Central University of Technology, Free State

The Investigation of Emerging Contaminants along the Modder River Catchment, Free State, South Africa

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BLOEMFONTEIN

July 2025

DECLARATION

I, Elias Katlego Mophosho, student number #########, declare that this research project submitted to the Central University of Technology, Free State, for the Master of Health and Environmental Sciences, is my own independent work; and complies with the Code of Academic Integrity, as well as other relevant policies, procedures, rules and regulations of the Central University of Technology, Free State; and has not been submitted before to any institution by myself or any other person in fulfilment (or partial fulfilment) of the requirements for the attainment of any qualification.

July 2025

Signature of the student Date

ABSTRACT

Today, human kind frequently employs a diverse range of synthetic organic compounds for household tasks, farming, industrial production, and the treatment of both human and animal health. The continuous manufacturing of new chemicals and their usages has now led to the type of pollutants recognised as emerging contaminants. Their accumulation in water sources has reduced water quality and made water risky for aquatic and human life. Consequently, this study was piloted with the aim of investigating emerging contaminants along the Modder River catchment in the Free State province. Samples were collected during the spring season using a grab sampling method from rivers (n = 5), dams (n = 5), tap water (n = 2), wastewater influent (n = 2) and wastewater effluent (n=2). The samples were analysed using high-performance liquid chromatography connected to a hybrid triple quadrupole ion trap mass spectrometer. Sources of emerging contaminants in the Modder River catchment were determined by multivariate statistical techniques, namely Pearson correlation and hierarchical cluster analysis. Among the targeted compounds in this study., namely 17-alpha-ethinylestradiol, ampicillin, atrazine, estradiol, ibuprofen, imidacloprid, lamivudine, progesterone, simazine, terbuthylazine, testosterone, and triclosan, 17-alpha-ethinylestradiol had the utmost mean values in rivers, dams, and tap water while lamivudine had the highest average concentrations in wastewater influent and effluents. The results of multivariate statistical analysis revealed that the occurrence of emerging contaminants in water sources around the Modder River catchment is associated with wastewater effluent discharge, illegal dumping, domestic sewage overflow, stormwater runoff and agricultural runoff. This study has revealed that the Modder River catchment is vulnerable to pollution by emerging contaminants as a result of man-made activities, which may adversely affect the aquatic ecosystem. The outcomes of this study may be helpful in protecting the aquatic environment. It is recommended that wastewater treatment managers develop and implement advanced treatment technologies for the removal of emerging contaminants in their plants to avoid further impairment of the Modder River catchment.

Keywords: emerging contaminants, source apportionment, Modder River catchment, Free State, wastewater treatment plants, rivers, dams, tap water

DEDICATION

I dedicate my dissertation work First to GOD who gave me strength and to my family and many friends who stood before me during the hardest times of producing this work. A special feeling of gratitude to my loving parent Emmah Matshipu Mophosho whose words of encouragement and push for tenacity ring in my ears. My brother Michael Aupaki Melato for being a great mentor in my academic life. I also dedicate this dissertation to my many friends and church families who have supported me throughout the process. I always appreciate all they have done, Thank you very much.

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LIST OF ABBREVIATIONS AND ACRONYMS

km	Kilometre
km^2	Square kilometre
ℓ	Litre
m	Metre
mg/ℓ	Milligram per litre
mℓ	Millilitre
m/z	Mass-to-charge ratio
ng/ℓ	Nanograms per litre
ppm	Parts per million
psi	Parts per square inch
µℓ	Microlitre
µg/ℓ	Micrograms per litre
DEET	N, N-diethyl-meta-toluamide
V	Voltage
%	Percentage
BPA	Bisphenol-A
EDCs	Endocrine disruptor compounds
GC	Gas chromatography
HPLC	High-performance liquid chromatography
LC	Liquid chromatography
LC–MS	Liquid chromatography–mass spectrometry
LC–MS/MS	Liquid chromatography–tandem mass spectrometry
<LOQ	Less than limit of quantification
MeOH	Methanol
MMM	Mangaung Metropolitan Municipality
MS	Mass spectrometry
PCPs	Personal care products
PPCPs	Pharmaceuticals and personal care products
WWTP	Wastewater Treatment Plant

CONTRIBUTION OF THE STUDY

One research output in the form of a journal article was published from this study (Chapter 2). Although the content of this dissertation chapter is the same as the published article, the article has been formatted and edited to present a single, continuous dissertation with the same style.

Published Article

Mophosho, E.K. and Oke, S.A. (2018). Research trends on endocrine disruptors compounds and personal care products as emerging contaminant in South African water systems. *International Journal of Energy, Environment and Economics*, 26(1), 13-29. http://hdl.handle.net/11462/2495

Chapter 1

INTRODUCTION

1.1 Research background

One of the most important resources for the survival of all life on Earth is fresh water. It is commonly known that human activity places a great deal of strain on water quality and that pollutants are finding their way into freshwater systems as a result (Archer et al., 2017a). Concern over artificial chemical pollutants that end up in our aquatic environment has recently been growing exponentially (Schoeman et al., 2017). Emerging contaminants pose a significant threat to human health and the environment, making them ubiquitous in environmental waters and are therefore a cause for concern (Riva et al., 2018). The term *emerging contaminants* refers to a class of environmental pollutants that have been associated with human health issues and ecological consequences since ancient times (Deblonde et al., 2011).

Miraji et al. (2016) discussed the history of emerging contaminants and how advances in science and technology have led to their discovery in water and aquatic environments. Since the 1970s, when emerging contaminants were discovered in the United States, Canada and Japan, the United States, China, and Germany have led the way in studies of emerging contaminants (Miraji et al., 2016). Many researchers reported that despite recent advancements and developments, Africa is still lagging behind in the study of emerging contaminants (Abafe et al., 2023; Archer et al., 2017; Ebele et al., 2017; Kanama et al., 2018; Miraji et al., 2016; Mugudamani et al., 2023; Oke et al., 2023; Sorensen et al., 2015). Nonetheless, countries like Tanzania, Zambia, and South Africa contributed to research on the number of newly identified pollutants in their water systems (Archer et al., 2017a; Kanama et al., 2018; Osunmakinde et al., 2013; Schoeman et al., 2017; Sorensen et al., 2015; Van Wyk et al., 2014).

The following categories of emerging contaminants have a negative impact on both the environment and human health: pharmaceuticals, personal care products (PCPs), artificial sweeteners, hormones, and illegal drugs. Because of their uncontrolled nature, these are recognised as a class of water contaminants in both surface and subsurface waters. Due to a lack of regulations and standards for environmental monitoring, these pollutants are emerging on a global scale (Madikizela and Chimuka, 2017; Miraji et al., 2016). The use of novel compounds in the fight against emerging diseases, the use of insect repellents containing N, N-diethyl-meta-toluamide (known as DEET), and societal demands for cosmetic products have led to the recent development of analytical technologies and the increased attention that these emerging contaminants are receiving.

Numerous emerging contaminant groups, including organic contaminants that negatively impact the endocrine systems of humans and wildlife, have been identified as significant water pollutants (Rodriguez-Narvaez et al., 2017). These micropollutants are thought to bioaccumulate in humans, micro invertebrates, and other aquatic food web organisms, making natural attenuation and conventional water treatment methods ineffective at eliminating them (Rodriguez-Narvaez et al., 2017). Out of the hundreds of pharmaceutical products that may have ended up in our water sources, only a small portion have been detected. Concerns about the possibility of oestrogenic and other harmful effects on humans have been raised by the small number of emerging contaminants discovered to be present in drinking water (Rodriguez-Narvaez et al., 2017; Zhang et al., 2015). The public is very concerned about the discovery of these new compounds in South African water sources, including drinking water, sewage treatment facilities, groundwater, surface water, and wastewater treatment facilities. This is especially true when no local and global guideline values based on human health are available (Archer et al., 2017a; Madikizela et al., 2017).

