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PART I

Monitoring techniques, current analytical approaches, and instrumental analyses

CHAPTER

1

c0145

Introduction to emerging freshwater pollutants

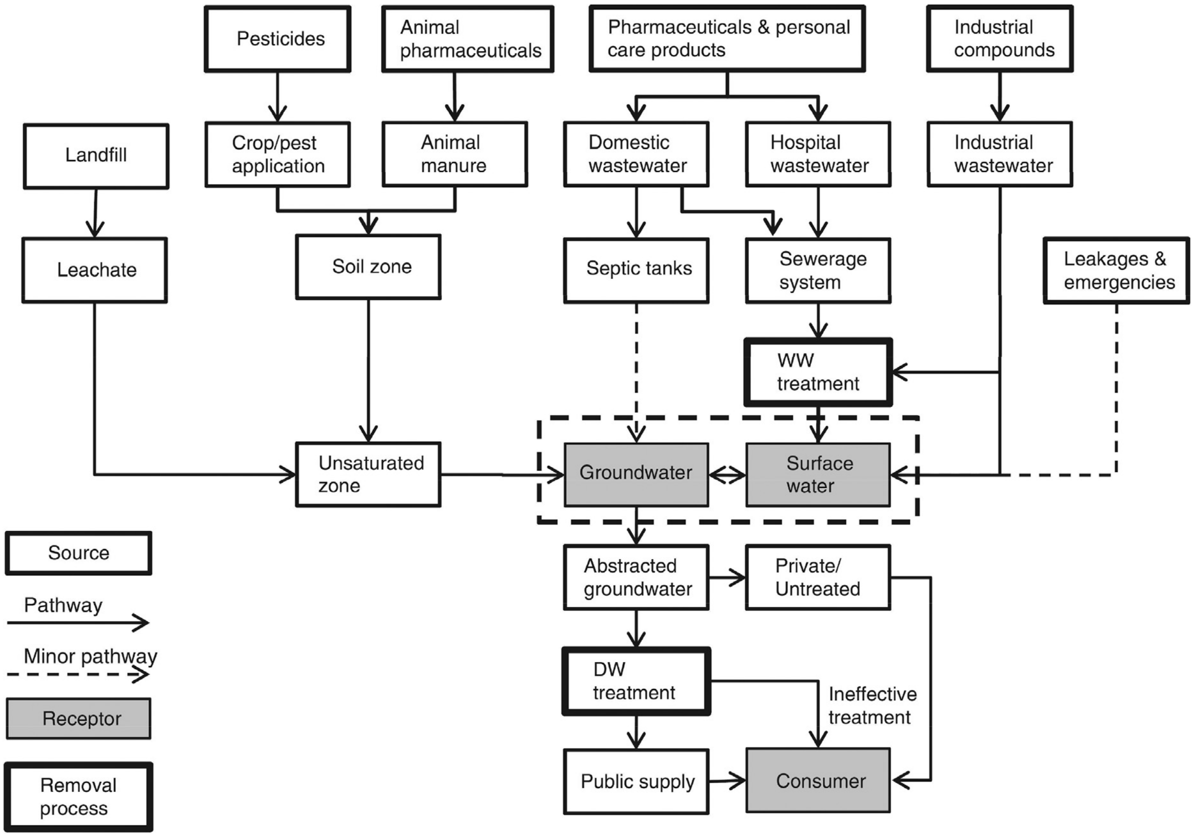
Nikita T Tavengwa and Tatenda Dalu Q4

1.1 Introduction s0010

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., 2021, Chapter 10), pesticides (Montagner et al., 2021, Chapter 12), industrial and household products (De Caroli Vizioli et al., 2021, Chapter 14), metals (Galhardi et al., 2021, Chapter 17), surfactants, industrial additives, and solvents (Cristale, 2021, Chapter 16; Hashemi and Kaykhaii, 2021, 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). p0010 Q5 Q6

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, 2021). 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., 2021; Sanganyando and Kajau, 2021, 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., 2021), 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., 2021, Chapter 9), pharmaceuticals and personal care products (Madikizela et al., 2021, Chapter 10), antibiotics (Ntshani and Tavengwa, 2021, Chapter 11), pesticides (Montagner et al., 2021), antiretrovirals p0015 Q7 Q8

https://doi.org/10.1016/B978-0-12-822850-0.00029-6



Q1 f0010 FIG. 1.1 Sources and pathways for emerging pollutants to reach various receptors *(in gray). Adapted from 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., 2021, Chapter 13), disinfection by-products (De Caroli Vizioli et al., 2021), azo dyes (Hashemi and Kaykhaii, 2021), flame retardants (Cristale, 2021), rare earth elements and radionuclides (Galhardi et al., 2021) and nanoparticles (Ajayi et al., 2021, 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. p0020

1.2 The fate of emerging pollutants in aquatic systems s0015

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 p0025 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, 2021). 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 s0020

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, 2021, 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. (2021, Chapter 8). Maximum allowable limits by international regulatory bodies and domestically the respective countries where these WWTPs are based are also presented. p0030

1.4 Monitoring techniques s0025

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. (2021, Chapter 2) and Kaserzon et al. (2021, 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. (2021). 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. p0035 Q9

1.5 Laboratory sample pretreatment s0030

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 p0040 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 s0035

