation products.

Considering the diversity and vastness of emerging contaminants present in freshwater systems, assessing the exposure and effects of all the contaminants is impractical. Early attempts on prioritization using suspect and nontarget screening involved determining the detection frequency and abundance and then ranking it with persistence, bioaccumulation potential, and toxicity data obtained from literature or estimated using quantitative structure–activity relationship models (Brack et al., 2018; Park et al., 2018; Posthuma et al., 2020). For example, 51 pharmaceuticals and personal care products were detected in Yeongsan River, Korea, using suspect and nontarget screening, and the top 12 priority compounds were identified based on the abundance, detection frequency, and toxicity data (Park et al., 2018). However, the reliability of this prioritization approach is highly dependent on the availability of quality ecotoxicological data. For many emerging contaminants, such quality data is scarce. Krauss et al. (2019) used site-specific prioritization to identify the emerging contaminants with the highest abundances at a particular site compared to other sites. However, this approach assumed that the emerging contaminants had similar toxicological profiles.

19.3.2 Advances in effect-directed analysis

Integrating suspect and nontarget screening with effect-directed analysis has demonstrated an immense potential to prioritize emerging contaminants and assess Effect-directed analysis involves bioassays (i.e., determining the molecular, cellular, or organismal biological response), fractionation, and toxicant identification and quantification (Brack et al., 2016). These steps are essential in reducing the complexity of the environmental matrices, making it possible to assess mixture toxicity or identify "ghost" compounds responsible for observed adverse health effects in organisms or populations. Recent studies used a combination of effect-directed analysis and nontarget screening to identify the emerging contaminants responsible for acute mortality in Coho salmon caused by exposure to stormwater (Peter et al., 2018; Tian et al., 2021). Peter et al. (2018) attributed the acute mortality to tire wear product leachates, particularly polyethylene glycols, polypropylene glycols, octylphenol ethoxylates, and a previously undetected family of (methoxymethyl) melamines. However, a subsequent study identified a transformation product of *N*-(1,3-dimethylbutyl)-*N*′-phenyl-*p*-phenylenediamine, which is widely used as a rubber antioxidant in tires as the leading cause of acute toxicity (Tian et al., 2021). A systematic review on the use of effect-directed analysis and nontarget screening in European rivers to support the implementation of the European Union Water Framework Directive found that by focusing on several endpoints (e.g., aryl hydrocarbon receptor effects, endocrine disruption, mutagenicity, and green algae toxicity), compounds that were not previously considered as emerging contaminants or regulated (e.g., substituted phenols, dinaphthofurans, synthetic estrogens and androgens, *N*-phenyl-2-naphthylamine, and 2-(2-naphthalenyl) benzothiophene) were identified as priority compounds (Brack et al., 2007).

19.4 Opportunities in environmental regulation of emerging contaminants

19.4.1 Effect-based approaches

In many countries, environmental policies and regulations are shifting from a focus on concentration levels, acute toxicity, and single compound toxicity towards holistic and integrated approaches that recognize the complexity of factors influencing the risk of emerging contaminants in freshwater systems. For example, the water and sediment quality guidelines in Europe now recommend effect-directed approaches in monitoring emerging pollutants, as discussed in a previous section. A holistic approach in ecological risk assessment of neonicotinoids in agriculture ecosystems in the European Union contributed to restrictions in their use and production. Effect-directed approaches are integral for the successful incorporation of mixture toxicity in environmental regulation. The US Environmental Protection Agency and the World Health Organization have developed guidelines on human health and safety testing that incorporate mixture toxicity. However, despite the absence of comprehensive guidelines that emphasize mixture toxicity in freshwater systems, previous studies have shown the current technical tools can provide the required data to support such guidelines (Bopp et al., 2019). For example, omics technology (transcriptomics, metabolomics, proteomics, and lipidomics) is widely used to unravel modes of action and toxicity pathways in complex mixtures as well as to elucidate the interactions of mixture components in biological systems at (sub)cellular level (Prat and

Degli-Esposti, 2019). High throughput in vitro toxicity screening has facilitated the replacement of animals in toxicity testing, the assessment of mixture toxicity, elucidation of modes of action of individual or group of substances while exponentially increased the number of chemicals that could be analyzed effectively at a given time (Bopp et al., 2019). In addition, integrating high throughput toxicity screening and in silico techniques (e.g., quantitative structure-activity relationship models and read-across methods) with machine learning and deep learning could facilitate a mechanistic understanding of ecotoxicological predictions for complex mixtures based on the adverse outcome pathways concept (Hemmerich and Ecker, 2020).