The extent to which the detected concentration of emerging contaminants impacts human health, remains to be determined. Due to their documented overuse (Becker and Stefanakis, 2016; Sangion and Gramatia, 2016), pharmaceuticals such as endocrine disruptor compounds (EDCs) and PCPs, are generally one of the most well-known groups of contaminants in surface water. However, little is known about their effects on aquatic life (Shaliutina-Kolesova et al., 2019). According to Shalutina-Kolesova et al. (2019), fluoxetine and antidepressants are common in aquatic environments, and their concentration can have an impact on the lives of aquatic macroinvertebrates.

The sources or introduction of these contaminants into water sources differ both in their numbers and nature. They can be categorised into two categories, point sources and non-point sources. Point sources can include excretion in human and animal urine and faeces, flushing of unused antibiotics, and house detergents. One of the major point sources of emerging contaminants is treated municipal and industrial wastewater at outflow of wastewater treatment plants (WWTPs) in urban, industrial and agricultural areas (Sangion-Kolesova et al., 2019). Non-point sources include stormwater runoff, urban areas and agricultural land. The use of pesticides is one example of a non-point source that is considered as a major agricultural contaminant (Becker and Stefanikis, 2016). Recently, research marked that the human infertility rate is gradually increasing, and reasons for the growing of infertility rate is hypothesised to the extent that it might be due to environmental contaminants that are spread throughout our environmental water and that human exposure is highly unavoidable (Ma et al., 2019). Therefore, this study aimed to investigate emerging contaminants in the Modder River catchment. It will also identify the possible sources of emerging contaminants in the Modder River catchment using multivariate statistical analysis. The outcomes of this study may be helpful in protection of the aquatic environment and public health as well as the sustainability of water resources along the Modder River catchment.

1.2 Problem statement

In Africa, there is an increasing use of synthetic organic compounds in the domestic context, within agriculture and industry, as well as the growing concern of exported toxic waste to Africa from richer countries (Sorensen et al., 2014). Due to anthropogenic activities, freshwater systems worldwide are confronted with thousands of compounds. The detection of many new compounds in water, groundwater and drinking water raises considerable public concern, especially when no human health-based guideline values are available, which calls to question whether detected concentrations affect human health (Heringa et al., 2009). According to Visca et al. (2021), the presence of emerging contaminants in water sources may cause acute or chronic effects such as carcinogenic, mutagenic and teratogenic effects. As a result of their continuous introduction into water sources, associated risks and lack of guideline values, there is a need for continuous monitoring of these contaminants. Therefore, the purpose of this study was to investigate the presence of emerging contaminants in rivers, dams, tap water and WWTPs along the Modder River catchment. The study also used multivariate statistical analysis to determine their possible sources and pathways.

1.3 Aim and objectives

The main aim of this study was to investigate the pollution of emerging contaminants along the Modder River catchment in South Africa. The aim of the study was achieved by setting the following specific objectives:

- To determine the extent of emerging contaminants within the Modder River catchment.
- To determine the source and pathways of emerging contaminants along the Modder River catchment.
- To recommend the possible mitigation measures for emerging contaminant pollution in the Modder River catchment.

1.4 Research questions

1. What is the extent of emerging contaminant pollution along the Modder River catchment?
2. What are the sources and pathways of emerging contaminants in the Modder River catchment?
3. What are the possible mitigation measures for emerging contaminant pollution in the Modder River catchment?

1.5 Research hypothesis

It is hypothesised that the Modder River catchment is vulnerable to emerging contaminant pollution.

1.6 Justification of the study

The existence of organic emerging contaminants in water sources at residual quantities ranging from nanograms to micrograms per litre can have detrimental impacts on aquatic animals and human health (Reyes et al., 2021), such as endocrine disruption, effects on red and white blood cells, as well as antibiotic and insomnia (Pei et al., 2022). Currently, both locally and internationally there was no formulated solutions to deal with the issues associated with the pollution of emerging contaminants (Wanda et al., 2017). Moreover, there are no based guideline values to protect the health of people (Heringa et al., 2009). Hence, it is very important to always conduct monitoring studies on emerging contaminant pollution to protect water resources and public health. The importance of this study cannot be ignored considering that most studies on emerging contaminant pollution in South Africa are concentrated in selected provinces such as the Western Cape (Archer et al., 2021; Ojemaye, 2020; Ojemaye et al. 2022), KwaZulu-Natal (Agunbiade and Moodley, 2016; Madikizela and Chimuka, 2017; Manickum and John, 2014; Matongo et al., 2015), the North West (Kanama et al., 2018, Wanda, et al., 2017), Gauteng (Madikizela et al., 2022; Van Zijl et al., 2017; Wanda et al., 2017), and the Eastern Cape (Vumazonke et al., 2020), with a scarcity of information in the Free State province. Investigating and determining the sources of emerging contaminants along the Modder River catchment will raise awareness on their concentration level and possible sources. This will help the relevant stakeholders in decision-making regarding pollution mitigation. The outcomes of this study will be important for the management and sustainability of the Modder River catchment.

1.7 Scope and limitation of the study

The study focused only on emerging contaminants identified from rivers, dams, tap water, as well as wastewater influent and effluent during the spring season. The occurrence of emerging contaminants in groundwater was not monitored. Moreover, the assessment of water quality based on physicochemical, hydro-chemical and microbiological parameters were not analysed in this study.

1.8 Structure of dissertation

Chapter 1: Introduction

It covers the background to the problem, problem statement, research questions, research hypotheses, aims and objectives, significance, as well as scope and limitations of the study.

Chapter 2: Literature review

It reviews the literature related to the occurrence of emerging contaminants in various water sources.

Chapter 3: Research methodology

Provides detailed information on methods adopted to answer the research questions of this study.

Chapter 4: Results and discussion

This chapter presents and discusses the results on the occurrence, sources and possible mitigation measures of emerging contaminants in water sources.

Chapter 5: Conclusion and recommendations

This chapter provides a conclusion on the findings of the study and the recommendations for future studies.

Chapter 2

LITERATURE REVIEW

Research trends on endocrine disruptors compounds and personal care products as emerging contaminant in South African water systems

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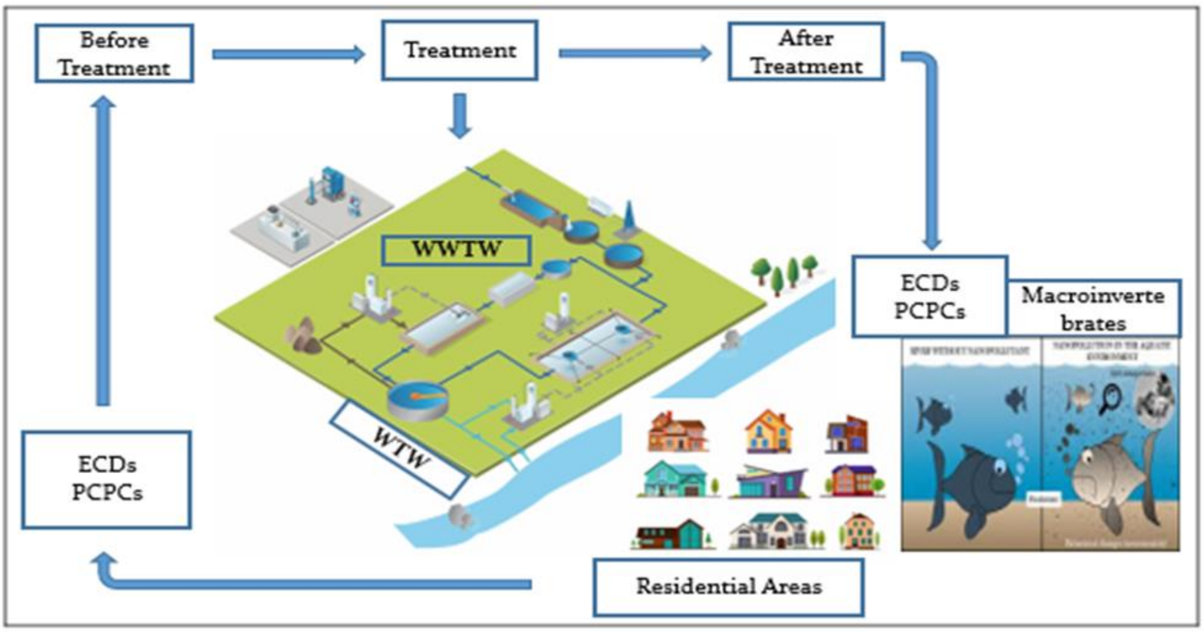
Graphical Abstract