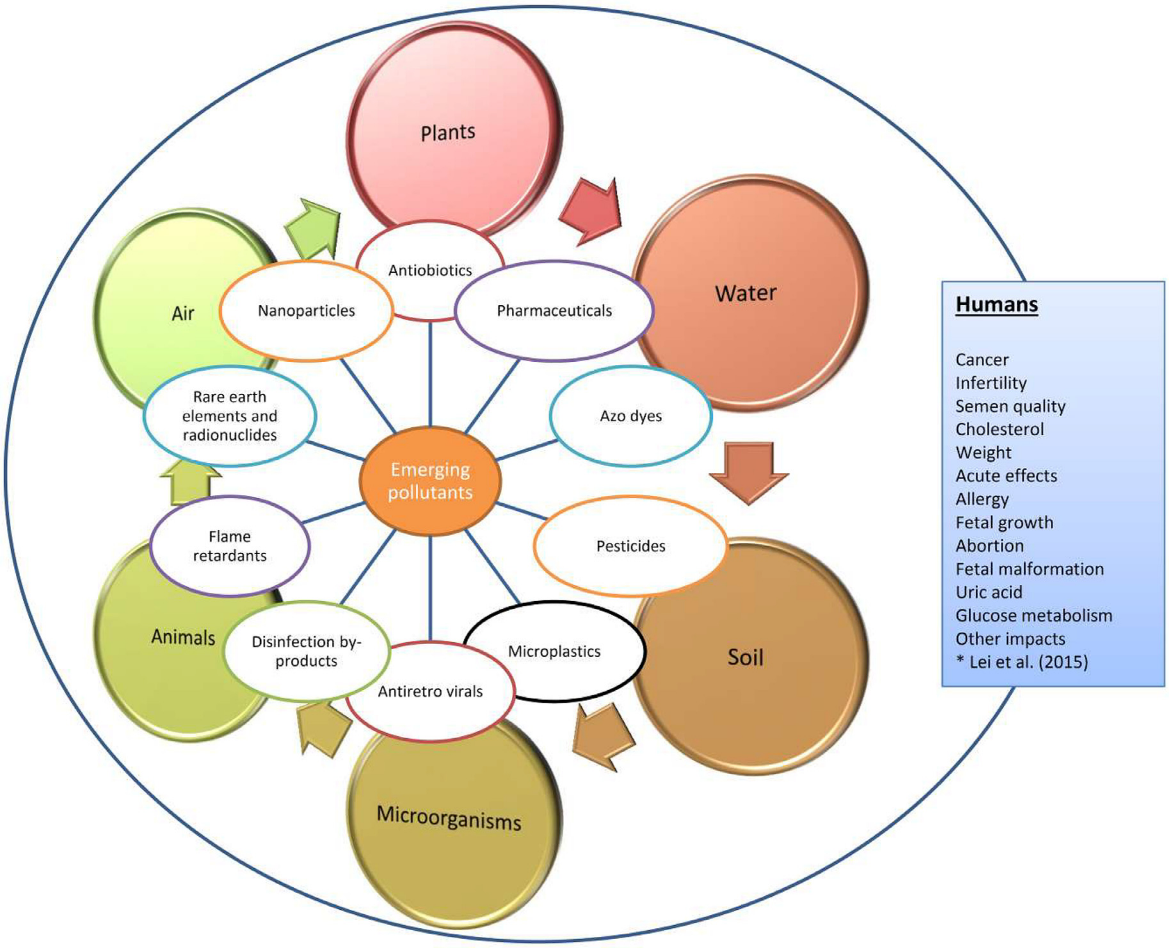
Liquid-liquid extraction and solid-phase extraction are some of the traditional techniques used for isolation and p0045 achieving the preconcentration of analytes in the environment. Besides their effectiveness in the extraction of antibiotics, these techniques are associated with some setbacks such 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 (2021, Chapter 4), Kebede et al. (2021, Chapter 5), and Kumar et al. (2021, 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 (2021), these miniaturization techniques have more advantages over conventional extraction techniques.

1.7 Management policies and legislations on emerging pollutants s0040

There is a need to have policies and intervention methods to control these emerging pollutants. The need to p0050 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 s0045

Some of the challenges posed by emerging pollutants are very diverse not only to freshwater environments but p0055 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. (2021, 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).



Q2 f0015 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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Non-Print Items

Abstract

There is a scarce of qualitative and quantitative information regarding the status of emerging pollutants in aquatic bodies within the developing world. Few pieces of literature are available from Africa and South America on emerging pollutants, with countries such as South Africa and Brazil leading the way in terms of research, leaving the rest of the developing world countries with little or no information on their distribution and fate in aquatic environments. This may be because of the lack of instruments and skilled personnel to carry out this research as these emerging pollutants occur in trace amounts. However, the scattered information has been put together comprehensively in this book which will become a reference point to researchers and environmentalists within the developing world. Therefore, the book aims to primarily document what is known and learned on freshwater emerging pollutants from a developing world perspective. The information on the concentration of emerging pollutants is a very important step towards remedial action (removal techniques). In this book, the most toxic and common emerging pollutants are treated separately as chapters, vis a vis, pharmaceutical and personal care products (PPCPs), pesticides, antiretrovirals (ARVs), microplastics and trace inorganic analytes. This book comprises 20 chapters (including this one), divided into three parts that examine (i) 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 which covers challenges and the future directions. This book will allow readers to better understand emerging freshwater pollutants in the developing world, and thereby assist them in responding to the challenge of addressing the problem.

Keywords: Emerging pollutants, Trace analysis, Azo dyes, Microplastics, Diatoms, Water management, Sampling techniques