19.4.2 "One substance—One assessment" approach

Synthetic substances are usually regulated according to their market type or use. For example, in the European Union, there are different directives and regulations for each group of synthetic substances such as pesticides, pharmaceuticals, and industrial chemicals; namely, Reg (EC) No 1107/2009, Directive 2001b/82/EC, and Reg (EC) No 1907/2006a (van Dijk et al., 2021). However, the regulations are often fragmented, resulting in a disparate and sometimes conflicting assessment of the same chemical (Table 19.2). For example, since ivermectin is registered as human and veterinary medicine and as a pesticide, its health and safety testing under Directive 2001b/82/EC focuses on efficacy, terrestrial mammal toxicokinetics, and toxicodynamics while under Reg (EC) No 1107/2009, data on environmental chemo-dynamics and toxicity to nontarget invertebrates are required. Therefore, requiring a single assessment for synthetic substances with multiple uses can help reduce fragmentation and disparities in chemical inventories. However, for the "one substance—one assessment" approach to work, harmonizing the regulations and directives is essential. This could be achieved by making: (i) ecological risk assessment mandatory despite the market type of the substance; (ii) environmental stewardship a common goal in all regulations and directives; (iii) the required chemo-dynamics and ecotoxicology data in different frameworks similar; and (iv) emissions inventory and consumption data public, as discussed in the review by van Dijk et al. (2021). The establishment in 2007 and the continued success of the Pesticide Properties Database demonstrate the feasibility and importance of a transparent, comprehensive, and harmonized chemical registry (Lewis et al., 2016). The Pesticide Properties Database currently has more than 2300 pesticide active ingredients and 700 metabolites covering more than 300 parameters on environmental behavior, ecotoxicity, and ecological risk (Lewis et al., 2016). There is a need for similar property databases, which could also include consumption data should be established as well. International and regional harmonization of chemical registries could be achieved by forming a global science-policy body that facilitates the interaction of scientists and policymakers across borders (Wang et al., 2021).

TABLE 19.2 Fragmentation and inconsistence in registration of synthetic substances in the European Union in 2019.

			Overlapping chemicals per framework				
	CAS registered chemicals	Multiple framework registered chemicals	Biocides	Industrial chemicals	Pesticides	Human medicines	Veterinary medicines
Biocides	148	73	–	49 (33%)	28 (19%)	1 (0.7%)	5 (3.4%)
Industrial Chemicals	9518	97	49 (0.5%)	–	28 (0.3%)	23 (0.2%)	5 (0.1%)
Pesticides	393	53	28 (7%)	28 (7%)	–	6 (2%)	2 (0.5%)
Human medicines	752	42	1 (0.1%)	23 (3%)	6 (0.8%)	–	16 (2%)
Veterinary Medicines	130	29	5 (4%)	5 (4%)	2 (2%)	16 (12%)	–
Nonapproved Biocides	35	17	–	15 (43%)	3 (9%)	0	0
Nonapproved Pesticides	743	114	19 (3%)	94 (13%)	–	5 (0.7%)	3 (0.4%)

From van Dijk, J., Gustavsson, M., Dekker, S.C., van Wezel, A.P., 2021. Towards 'one substance—one assessment': an analysis of EU chemical registration and aquatic risk assessment frameworks. J. Environ. Manag. 280. https://doi.org/10.1016/j.jenvman.2020.111692. Used with permission of Elsevier Limited.

19.4.3 Chemical class-based approach

Traditional regulations where substances are assessed at chemical-by-chemical approach often led to the treatment of lack of data and untested replacement substances as proof that a substance is not hazardous. The class-based approach assesses multiple synthetic substances which share similar physicochemical characteristics and chemical structure based on the assumption that their biological activities and environmental chemo-dynamics are also closely similar (National Academies of Sciences, Engineering, and Medicine, 2019). This approach has been successfully used to evaluate the risk of phthalates and pesticides in the US (National Academies of Sciences, Engineering, and Medicine, 2019). New class-based hazard assessment approaches are currently being proposed globally for per- and polyfluoroalkyl substances (Kwiatkowski et al., 2020), under development for organohalogen flame retardants in the US (National Academies of Sciences, Engineering, and Medicine, 2019), and recently under implementation for per- and polyfluoroalkyl substances in the European Union (Kwiatkowski et al., 2021). However, for a class-based approach to succeed, the implications of stereochemistry on differences in environmental behavior and ecotoxicology should not be overlooked. Enantiomers of chiral substances have been shown to have different biological activities. For that reason, pharmaceutical and pesticide registration frameworks often recommend conducting tests that assess enantiomer-specific differences in fate and toxicity (Sanganyado et al., 2017).

19.4.4 Green synthesis approach

The green synthesis approach to mitigating chemical pollution is based on the understanding that since the environmental chemo-dynamics and ecotoxicology of emerging contaminants are mainly influenced by their chemical structure, it is possible to design chemicals that are nonpersistent, nondepleting, and nontoxic (Zimmerman et al., 2020). Adopting a green synthesis approach in the development of replacement products could help severe the current vicious cycle in chemical development where a persistent, bio-accumulative, and toxic substance is replaced by a similarly troublesome compound (see Ajayi et al., 2022, Chapter 18). However, the whole production process needs to be environmentally friendly to ensure minimal to zero emissions of emerging contaminants. For example, a previous study found that bioethanol production contributed to the emergence and proliferation of antibiotic-resistant genes in receiving freshwater systems (Muthaiyan et al., 2011). Green approaches, such as using solid biowaste to treat industrial effluent, can be embedded in the process design to reduce the discharge of emerging pollutants into the environment (Chingono et al., 2018). Therefore, green design and production process should be the goal to reduce freshwater pollution in green synthesis rather than just the commercialization of green products.