Abstract

The presence of pharmaceuticals, herbicides, endocrine disruptors and personal care products have recently attracted the interest of researchers due to their concern with regards to a wide variety of human health risk arising from their prevalence in surface water resulting from inadequate waste water treatment processes. In this study, a recent trend in the fate and occurrence of personal care products such as triclosan, nitro, polycyclic, macrocyclic musk, surfactants, alkylphenols, ethylates, 4-nonylphenol carboxylates, octyl-phenol, and endocrine disrupting compounds such as 17B-estradiol, estriol, estrone, alkylphenols, bisphenol A, will be reviewed for South Africa. These compounds are found at WWTPs, domestic and industrial pathways, agricultural sources and surface waters of South Africa. Sample analysis includes extraction with a solid phase process of chemical compounds, with techniques such as liquid chromatography, gas chromatography, mass spectrometry and high-performance liquid chromatography. The identification and quantification of these emerging chemical compounds in surface water and wastewater has become a major scientific responsibility, which is currently lacking regulation in South Africa, especially when endocrine disruptors and personal care products have an adverse impact on pregnant women and human hormones.

Keywords: emerging contaminants, endocrine disrupting compounds, personal care products, environmental waters

2.1 Introduction

Fresh water is one of the essential resources for the support of all life on earth. It is well recognised that anthropogenic activities are creating a huge amount of pressure on water quality, and through such human activities, pollutants are entering fresh water systems (Archer et al., 2017a). There has recently been an exponentially growing concern regarding synthetic chemical pollutants that reach our aquatic environment (Schoeman et al., 2017). Emerging contaminants are pervasive in environmental waters and are raising a concern due to their potential risks on human health and the environment (Riva et al., 2018). Emerging contaminants are part of environmental pollutions which are linked to ancient times with the main focus on the regulated pollutants that impacted human health with antecedent ecological effects (Deblonde et al., 2011).

Miraji et al. (2016) pointed to the history of emerging contaminants since it was discovered in water and aquatic environments due to the improvement in science and technology. Since the discovery of emerging contaminants in the United States around the 1970s, leading countries in studies of emerging contaminants are Canada, Japan, the United States, China and Germany (Miraji et al., 2016). Africa is reported to lack behind in the study of emerging contaminants even though there have been recent improvements and developments (Archer et al., 2017b; Ebele et al., 2017; Kanama et al., 2018; Miraji et al., 2016; Sorensen et al., 2015). However, countries like South Africa, Tanzania and Zambia have contributed to studying the extent of emerging contaminants in their water systems (Archer et al., 2017a; Kanama et al., 2018; Osunmakinde et al., 2013; Schoeman et al., 2017; Sorensen et al., 2015; Van Wyk et al., 2014).

Types of emerging contaminants that have adverse effects on human health and the environment are antibiotics, pharmaceuticals, PCPs, hormones, artificial sweeteners and illicit drugs. These are recognised classes of water contaminants in surface water and underground water due to their unregulated state. Globally, these contaminants are known as emerging because they lacked standards and guidelines for their environmental monitoring (Madikizela and Chimuka, 2017; Miraji et al., 2016). The attention these emerging contaminants are receiving is due to recent development of analytical technologies and in the use of new compounds prevalent in fighting emerging diseases, insect repellent (DEET) and societal demands in cosmetic products.

The presences of a group of emerging contaminants have been documented as significant water pollutants, such as organic contaminants that have been having adverse effects on human and wildlife endocrine systems (Rodriguez-Narvaez et al., 2017). It is believed that natural attenuation and conventional water treatment processes are unable to remove these micropollutants which are reported to bioaccumulate in humans, micro-invertebrates and other organisms in the aquatic food web (Rodriguez-Narvaez et al., 2017). Only a small fraction of the hundreds of pharmaceutical products that have found their way into our water sources have been detected. The few emerging contaminants found to be present in drinking water has generated significant concerns regarding the risk of oestrogenic and other adverse effects on human beings (Rodriguez-Narvaez et al., 2017; Zhang et al., 2015). The detection of these new compounds in South Africa are found in sources such as surface water, groundwater, drinking water, sewage treatment works and WWTPs, which raises considerable public concern, especially when human health-based guidelines values are not available both globally and locally (Archer et al., 2017a; Madikizela et al., 2017).

It is still to be questioned if and how much of the emerging contaminant-detected concentrations affect human health. Generally, pharmaceuticals such as EDCs and PCPs make up some of the most familiar groups of contaminants in surface water due to their over-usage that has been documented (Becker and Stefanakis, 2016; Sangion and Gramatia, 2016) and little is known concerning their impact on aquatic life (Shaliutina-Kolesova et al., 2019). Fluoxetine and antidepressants are prevalent in the aquatic environment and a range of concentrations can result in alterations in the life of aquatic macroinvertebrates (Shaliutina-Kolesova, et al., 2019).

The advancement of suitable quantitative methods for the analysis of EDC and PCP contaminants in South African water is continuous with increasing attention aimed at analysis of water contaminants (Madikizela and Chimuka, 2017; Van Wyk et al., 2014). Liquid chromatographic procedures were used to investigate and determine emerging chemical compounds in surface water (Matongo et al., 2015), and both gas and high-performance liquid chromatography (HPLC) have been reported in the literature to analyse the emerging contaminants in South African water with the HPLC preferred method for non-volatile chemical compounds (Madikizela et al., 2014; Olaitan et al., 2014). Other methods used for analysis of EDCs and PCPs are the Liquid chromatography–tandem mass spectrometry (LC–MS/MS) (Olarinmoye et al., 2016). However, there is a need for the development of standardised analytical technologies that allows for EDCs, PCPs and other emerging contaminants in the identification and quantification of chemical compounds at very low concentrations in drinking water (Odendaal et al., 2015).

Emerging contaminant sources differ both in their numbers and nature. They can be categorised into two sources, mainly point sources and non-point sources. Point sources can include excretion in human and animal urine and faeces, flushing of un-used antibiotics and house detergents. One of the major point sources of emerging contaminants is treated municipal and industrial wastewater at outflow of WWTPs in urban, industrial and agricultural areas (Sangion-Kolesova et al., 2019). Non-point sources include stormwater runoff, urban areas and agricultural land. The use of pesticides is one example of a non-point source that is considered a major agricultural contaminant (Beekar and Stefanikis, 2016). Recently, research marked that the human infertility rate is gradually increasing, and reasons for the growing infertility rate is hypothesised to the extent that it might be due to environmental contaminants that are spread throughout our environmental water, and human exposure is highly unavoidable (Ma et al., 2019). Due to anthropogenic activities, freshwater systems worldwide, including in South Africa, are confronted with thousands of emerging contaminant compounds (Shricks et al., 2016).

