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C H A P T E R

20

c0080 Challenges and future directions in the analysis of emerging pollutants in aqueous environments

Nikita T Tavengwa, Babra Moyo, Herbert Musarurwa, and Tatenda Dalu

Q1

20.1 Challenges and future directions

s0010

20.1.1 Dearth of information

s0015

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. p0010

20.1.2 Low concentrations and matrix effects

s0020

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, 2021, Chapter 1](#)). Though they may occur in trace amounts, they might be unexpected of high toxicity as well (see [Sanganyando and Kajau, 2021, Chapter 7](#); [Mashile et al., 2021, Chapter 8](#); [Yardy et al., 2021, Chapter 9](#); [Madikizela et al., 2021, Chapter 10](#); [Ntshani and Tavengwa, 2021, Chapter 11](#); [Montagner et al., 2021, Chapter 12](#); [Moodley et al., 2021, Chapter 13](#); [De Caroli Vizioli et al., 2021, Chapter 14](#); [Hashemi and Kaykhaii, 2021, Chapter 15](#); [Cristale, 2021a,b, Chapter 16](#); [Galhardi et al., 2021, Chapter 17](#)). Their occurrence in trace amounts might also pose a great analytical challenge in that they may not be detected by common analytical instruments because they might have concentrations of low limits of detection (see [Kaserzon et al., 2021, Chapter 3](#); [Kaykhaii and Hashemi, 2021, Chapter 4](#); [Kebede et al., 2021, Chapter 5](#); [Kumar et al., 2021, 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. p0015 Q4 Q5 Q6 Q7

20.1.3 Occurrence of pesticides as racemic mixtures

s0025

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 p0020

freshwater systems (see [Montagner et al., 2021, 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

s0030

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., 2021, Chapter 8](#)).

p0025

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., 2021, Chapter 8](#); [Sanganyado, 2021, 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](#)).

p0030

Even though some flame retardants have been banned in several countries, as pointed out by [Cristale \(2021a,b\)](#) in [Chapter 16](#), they are still being detected in the present day. [Cristale \(2021a,b\)](#) 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.

Q8

p0035

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.

p0040

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](#)).

p0045

20.1.5 Grab versus passive sampling

s0035

Most aquatic monitoring programs rely on collecting discrete grab, spot, or bottle samples of water at a given time (see [Kaserzon et al., 2021, 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

p0050

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

s0040

Dyes have a unique way of causing water impairment (see Hashemi and Kaykhaii, 2021, 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, 2021, 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).

p0055

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, 2021, 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.

p0060

20.1.7 Use of living organisms—Biomonitoring

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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. (2021, 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., 2021, 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.

p0065

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,

p0070

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. p0075

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). p0080

20.1.8 Analysis of physical emerging pollutants: Microplastics

s0050

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., 2021, 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., 2021, 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 inter-laboratory 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; Pereo 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. p0085

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 p0090

(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. p01095

20.2 Conclusion

s0055

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., 2021, Chapter 18). Thus, research efforts should be directed to the development of effective but less sophisticated electrochemical sensors for emerging pollutants in freshwater. p0100

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. p0105

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. p0110

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Non-Print Items

Abstract

New emerging analytes are always made and discharged into any of the environmental compartments, including freshwaters where they cause pollution. It has always been difficult to cope with a wide range of these emerging pollutants with different chemistries. Emerging contaminants have widely been detected in water bodies and there is a high possibility of them being ingested by aquatic animals. More so, most emerging pollutants end up in wastewater treatment plants where, unfortunately, they are released into the environment as these facilities are not designed to remove emerging pollutants. Discharge of emerging pollutants into freshwater bodies will not slow down in the foreseeable future as industrialization and urbanization continue. The animal and environmental health and effects of these emerging pollutants are not immediately known until the new emerging pollutants have been detected and quantified, which itself is a challenge to scientists as the physicochemical properties need to be established first. Even crucial regulatory parameters such as the maximum allowable limits are not immediately established for emerging pollutants. This concluding chapter aims to spell out more challenges that are faced regarding the handling and analysis of various emerging pollutants.

Keywords: Challenges, New pollutants, Environmental contamination, Trace analysis