19.5 Conclusion

Traditional chemical-by-chemical environmental regulation approaches are inadequate for mitigating the pollution of freshwater systems (see Tavengwa et al., 2022, Chapter 20). In traditional approaches, the absence of evidence is often interpreted as proof of environmental friendliness. This has resulted in a vicious cycle where troublesome synthetic substances are replaced by similarly troublesome substances, with manufacturers altering minor functional groups while preserving the overall physicochemical and biological properties. However, advances in chemical and biological analysis such as suspect and nontarget screening and effect-directed analysis have contributed significantly towards a shift from traditional approaches to effect-based, “one substance—one assessment,” class-based, and green synthesis-based approaches. A major hindrance to such paradigm shift in environmental regulations of emerging contaminants is a lack of sustainable infrastructure for science-policy interface forums for scientists, policymakers, and the public at the national, regional, and global levels. A lack of bi-directional communication between scientists and legislators has contributed to the dominance of chemical-by-chemical approaches and, in some cases, the relaxation of environmental regulations to profit polluting industries. Hence, creating a global science-policy interface platform should be a priority to ensure minimal to zero-emission of emerging contaminants to protect the health of freshwater ecosystems.

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CHAPTER

20

Challenges and future directions in the analysis of emerging pollutants in aqueous environments

Nikita T. Tavengwa, Babra Moyo, Herbert Musarurwa, and Tatenda Dalu

20.1 Challenges and future directions

20.1.1 Dearth of information

The amount of available information regarding emerging pollutants in different countries/continents varies greatly. Furthermore, there is little or no data/information recorded in most tropical regions. This observation has a general correlation with how well the countries perform economically. Those countries or states with more financial resources and functionally equipped laboratories tend to have more information on emerging pollutants. A good example is the distribution of the LC-MS/MS in South African provinces, with great numbers of this instrument being concentrated in the Gauteng and Western Cape provinces, while poorer provinces have few or none. This distribution pattern is reflective of the situation within the continents or regions as well.

20.1.2 Low concentrations and matrix effects

Emerging pollutants are new compounds, which means they are likely to be discharged into large water bodies where they are not going to be saturated but will occur in trace amounts (see Tavengwa and Dalu, 2022, Chapter 1). Though they may occur in trace amounts, they might be unexpected of high toxicity as well (see Sanganyando and Kajau, 2022, Chapter 7; Mashile et al., 2022, Chapter 8; Yardy et al., 2022, Chapter 9; Madikizela et al., 2022, Chapter 10; Ntshani and Tavengwa, 2022, Chapter 11; Montagner et al., 2022, Chapter 12; Moodley et al., 2022, Chapter 13; Vizioli et al., 2022, Chapter 14; Hashemi and Kaykhaii, 2022, Chapter 15; Cristale, 2022, Chapter 16; Galhardi et al., 2022, Chapter 17). Their occurrence in trace amounts might also pause a great analytical challenge in that they may be not be detected by common analytical instruments because they might have concentrations of low limits of detection (see Kaserzon et al., 2022, Chapter 3; Kaykhaii and Hashemi, 2022, Chapter 4; Kebede et al., 2021, Chapter 5; Kumar et al., 2022, Chapter 6). This implies that more sophisticated/advanced instruments might be the answer to this analytical challenge. However, this presents yet another challenge as these instruments are costly. This is especially so for most developing countries within the tropical regions as they end up neglecting research-related activities to focus more on food security. These countries then rely on research results from foreign institutions, nongovernmental organizations, and first-world countries that are well resourced and take environmental research seriously.

20.1.3 Occurrence of pesticides as racemic mixtures

The application of pesticides is known to increase the efficiency of crop production, by farmers. However, the indiscriminate use associated with the use of cheaper and nonselective pesticides, (often banned in other countries due to the toxic potential to the environment) and the lack of efficient regulation, escalate the environmental contamination of

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freshwater systems (see Montagner et al., 2022, Chapter 12). This problem is further compounded by the existence of pesticides as racemic mixtures. When racemates are used in pest management, only the active enantiomer would be involved in destroying the pest. The other enantiomer(s) will be inactive and would be discharged into the environment which can be toxic to nontargeted species (Musarurwa and Taveng, 2020). The solution to this might be in chiral switching where there is a replacement of racemic chiral pesticides with single enantiomer-enriched formulations. This is because enantiomers of the racemic chiral pesticides do not have the same bioactivity on the target organisms as well as toxicity on nontarget organisms (Corcellas et al., 2015; Duan et al., 2018; Kaziem et al., 2020). Usually, the inactive enantiomer(s) of the chiral pesticides would end up discharged into freshwater systems.

20.1.4 Unpredictable physicochemical properties

Emerging pollutants are new compounds that can be very stable and resistant to any form of degradation such as biodegradation and photodegradation, and might have high thermal stabilities. This means they can have long half-lives implying they can remain intact in the environment for a long period of time even far from the point of discharge. In a study in South Africa, Chimuka et al. (2016) found traces of PAHs in Limpopo Province which is not highly industrialized as compared to Gauteng Province. The most plausible explanation for this observation is that these groups of compounds can travel for long distances, and be detected away from point sources. Most contaminants, including emerging pollutants, are solubilized in water which ends up in wastewater treatment plants where they are removed before the water is discharged back into freshwater systems (see Mashile et al., 2022, Chapter 8).