2.2 Types of emerging contaminants

2.2.1 Endocrine disrupting compounds

The human endocrine system is the human system that is responsible for production of hormones in the body. In the 1990s, evidence has been collected that certain synthetic and natural chemicals in the environment can disturb the hormonal system (endocrines, e.g., testosterone) of exposed organisms by mimicking or blocking the action of hormones. The human endocrine system is comparable to that of fish; therefore, exposure to endocrine disrupting contaminants can also cause certain health risks to humans (Houtman, 2010). Types of EDCs are 17-beta estradiol, estriol, oestrone, alkylphenols, bisphenols A and alkylphenol ethoxylates. Figure 2.1 shows the chemical structures of some endocrine disruptor compounds.

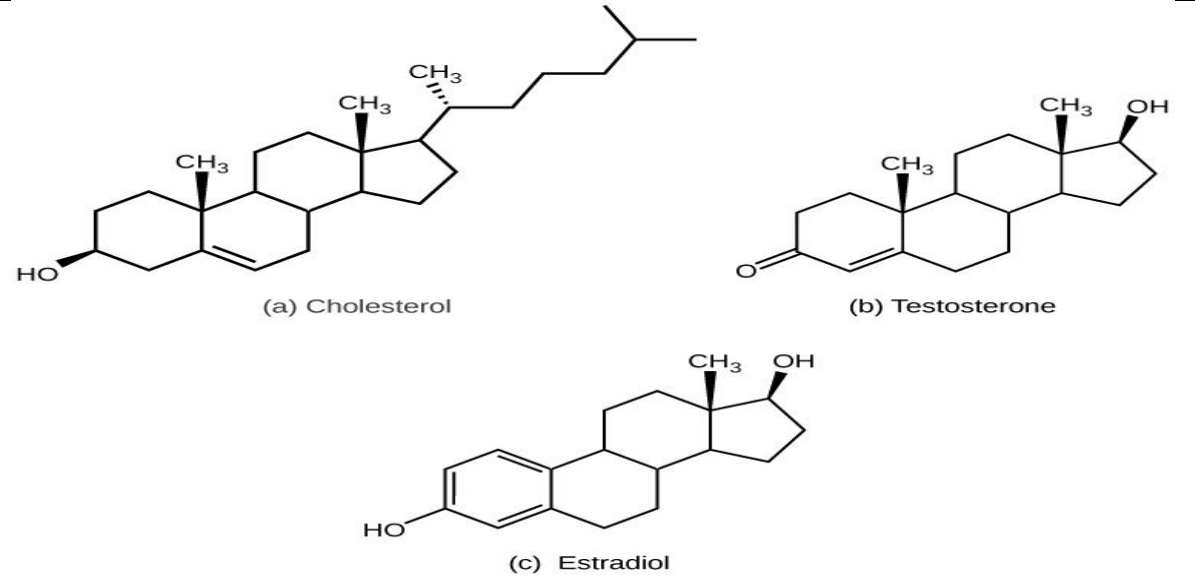


Figure 2.1 Chemical structures of endocrine disruptors *(Malnor and Gair, 2013)*

2.2.2 Pharmaceutical compounds

Pharmaceuticals are chemical compounds that are used for the diagnosis, treatment, or prevention of disease in humans and animals. Hundreds and thousands of different pharmaceuticals are currently used and distributed both in the public and private sector, antibiotics, anti-diabetics, beta-blockers, lipid regulators, antidepressants, anti-epileptics (Houtman, 2010). The study of pharmaceuticals and their metabolites in the environment has rapidly become a field of scientific research under environmental studies with rising interest (Agunbiade and Moodley, 2014). A variety of drugs are used for medicinal purposes and human health care globally, and diverse pharmaceuticals are used for veterinary science for animal treatment. About 3 000 pharmaceutical compounds are approved as medicinal products. The occurrence of pharmaceuticals in the environment also poses a threat both to the scientific community and the public (Agunbiade and Moodley, 2014). Figure 2.2 shows chemical structures of pharmaceutical compounds.

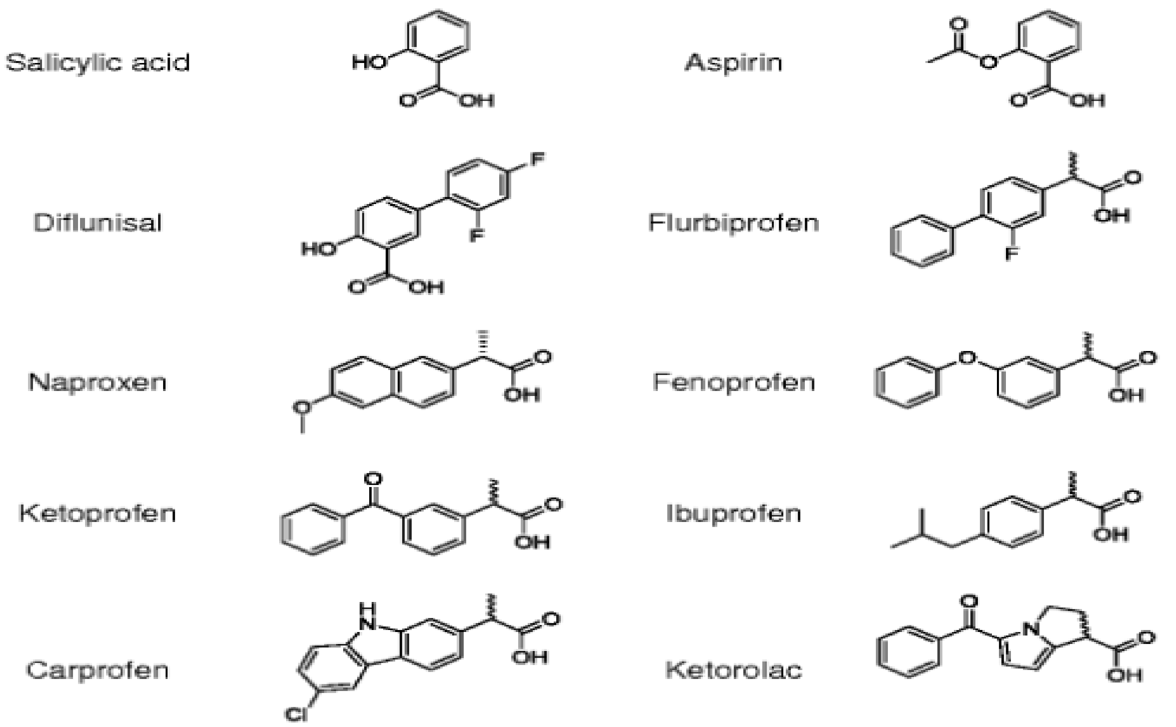


Figure 2.2 Chemical structures of pharmaceutical compounds *(Edink et al., 2011)*

2.2.3 Personal care products

PCPs are those products that are applied directly to the human body and are not ingested; such products consist of cosmetics, toiletries and fragrances. One of the group of PCPs used as fragrance is polycyclic musks, and the second group consists of preservatives such as parabens applied in shampoos, creams and body lotions. An emerging chemical contaminant known as Triclosan has been used for years in a wide variety of consumer products, for example toothpaste, bath soaps, and hand soaps (Houtman, 2010).

Some PCPs are a very unique category of micropollutants due to their special degradation characteristics. Some examples of this class of emerging contaminants are fragrances (nitro, polycyclic, macrocyclic musks), surfactants, alkylphenol and ethylates, 4-nonylphenol carboxylates, octylphenol ethoxy carboxylates. The European Union included some of them in the priority list of hazardous substances in the water policy (Vlachogianni and Valavanids, 2013). Some PCPs do not fall within cosmetic regulations and are constantly finding its way into the aquatic environment (Juliano and Magrini, 2017). Figure 2.3 shows the chemical structures of some PCPs.

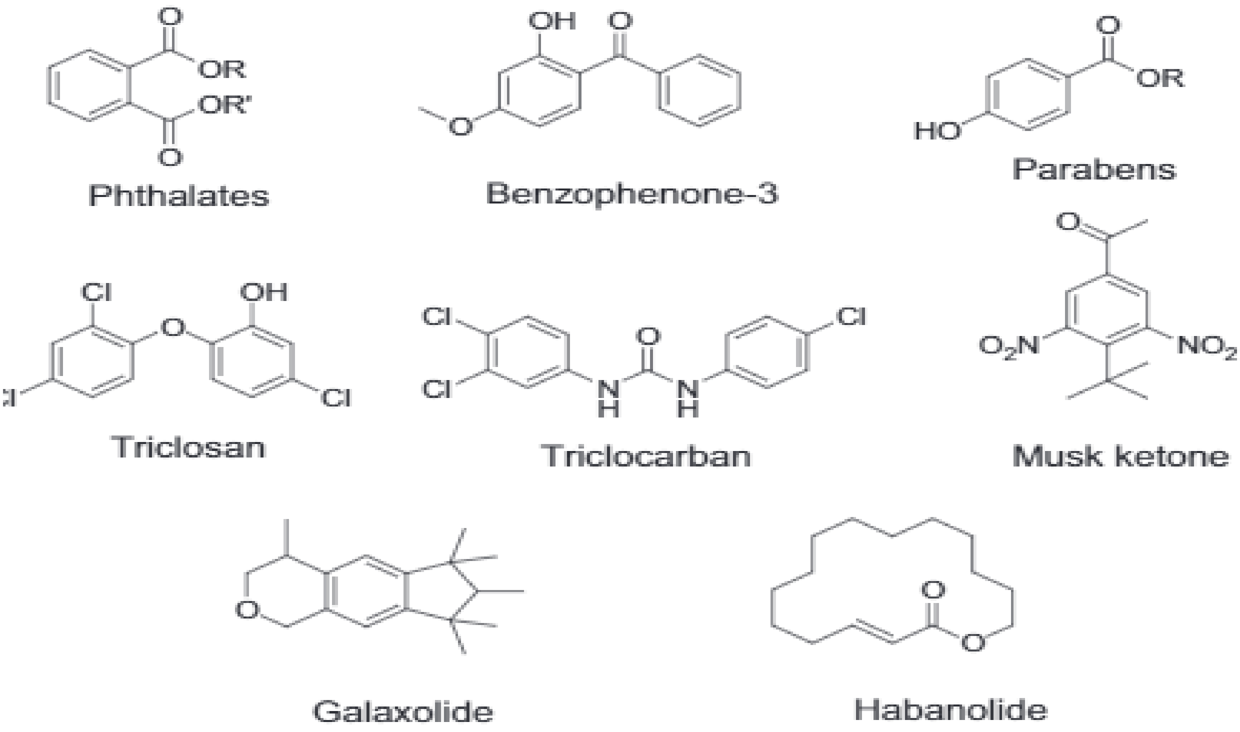


Figure 2.3 Chemical structures of personal care products *(Karthikraj and Kunnan, 2017)*

2.2.4 Pesticides and agricultural contaminants

Pesticides are products that are used merely in agriculture and crop production. They vary from herbicides, fungicides, insecticides and bactericides; they have also become a concern in surface water quality for years. Extensive use in agricultural practices and industrial emission during their production are important sources of pesticides and their residues in the aquatic environment. Currently a number of registered pesticide compounds, which include glyphosate, triazines, organophosphorus herbicides, thiocarbamates, and chlorophenyl acetic acids. These compounds, when applied in agricultural fields, contaminate the surface water by run-off, drainage and leaching (Houtman, 2010). Figure 2.4 shows the different classifications of pesticides by use that emanate as agricultural emerging contaminants.

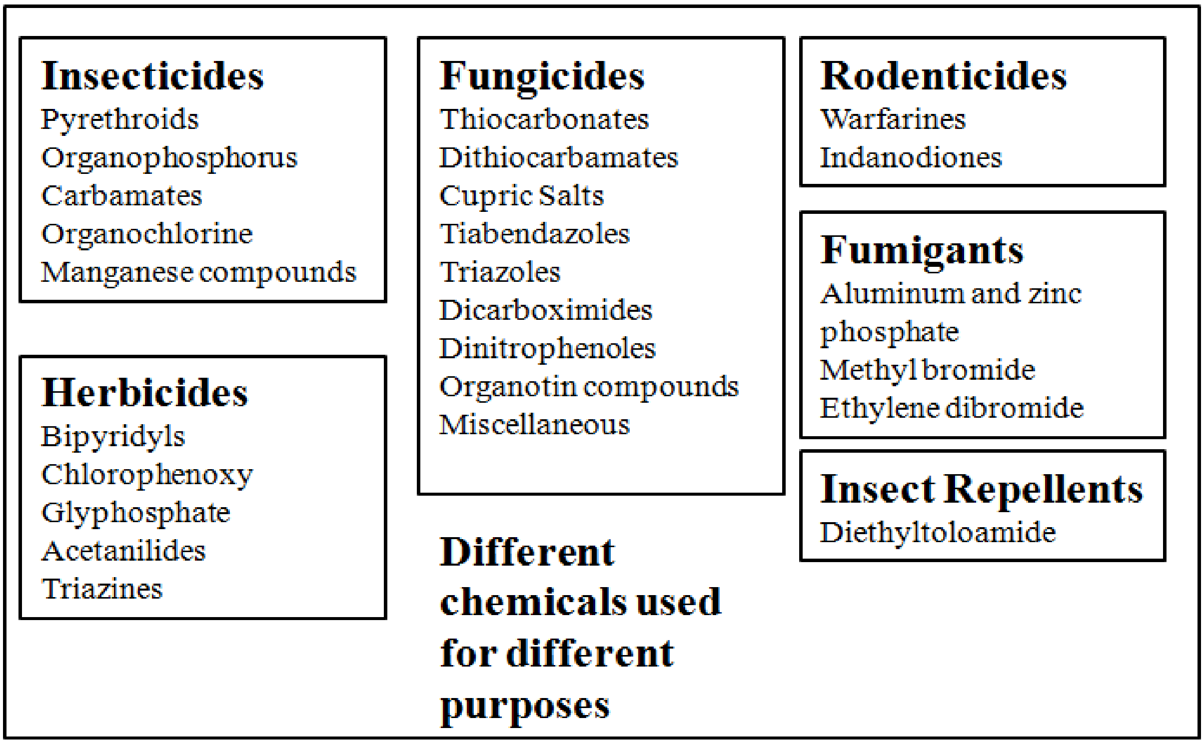


Figure 2.4 ***Different types of pesticides that emanate as agricultural emerging contaminants*** *(Adapted from World Health Organization, 2008)*

2.3 Sources and pathways of endocrine disruptor compounds and personal care products

Surface water is one of the largest water sources after oceans, and it emanates from rivers, lakes, canals, dams and streams, and these water sources serve as sources of drinking water for consumption by the public. Groundwater is generally of certain amounts of bacteriological concentrations with a slightly constant chemical quality, whereas surface water quality differs considerably due to anthropogenic upstream activities with a varying discharge volume and flow rate (Houtman, 2010). Emerging contaminants are brought in by human activities, which include agriculture, household use detergents, WWTPs, the industry and spillages. Wastewater (sewage water) is considered to be one of the most significant sources of PCPs in environmental water (Juliano and Magrini, 2017). Figure 2.5 shows sources and pathways of emerging contaminants that reach various receptors.