Many municipal wastewater infrastructures are not in order in many tropical countries. Also of great concern is that nearly all wastewater treatment plants are not designed to remove some pollutants, especially the emerging ones (see Mashile et al., 2022, Chapter 8; Sanganyado, 2022, Chapter 19). In general, most water treatment plants are not planned to remove trace levels of emerging pollutants such as pesticides. Since these pesticides are known to have adverse impacts on the environment, not only habitats at the site of discharge (wastewater treatment plant effluents) will be affected, but also those in other places through diffusive routes (Børgensen et al., 2015).

Even though some flame retardants have been banned in several countries, as pointed out by Cristale (2022) in Chapter 16, they are still being detected in the present day. Cristale (2022) pointed out that emerging pollutants such as high brominated flame retardants can degrade to lower brominated congeners which are more soluble than their respective parent compounds. This implies that they are more hydrophilic and can be transported for longer distances in water. If the degradation product compounds are toxic, consequences can be suffered by habitants downstream, where there are no industrial activities. Another challenge, still in the case of flame retardants, which are used to reduce the effect of fires, by-products can be produced after ignition to produce which can be classified as emerging pollutants themselves.

Another problem is the attachment of flame retardants on carrier bags has been noted to be weak. A possible problem is a contamination of the food carried, especially the ready-to-eat. This weak binding also presents a possibility of flame retardants being inhaled, in the case of volatile and semivolatile ones. There is, therefore, need to do further investigation of this group of compounds on plastic carrier bags.

With the good intention of adding chlorine to the water to make it fit for human consumption, new challenges arise in the form of new products forming other products. These products have been confirmed to cause an array of negative health problems, including cancer. More so, chlorine on its own and its reaction products can react with organic matter such as fulvic acid to form cancer-causing compounds, e.g., chlorinated organic compounds (Tavengwa et al., 2016).

20.1.5 Grab versus passive sampling

Most aquatic monitoring programs rely on collecting discrete grab, spot, or bottle samples of water at a given time (see Kaserzon et al., 2022, Chapter 3). Often, where pollutants are present at only trace levels, huge amounts of water need to be collected when the pollutants are present at trace levels. The information obtained in laboratory analysis of the sample provides only a snapshot of the levels of pollutants at the time of sampling. This approach has many drawbacks in environments where contaminant concentrations vary over time hence episodic pollution events are likely to be missed. To circumvent this problem, the sampling frequency can be increased, or installation of automatic sampling systems that can take numerous water samples over a given period can be done. All these approaches are costly, and in many cases, impractical, since a secure site and significant pretreatment of water are required. Such systems are rarely used in widespread monitoring campaigns. Spot sampling can also result in different apparent concentrations of pollutants depending on the pretreatment method applied. This does not reflect true levels of dissolved, bioavailable fraction of the contaminants. With all these disadvantages of grab sampling, passive sampling is now widely seen as a solution. Passive samplers are in many forms. These include the semipermeable membrane device (SPMD) which is made of a low-density polyethylene membrane, it is transparent to ultraviolet *a* and *b* waves. Unfortunately, chemicals that are sensitive to light, like PAHs, can degrade before correct concentrations are measured (Alvarez, 2010). SPMDs are designed to accumulate low-level concentrations of chemicals and those that are exposed to air for more than 30 min can concentrate airborne pollutants. In addition, while an SPMD can account for surge events of contaminants, it is difficult to determine when this event took place during the sampling period because the SPMD does not track time (Alvarez, 2010). Another disadvantage is that an SPMD will not be able to detect contaminants that readily dissolve in water (Alvarez, 2010).

20.1.6 Physical removal techniques

Dyes have a unique way of causing water impairment (see Hashemi and Kaykhaii, 2022, Chapter 15). For instance, a very small amount of dye(s) in water can be highly visible. Discharging even a small amount of these pollutants into the water can affect aquatic life and food webs due to the carcinogenic and mutagenic effects of synthetic dyes (Ertugay and Malkoc, 2014). Consequently, treatment of dye-contaminated wastewaters with decontamination processes is necessary before their discharge. Most of the commercially available chemical and physical treatment processes are inefficient in the removal of azo dyes from wastewater (Yaseen and Scholz 2018; Hashemi and Kaykhaii, 2022, Chapter 15). These methods present disadvantages such as, high costs, excessive use of chemicals that maybe toxic, concentrating these pollutants, and production of enormous amounts of sludge which result in secondary pollution (de Campos Ventura-Camargo and Marin-Morales, 2013; Ajaz et al., 2019).

As alluded to earlier, accurate analysis of trace emerging pollutants has always been a challenge due to the complexity of this matrix and the varying physicochemical properties of these analytes (see Sanganyando and Kajau, 2022, Chapter 7). The most common sample preconcentration technique is the application of sorptive materials which have recently been critically reviewed by Moyo et al. (2020) in the case of antibiotics. The challenge regarding the use of these materials is their nonselectivity. This is especially a problem when a specific analyte has to be removed from closely related analogs. Activated carbon is one of the most effective adsorbents for emerging pollutants, e.g., dyes, nonetheless, it lacks selectivity and most are expensive. Nonselectivity is a result of the nonpolar nature of carbon and the hydrophilicity of the water-soluble azo dyes (Singh and Arora, 2011). However, alternative low-cost sorbents derived from waste such as rice husks, orange peels, and groundnut shells have been explored in recent years. The problem of selectivity has necessitated the introduction of very selective material in the form of molecularly/ion-imprinted polymers.