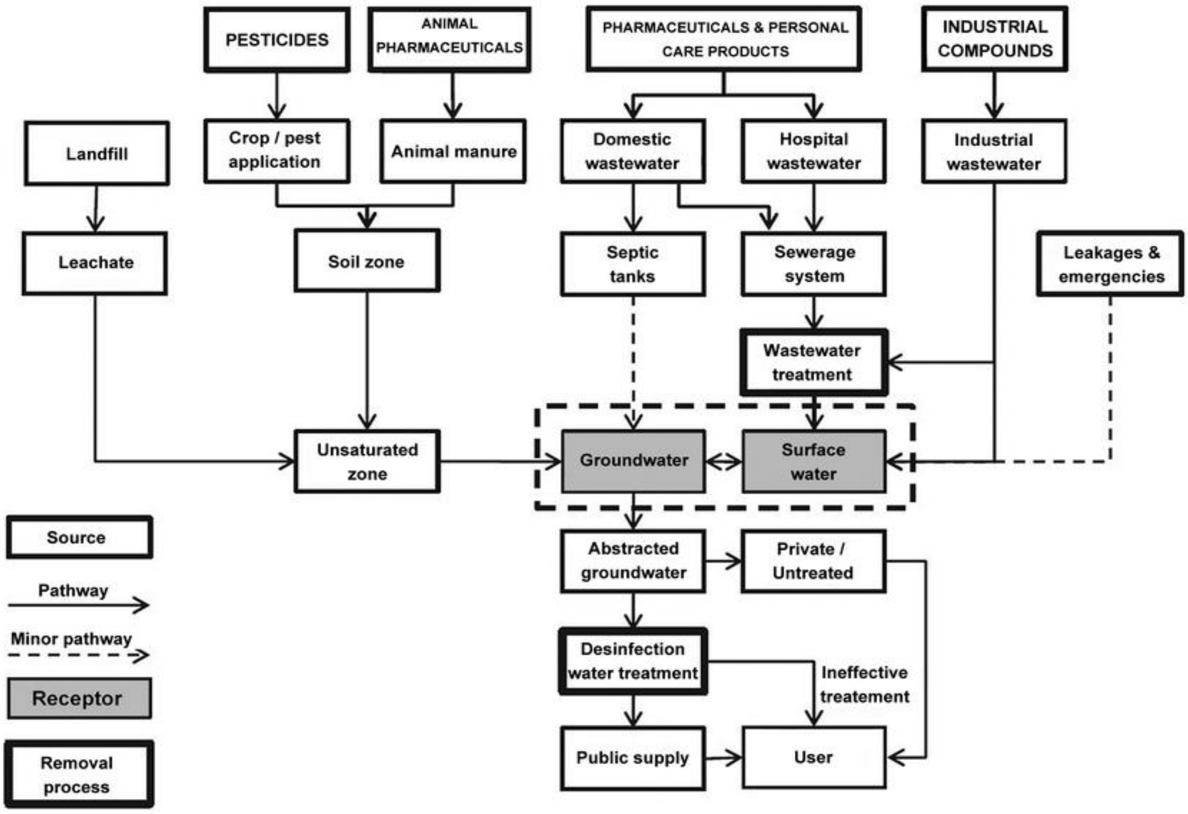


Figure 2.5 Sources and pathways for emerging contaminants that reach various receptors *(Stuart et al., 2012)*

2.3.1 Wastewater treatment plants

Huge amounts of emerging contaminants are persistent in surface water and they create pressure on the WWTPs for their detection and removal. A study conducted by Archer et al. (2017b) on WWTPs and environmental waters showed that eight emerging contaminants, classified as illicit drugs, were identified in wastewater influents (Archer et al., 2017a). Emerging contaminants have become a concern in WWTPs, and primary sources such as hospitals, funeral homes, residential houses and abattoirs (Shaver, 2011), that effectively contribute to the WWTPs, make emerging contaminants from WWTPs as a secondary source, as effluent that contaminate our surface water.

According to Gogoi et al. (2018), emerging contaminants such as endocrine disrupting compounds and PCPs have been present in surface water, groundwater, as well as in drinking water and in WWTP discharge. Municipal wastewater works are viewed as one of the discharge sources for the emanation of emerging contaminants such as non-point and point sources, industries and stormwater, wastewater from households and water treatment facilities into the environment (Gogoi et al., 2018). Many sources of pharmaceutical compounds are effluents from WWTPs. According to an article by Schoeman et al. (2017), concentrations of efavirenz, a pharmaceutical compound found in WWTPs, were ranging between 5 500 and 14 000 ng/ℓ. WWTPs have been studied in depth as one of the major sources of emerging organic contaminants, in particular municipal solid waste (Kapelewska et al., 2018). Numerous studies have demonstrated the presence of PCPs and EDCs in urban wastewater, excreted original or metabolised in sewage from hospitals and surface water. They have also been detected in groundwater and even in some drinking water (Deblonde et al., 2011).

2.3.2 Agricultural use

Agriculture is responsible for the spreading of contaminants of emerging concern from domestic and industrial sources where biosolids and manure are used as soil conditioners and fertilisers and wastewater for irrigation (Evans et al., 2019). Human exposure to pesticides can occur in the workplace, in the households and through the ambient environment. It was found that women with a history of working in the agricultural industry had an elevated risk of infertility. To determine the effect of pesticide exposure on reproductive health, agricultural workers in several different countries were evaluated. In a Canadian study, exposure to the phenoxy herbicides 2,4-dichlorophenoxyacetic acid (known as 2,4-D) was associated with spontaneous abortion. High exposure to organophosphate pesticides may be considered as an important cause of idiopathic preterm delivery in women (Dai et al., 2018).

2.3.3 Industrial and domestic sources and pathways

Over recent years, the manufacturing and widespread applications of synthetic chemical compounds have become crucial in industrial sectors. Significant interest, therefore, continues to grow in the treatment and remediation of these compounds, including endocrine disruptors, hormones, pharmaceuticals and synthetic textile dye pollutants, because these substances may cause disorders of the nervous, hormonal and reproductive system, thus posing adverse health outcomeS (Bilal et al., 2019). About 300 million tons of synthetic compounds annually used in industrial and consumer products, partially find their way to natural waters (Shricks et al., 2016).

In addition to their introduction through human use, pharmaceuticals are also used in livestock, poultry, and fish farming. A variety of drugs are commonly given to farm animals to reduce illnesses and diseases in these animals and also to increase the size of the animals. Despite the fact that approximately 3 000 substances are used in pharmaceutical ingredients, only a small fraction has been examined in the environment (Richardson and Kimura, 2017). The presence of pharmaceutical drugs and PCPs in the aquatic environment may pose potential threats to the ecosystem and human health; hence, PCPs have aroused much concern over the world (Sui et al., 2015). An increased number of PCPs have been detected in the South African aquatic environment in recent years (Walters, 2017). These synthetic organic products are found in Africa through domestic (pit latrines), agricultural and industrial sources (Sorensen et al., 2015).

2.4 South African studies on endocrine disruptor compounds and personal care products

South Africa is one of the developing countries in Africa with a population that is estimated at about 56.5 million people from its 2017 census results (StatsSA, 2017), with increased urbanisation. A study conducted by Kanama et al. (2018) in the North West province of South Africa showed a presence of triclosan, a personal care product compound with a precursor of 286 m/z and a product of 35:141.8, with a cone voltage of 22 V and energy collision of 11 eV. Endocrine disruptors were also studied in the North West, namely Estrone (E1) with a precursor of 269.2 m/z, products of 145.10; 143.05 cone voltage of 149 V and collision energy of 45 eV. 17β estradiol (β-E2) with a precursor of 271.2 m/z, product of 145; 10; 183.10, cone voltage of 14 V and energy collision of 47. Estriol (E3) has a precursor of 287 m/z and product of 143.05; 171.15, cone voltage of 15 V and energy collision of 43 eV. 17α-ethinylestradiol (EE2) has a precursor of 295.3 m/z, product of 145.05; 187, cone voltage of 11 V and collision energy of 47 eV.

A study conducted by Madikizela et al. (2014) in KwaZulu-Natal, South Africa, showed the presence of triclosan in three different sources, namely surface water at 0.4–0.9 ug/ℓ, WWTW influent at 2.1–9.0 ug/ℓ and WWTP effluent at 1.3–6.4 ug/ℓ. In Gauteng, South Africa, the presence of triclosan was also traced in WWTP influent at 78.4 ug/ℓ and WWTP effluent at 10.7 ug/ℓ. Steroidal hormones in a group of EDCs were studied across the South African environmental waters (see Table 2.1). Initially, detection of endocrine disruptor studies in South Africa was mainly steroidal hormones, particularly oestrogen, in water systems.

This is as a result of the usage of synthetic oestrogen contraceptives and hormone replacement therapy by a large number of South African populations (Archer et al., 2017a). However, it is well known in South Africa that PCPs and endocrine disruptors are accumulating in the water systems at the same rate as contraceptive medications. Table 2.1 shows a summary of endocrine disruptors and personal care products in South African water systems at different sources and locations.

2.5 Exposure and human health risk

Human exposure to environmental contaminants occurs through various routes, and are detected at low concentrations in drinking water, which raises considerable human health concerns. It acknowledged that environmental exposure to emerging chemical compounds are potential risk factors for infertility and pregnancy in women. Endocrine disrupting compounds interferes with the synthesis, secretions, and transport, metabolism and elimination processes of hormones in the human body that are responsible for reproduction (Ma et al., 2019). In a study that was conducted by Pualose et al. (2015), it was found that xenoestrogen bisphenol-A (BPA) an endocrine disruptor compound "increases the propensity to develop mammary cancer during adulthood, long after cessation of exposure". Exposure to BPA are associated with female infertility and affect the functions of the uterus and the ovaries as well as embryo implantation (Ma et al., 2019). Figure 2.6 shows BPA exposure of PCPs and EDCs to human organs.

Table 2.1 A review summary of endocrine disruptors and personal care products in South African surface waters

Name and group of emerging contaminants	Concentration in ug/ℓ	Location	Source	References
Endocrine disrupting compounds				
Oestrogen (E1)	0.001–0.03	KwaZulu-Natal	WWTW Downstream	Manickum and John, 2014
	0.01–0.02	Western Cape	STW Downstream	Swart et al., 2011
	0.009–0.011	Western Cape	STW Effluent	Swart and Pool, 2007
	0.01	Western Cape	STW Effluent	Swart and Pool, 2007
	0.003–0.02	KwaZulu-Natal	STW Effluent	Manickum et al., 2011
	0.01–0.35	KwaZulu-Natal	WWTW influent	Manickum and John, 2014
	0.003–0.08	KwaZulu-Natal	WWTW effluent	Manickum and John, 2014
	0.02–0.02	Western Cape	STW influent	Swart et al., 2011
	0.01–0.02	Western Cape	STW Downstream	Swart et al., 2011
	0.002–0.004	Gauteng	Drinking Water	Van Zijl et al., 2017
	0.0004–0.001	Western Cape	Drinking Water	Van Zijl et al., 2017
Estradiol (E2)	0.001–0.03	KwaZulu-Natal	WWTW Upstream	Manickum and John, 2014
	0.002–0.07	KwaZulu-Natal	WWTW Downstream	Manickum and John, 2014
	0.001	Western Cape	STW Effluent	Swart and Pool, 2007
	0.005	Western Cape	STW Effluent	Swart and Pool, 2007
	0.01–0.02	KwaZulu-Natal	STW Effluent	Manickum et al., 2011
	0.02–0.20	KwaZulu-Natal	WWTW influent	Manickum and John, 2014
	0.004–0.11	KwaZulu-Natal	WWTW effluent	Manickum and John, 2014
	0.001–0.03	Mpumalanga	Surface Water	Van Wyk et al., 2014
	0.04–0.37	Gauteng	Drinking Water	De Jager et al., 2013
	0.05–0.37	Western Cape	Drinking Water	De Jager et al., 2013
	0.00003	Gauteng	Drinking Water	Van Zijl et al., 2017
	0.00002	Western Cape	Drinking Water	Van Zijl et al., 2017
Ethynyl-estradiol (EE2)	0.003	KwaZulu-Natal	WWTW Upstream	Manickum and John, 2014
	0.001–0.004	KwaZulu-Natal	WWTW Downstream	Manickum and John, 2014
	0.01–0.095	KwaZulu-Natal	WWTW influent	Manickum and John, 2014
	0.001–0.008	KwaZulu-Natal	WWTW effluent	Manickum and John, 2014
	0.001–0.01	Mpumalanga	Surface Water	Van Wyk et al., 2014
	0.00002	Gauteng	Drinking Water	Van Zijl et al., 2017

Name and group of emerging contaminants	Concentration in ug/ℓ	Location	Source	References
Progesterone(P)	0.01	KwaZulu-Natal	WWTW Upstream	Manickum and John, 2014
	0.06	KwaZulu-Natal	WWTW Downstream	Manickum and John, 2014
	0.16–0.90	KwaZulu-Natal	WWTW influent	Manickum and John, 2014
	0.03	KwaZulu-Natal	WWTW effluent	Manickum and John, 2014
Testosterone (T)	0.005–0.02	KwaZulu-Natal	WWTW Upstream	Manickum and John, 2014
	0.003–0.02	KwaZulu-Natal	WWTW Downstream	Manickum and John, 2014
	0.12–0.64	KwaZulu-Natal	WWTW influent	Manickum and John, 2014
	0.03	KwaZulu-Natal	WWTW effluent	Manickum and John, 2014
Personal care products				
Triclosan	78.4	Gauteng	WWTW influent	Amdany et al., 2014
	10.7	Gauteng	WWTW effluent	Amdany et al., 2014
	127.7	Gauteng	WWTW influent	Amdany et al., 2014
	22.9	Gauteng	WWTW effluent	Amdany et al., 2014
	0.4–0.9	KwaZulu-Natal	Surface Water	Madikizela et al., 2014
	2.1–9.0	KwaZulu-Natal	WWTW influent	Madikizela et al., 2014
	1.3–6.4	KwaZulu-Natal	WWTW effluent	Madikizela et al., 2014
	35 m/z	North West	WWTW influent	Kanama et al., 2018

Note: STW = Sewage treatment works; WWTW = wastewater treatment works Adapted from Archer et al. (2017a); Kanama et al. (2018)