20.1.7 Use of living organisms—Biomonitoring

Biomonitoring has been on the rise in recent years due to increasing anthropogenic impacts on freshwater systems. Challenges and opportunities related to this technique have been well highlighted by Mwedzi et al. (2022, Chapter 2). For example, on a global scale, there is generally a need for new aquatic biomonitoring approaches which consider other important taxonomic groups (e.g., amphibians, birds, mammals, microbes, reptiles) and new freshwater emerging pollutants (e.g., microplastics; see Su et al., 2019; Yardy et al., 2022, Chapter 9). For example, Su et al. (2019) concluded that eastern mosquitofish *Gambusia holbrooki* can be used as an appropriate biomonitoring organism for microplastic pollution in urban wetlands as polyester and fibers were found to be the dominant plastic-type and common shape on fish heads and guts, and they further recommended that future studies should consider measuring microplastic content in different fish body parts to identify critical uptake pathways that need to be considered in risk assessments and field monitoring program designs. de Oliveira Barbosa et al. (2019) highlighted that for freshwater fish, the ecological classification provides useful information, but with a lower level of concordance. Thus, in a cost-effective perspective, habitat use could be a good option due to its simplicity in classifying fish independently of taxonomic identification, which could make the biological assessment easy for a less qualified professional.

The collection of biomonitoring samples for water quality determination should be complemented by sound taxonomical investigations to update knowledge of key biomonitoring taxa such as diatoms, macroinvertebrates, and fishes. In terms of diatom and macroinvertebrate tolerances, ecological preferences, and ecophysiology, much work still needs to be done. Therefore, attention should be paid to both the biology and ecology of biomonitoring taxa occurring in moderate to high water quality environments (Dalu and Froneman, 2016; Mangadze et al., 2019). Furthermore, biomonitoring methods development based on intermediate taxonomy, i.e., genus level, will make the process faster and easier for other biomonitoring taxa such as diatoms and fishes, while not compromising bioindicator taxa model inferences.

While the lack of skilled human capacity, skills, and baseline information on bioindicator taxa community composition and ecological requirements represent significant hurdles. Across the developing world, taxa identification is moving towards the use of molecular tools, however, that is not the case across the developing world. It must be recognized that in many developing tropical countries, traditional identification techniques will still be required in the foreseeable future due to a lack of funding to purchase molecular analysis equipment.

Currently, there is also a lack of good long-term and large-scale data sets on autecology and taxonomy for a large number of bioindicator taxa which make biological indices not to be so powerful tools for river health monitoring across the developing world (Dalu and Froneman, 2016). There is also a need to adapt and strengthen existing biotic indices because they are reliable in identifying source impairment and can also be used as a monitoring and evaluation tool to identify freshwater systems where restoration activities are needed and to monitor trends in biotic integrity and biodiversity over time. Thus, extensive biomonitoring protocols are still needed within the tropical regions to develop standard methods (Mangadze et al., 2019).

20.1.8 Analysis of physical emerging pollutants: Microplastics

The effects of microplastic pollution on tropical freshwater environments is still basically speculative and there is still a lack of empirical data (Alimi et al., 2020; Yardy et al., 2022, Chapter 9), but it is important to monitor and characterize the microplastic abundance, distribution, and potential sources especially in wastewaters to carefully and comprehensively assess the risks associated with microplastics and develop better policy (see Yardy et al., 2022, Chapter 9). Due to the minute size of microplastic particles, this type of pollution is not necessarily visually unappealing but it has major mechanical and chemical implications for freshwater organisms, i.e., mechanically clogging organism digestive tracts and hindering mobility, both aspects that need to be studied further. Microplastics may also leach chemical additives into the freshwater environment, as well as accumulate pollutants with a high affinity for plastic particles (Boucher and Friot, 2017). There is also limited information on the interaction of metals and microplastics and more studies are needed in this area to fully understand the risks associated with microplastics, as this crucial to the overall risk assessment of freshwater microplastics in the tropics (Alimi et al., 2020). It is important to note that some studies do not include appropriate procedural or experimental controls which is not a good practice as it can lead to under or overestimation of microplastic concentrations within the tropical freshwater regions. Therefore, there is a need for standardization or homogenization of the methods to facilitate comparison of the results obtained in different studies, the establishment of guidelines to validate analytical methods, development of reference materials, and interlaboratory exercises, should be pursued further. Also, most studies (>50%) still rely on visual microplastic identification, thus, efficient sampling and detection methods are vital to understanding the microplastic distributions across tropical freshwater systems (Alimi et al., 2020). Furthermore, there is a lack of modern scientific equipment (e.g., Fourier-transform infrared spectroscopy, Raman, pyrolysis gas chromatography-mass spectrometry) which is a major setback for microplastic research in tropical freshwater studies, as most of the equipment is quite expensive and are not readily available to researchers in this region. Furthermore, there is a huge gap in our understanding of the microplastic fate and possible toxicological risk impacts (Alimi et al., 2020; Pereao et al., 2020). At present, although there is no reason to be an alarmist about the human health effects, more research is needed to establish microplastic hazards to humans (Picó and Barceló, 2019). However, recent findings of microplastics in drinking water have raised concern on human exposure to these particles. Furthermore, there is also a need to investigate and determine microplastic effects on freshwater organisms, especially economically important species consumed by the human population.

Action-orientated strategies to mitigate the microplastic problem should be identified and implemented, through changing the human perceptions towards microplastic pollution (Nel and Froneman, 2015). Governments are currently dealing with the microplastics problem in different ways and we hope to see in the next coming years more measures on pollution prevention, like restricted use of plastic materials such as bags, bottles, and cutlery. The government at all levels should encourage research to enhance knowledge acquisition on plastic pollution in the freshwater environment, as this will, in turn, assist the government in policy formulation and regulation of plastic pollution in the environment (Alimi et al., 2020). Thus, these legislative decisions need to be supported by the development of smarter and more recyclable plastics materials, making recycling processes more efficient, and tracing and removing microplastics through advanced wastewater treatments. Furthermore, continuous dissemination of information to the public in general from governments, nongovernmental organizations, and scientists is needed to reduce plastic use

(Picó and Barceló, 2019). Based on the principle that you can improve only what you can measure, metrics and indicators should be developed to set targets and monitor progress; and this should include integration in target settings frameworks and policies (e.g., Sustainable Development Goals) (Boucher and Friot, 2017).

It is important to note that once microplastics enter freshwater systems there are extremely difficult to remove as their presence at regional scales is governed by water circulation. Thus, future studies are needed to elucidate the role of large- and meso-scale limnological features in the distribution of microplastics within the tropical freshwater environment. This is a major cause for concern as the ill management of waste in localized areas has a global effect (Nel et al., 2017). We believe that further exploration and gap analysis are of great importance for determining priorities in implementing solutions and developing new approaches important in the future (Picó and Barceló, 2019). However, there is still little knowledge on the effect in different species as well as the effects of several types of plastics with different chemical compositions and different forms.

20.2 Conclusion

Emerging pollutants are usually found in freshwater in trace concentrations. They, however, have the potential of adversely affecting the environment at these trace levels. Thus, sample preconcentration is imperative during their analysis to enable their detection using simple analytical instruments. During their preconcentration, concerted efforts should be directed towards the replacement of toxic organic solvents with green alternatives such as deep eutectic solvents and bio-solvents. This would result in the minimization of secondary pollution of the environment during the preconcentration of these emerging pollutants. In addition, the conventional, environmentally unfriendly sorbents used during sorptive extraction of emerging sorbents in freshwater should be replaced with green biological polymeric sorbents such as polydopamine-based sorbents and bio-metal organic frameworks. In the same vein, the level of sophistication of analytical instruments for emerging pollutants in fresh water should be reduced to enable their quick detection even by less experienced researchers. The cumbersome and sophisticated chromatographic instruments should be replaced with portable electrochemical sensors that can enable on-site detection of emerging pollutants in freshwater (see Ajayi et al., 2022, Chapter 18). Thus, research efforts should be directed to the development of effective but less sophisticated electrochemical sensors for emerging pollutants in freshwater.

The increase in the number of emerging pollutants in freshwater is largely a result of anthropogenic activities. For instance, the excessive use of plastic materials by humans has caused an exponential increase in the number of microplastics in freshwater. Thus, there is a need to scale down the use of plastic materials, in a bid to save the environment and replace them with green alternatives such as polylactic acid. Polylactic acid is a biodegradable polyester that can be used as a food packaging alternative to plastics. Some emerging pollutants such as pesticides and pharmaceuticals are manufactured, as already alluded to, as racemates. Usually, one enantiomer in the racemic mixture will be bioactive while the other ones will be discharged into the environment where they cause toxicity to nontarget organisms. To mitigate pollution of the environment by the inactive enantiomers of chiral pesticides and pharmaceuticals, great advocacy should be directed towards the manufacture of enantiopure formulations of these chemicals. This can be coupled with stepping-up research in slow-release techniques, such as encapsulation, of pesticides and pharmaceuticals after their application. This will go a long way in keeping their concentrations in the environment within maximum allowable limits.

Developing countries, due to limited resources, usually get processed data on bio-monitoring emerging pollutants in fresh water from the western world. This overreliance on the western world usually makes the developing countries to be recipients of scientific data that may be irrelevant to their peculiar situations. It is, therefore, mandatory that developing countries should step up efforts to monitor emerging pollutants in fresh water by way of equipping learning and research institutions with state-of-the-art analytical instruments. This would facilitate the rapid risk assessment of these emerging pollutants in the environment. It is through such commitments that the developing countries would get relevant and unbiased scientific data pertaining to emerging pollutants in freshwater.

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Appendix

TABLE A1 Passive sampler (configurations) reported in the literature for quantitative assessment of chemical pollutants in water (Vrana et al., 2005; Seethapathy et al., 2008).

Passive sampler name	Receiving phase	Membrane type	Operating region	Target analytes	Deployment duration	References
Passive samplers designed for polar and moderately polar pollutants						
Chemcatcher©	Immobilized chelating acceptor resin coated on PFTE Housing—containing C18 or SDB RPS Empore disks	Cellulose acetate, polyether sulfone, polyethylene	Kinetic, Equilibrium	Polar and nonpolar organic chemicals, some POPs, organochlorine pesticides, PCBs, PAHs	14 days—1 month (several days if the membrane is not employed)	Kingston et al. (2000), Vrana et al. (2006)
Dosimeter (DiGiano et al. Sampler)	Activated carbon	Diffusion through holes drilled into polyacrylate	Kinetic	Atrazine	<1 month	DiGiano et al. (1988)
Polar organic chemical integrative sampler (POCIS)	Pharmaceuticals: 200 mg of Oasis HLB. Herbicides: 80 mg solute ENV+ and 20 mg Biobeads S-X3 with 100 mg Ambersorb 1500	Polyether sulfone membrane (130 μm thick, 47 mm diameter, 0.1 μm pore size)	Kinetic	Polar organic chemicals (pesticide, pharmaceuticals, sulfa drugs, alkylphenols, EDCs)	<1 month	Jones-Lepp et al. (2004); Alvarez et al. (2004)
Gradient time integrative passive sampler (G-TIPS)	Nylon cylinder (7.5 cm) filled with water (300 mL)	Polyethylene diffusion membrane (5 mm thickness, 35% porosity, 2.5 μm pore size)	Kinetic	Very hydrophilic chemicals, illicit drugs, pharmaceuticals	<1 month	Verhagen et al. (2020)
MPT (Microporous Polyethylene Tubes)	Microporous polyethylene tubes (2 mm thick, Area 17.6 cm^2, 35% porosity, 2.5 μm pore size) filled with sorbents		Kinetic	Polar organic pollutants, pesticides, pharmaceuticals, illicit drugs, PFAS	<9 months	Mckay et al. (2020); Fauvelle et al. (2017)
Organic diffusion gradient in thin film (o-DGT)	Teflon housing with a surface area of 3.1 cm^2 containing gel diffusive gel embedded with XAD-18 or HLB sorbents	Agarose or polyacrylamide gel as diffusive media with the embedded sorbent, sometimes covered by a nylon or polyether sulfone membrane	Kinetic	Organic compounds (pesticides, pharmaceuticals, hormones, endocrine disrupting chemicals, household, and personal care products), selected PFAS	<14 days	Guibal et al. (2017); Challis et al. (2016); Wang et al. (2020)
Regenerated cellulose dialysis membrane	Deionized water	Cellulose dialysis membrane (18 Å pore size)	Equilibrium	Organic, inorganic chemicals	1 month	Ehlke et al. (2004)
Solvent filled dialysis membrane sampler	Hexane or heptane	Dialysis membrane	Kinetic	Lipophilic chemicals	1 month	Soedergren (1987)
De Jonge and Rothenberg	A water-permeable porous sampler		Flux-proportional sampling in groundwater	Range of organic chemicals	1 month	De Jonge and Rothenberg (2005)
Trimethylpentane containing passive sampler (TRIMPS)	2,2,3-Trimethyl pentane	Polyethylene membrane	Kinetic	Pesticides	1 month	Leonard et al. (2002)

Zhang and Hardy sampler	XAD-7, Tenax	Polycarbonate	Kinetic	Phenolic chemicals	Up to 1 day	Zhang and Hardy (1989)
Lee and Hardy sampler	Adsorbent receiving phase	Silicone polycarbonate permeation membrane	Integrative	Chlorobenzenes, nitrobenzenes, and nitrotoluenes	Up to 1 day	Lee and Hardy (1999)
Ceramic dosimeter	Various—ion exchange resin, Tenax	Diffusion through porous ceramic membrane	Kinetic	PAHs, volatile aromatic chemicals, chlorinated hydrocarbons, alkyl naphthalenes, BTEX	<2 months—1 year in groundwater	Bopp et al. (2005); Martin et al. (2003); DiGiano et al. (1988)
Gore-sorber sampler	Various sorbents depending on analyte	Gore-tex membrane (PTFE)	Kinetic	BTEX, MTBE, PAHs, VOCs, SVOCs	Approx. 14 days	Mehltretter and Sorge (1995); Kless (1995)
Kot et al. sampler	Hexane or iso-octane	Polypropylene or PTFE	Kinetic, Equilibrium	Phenols, acid herbicides, triazines	1 month	Kot et al. (2000)
Lee and Hardy passive sampler	Porapak-Q and Tenax-TA	Silicone polycarbonate	Kinetic	Chlorobenzenes, nitrobenzenes, nitrotoluenes	>1 day	Lee and Hardy (1999)
Passive samplers designed for moderately polar to non-polar pollutants						
Low density polyethylene (LDPE) and silicone strips	Low density polyethylene	None	Integrative	Hydrophobic chemicals including PAHs, PCBs, petroleum hydrocarbons, organochlorine pesticides	<1 month	Rusina et al. (2007)
MESCO sampler (membrane enclosed sorptive coating)	PDMS (coated on stir bar	Cellulose or low density, polyethylene	Kinetic	PAHs, PCBs, and organochlorine pesticides, selected POPs	2 weeks	Paschke et al. (2006)
Passive in situ concentration extraction sampler (PISCES)	Hexane or iso-octane	Low density polyethylene	Kinetic	PCBs	Approx. 2 weeks	Litten et al. (1993)
Polydimethylsiloxane (PDMS)	Silicone rubber		Kinetic/ Equilibrium	PAHs, PCBs and organochlorine pesticides, other POPs	1 to several months	O'Brien et al. (2012)
Polyethylene diffusion bag (PDB)	Deionized water	Low density polyethylene	Equilibrium	VOCs, metals, trace elements	Approx. 2 weeks	Vroblesky and Hyde (1997)
Semipermeable membrane device (SPMD)	Triolein	Low density polyethylene (silicone, polypropylene, and polyvinyl chloride)	Equilibrium. Linear/ nonlinear	PAHs, PCBs, organotin chemicals	Hours - days	Huckins et al. (2002); Huckins et al. (2006)

Continued

TABLE A1 Passive sampler (configurations) reported in the literature for quantitative assessment of chemical pollutants in water (Vrana et al., 2005; Seethapathy et al., 2008)—cont'd

Passive sampler name	Receiving phase	Membrane type	Operating region	Target analytes	Deployment duration	References
Solid phase microextraction (SPME)	Various sorbents coated on the SPME fiber	None	Kinetic, Equilibrium	Hydrophobic chemicals including PAHs, PCBs, petroleum hydrocarbons, organochlorine pesticides, aniline, phenols, algal cells	Hours - days	Chen and Pawliszyn (1995); Ouyang and Pawliszyn (2008)
Thin-layer chromatography plate (TLC)		No membrane		Organophosphates	>1 month	Leblanc et al. (2003)
Passive samplers designed for metals, nutrients, and algal toxins						
Diffusion gradient in thin film (DGT)	Metal binding resin incorporated into acrylamide gel	Acrylamide gel	Kinetic	Metals (Cd, Ni, Pb, Ca, Mg, Zn, Mn)	1 week	Davison and Zhang (2012); Tusseau-Vuillemin et al. (2003); Teasdale et al. (1999)
Nylon screen passive diffusion sampler	Deionized water	Nylon screen (125 μm pore size)	Equilibrium	Organic and inorganic chemicals	3 months	Team (2006)
Permeation liquid membrane (PLM) sampler	1,2-Cyclohexylene-aminotetraacetic acid (CDTA) or pyrophosphate solution	1,10-Didecyldiaza-18-crown-6 (22DD) and lauric acid (1:1) ratio in 1:1 (v/v) toluene/phenylhexane	Kinetic	Cu, Pb, Ni	Several hours	Slaveykova et al. (2004); Domingos et al. (2007)
Solid phase adsorption toxin tracking (SPATT) bags	Porous hydrated adsorption resin	Polyester mesh (95 μm)	Kinetic	Biotoxins, microalgal bloom components	1 week	Mackenzie et al. (2004)
Stabilized liquid membrane device (SLMD)	Solution of acidic compounds like oleic acid	Low density polyethylene lay-flat tube	Kinetic	Doubly charged metal ions	Days - weeks	Brumbaugh et al. (2002)

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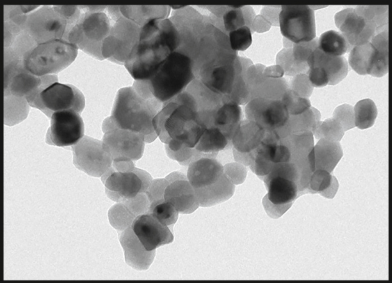

EMERGING FRESHWATER POLLUTANTS

ANALYSIS, FATE, AND REGULATIONS

Edited by **Tatenda Dalu and Nikita T. Tavengwa**

Emerging Freshwater Pollutants: Analysis, Fate, and Regulations comprises 20 chapters, all of which are written by leading experts. The book is written in the most practical terms and is easy to comprehend, with numerous helpful examples and case studies. The book is meant to be used as a practical guide and serves as an important educational tool to address issues concerning freshwater emerging pollutants. The book is organized in a way that exposes the reader in logical succession to the full range of complex scientific and management aspects of emerging freshwater pollutants in the developing world. The book recognizes that water chemistry, emerging freshwater pollutants, and management are interdependent disciplines. The book covers (i) the various monitoring techniques, current analytical approaches, and instrumental analyses; (ii) fate and occurrence of emerging pollutants in aquatic systems; and (iii) management policies and legislations on emerging pollutants. Thus, subsequent chapters elucidate chemicals with pollution potential, multi-detection approaches to the analysis of organic pollutants in water, the effects of microplastics, and photochemical transformation of emerging pollutants in freshwater systems. Whereas other chapters address the oxidation of organic compounds in aquatic systems, biomonitoring systems for the detection of toxic levels of water pollutants, and the health aspects of water recycling practices.

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About the Editors

Dr. Tatenda Dalu is Lecturer in the School of Biology and Environmental Sciences at the University of Mpumalanga, South Africa, and Research Associate at the South African Institute for Aquatic Biodiversity.

Dr. Nikita T. Tavengwa is Senior Lecturer in the Department of Chemistry at the University of Venda, South Africa.

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