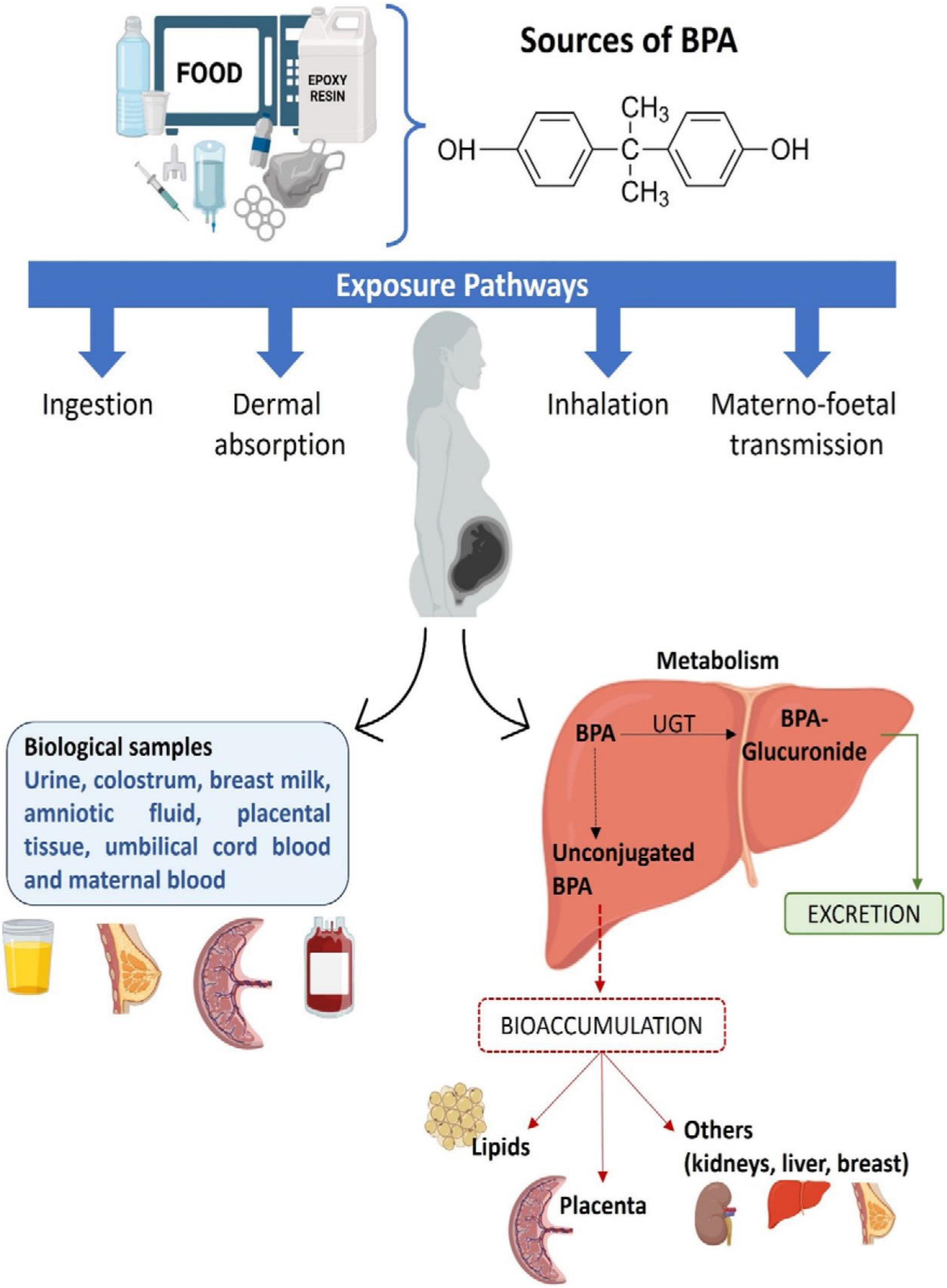


Figure 2.6 Human organs that are exposed to BPA, an endocrine disrupting compound (Henrique et al,2025)

2.6 Regulations on emerging contaminants

According to the Guideline for drinking-water quality (World Health Organisation, 2017) and the US Environmental Protection Agency (year), the levels of concern of emerging contaminants were below the maximum levels, but the range of emerging contaminants detected in drinking water requires a seasonal and more frequent screening programme (Odendaal et al., 2015). Many of the emerging contaminants elevate significant toxicological and public health concerns, particularly when no human health guideline values are available (Shricks et al., 2016). In addition, there has been a lack of publications to provide health standards and guidelines in treating emerging pollutants (Kapalewska et al., 2018).

Developing and enforcing regulations pertaining to pharmaceuticals and PCPs may be needed. A review has highlighted that critical information on interventions to improve the use of antibiotics and other pharmaceutical products is needed (Hindricks, 2012). It is well recognised that the existing South African water quality management policy was last dated in 1991 and resource directed management of water quality in 2006. While innovations are taking place, revision of the policy needs to be dealt with in order to align with current overarching policy and legislative frameworks (Department of Water and Sanitation, 2015). Currently, there are no guidelines and values in South Africa regarding emerging chemical compounds for pharmaceuticals, endocrine disruptors, and PCPs, with an exception only for pesticides that are agricultural contaminants. However, preventive measures such as rational drug use and education of those who prescribe the medication, and the public to reduce disposal and discharges to the environment, will likely reduce human exposure (World Health Organization, 2017).

2.7 Methodology, quantification, and analysis

2.7.1 Solid phase extraction

Odendaal et al. (2015) described the methodology of quantifying and analysing electrical conductivity through solid phase extraction: Samples of compounds are prepared with extraction and reconstitution in 1 mℓ of H_2O/0.1% formic acid. Different solid phase extraction cartridges with varying sorbent characteristics are analysed to identify the cartridges with the best optimum recovery. Before extraction, cartridges are equilibrated with 6 mℓ pure methanol (MeOH). After equilibration, samples are loaded at a flow of 6 mℓ/min. After loading of samples, cartridges must be washed with 6 mℓ tubes using 2 mℓ MeOH and 2 mℓ of acetonitrile. Eluates are evaporated using a savant SC 210A speed-vac concentrator with a thermo RVT 4104 refrigerated vapour trap. Extracts are reconstituted in 1 mℓ of H_2O/0.1% formic acid and suspended using a vortex (Velp Scientifica, Italy) as well as by sonication (Branson, United States) (Odendaal et al., 2015).

2.7.2 LC−MS/MS/GC analysis/quantification

The analysis using LC−MS is performed on a HPLC (Agilent 1200) linked to a 3200 QTRAP hybrid triple quadrupole mass spectrometer (AB Sciex, Framingham, Massachusetts, United States). The HPLC is fitted with 3-micro-meter Gemini-NX-C18 110-Å (150 × 2 mm) column (Phenomexe, CA, Torrance, United States). Formic acid (0.1% v/v) in water (solvent A) and formic acid (0.1% v/v) in MeOH (solvent B) are used as elution to positively charge analytes (Odendaal et al., 2015).

2.8 Conclusion

The literature study has shown that emerging contaminants are available in South African surface water systems, with increasing human health risk associated with these contaminants. Urbanisation and overpopulation has led to the increasing use of pharmaceutical products, PCPs and endocrine disrupting compounds in South Africa. These products require a more in-depth research in terms of their occurrence, fate and behaviour. Since there are no regulations in South Africa, there will be a need to educate the public about emerging contaminants and their associated health effects to human and animals.

Chapter 3

RESEARCH METHODOLOGY

3.1 Introduction

This chapter discusses the methods that were used to answer the research questions of the study. The chapter starts by giving an overview of the study area: the Modder River catchment. The material and methods used in this study are described, namely sample collection and handling procedures; sample preparation and extraction; sample analysis; method verification and quality control. Furthermore, the methods that were used to determine the sources of emerging contaminants are defined.

3.2 Description of the study area

The Modder River catchment can be found between latitudes 28° 50' and 29° 40' south, and 24° 40' and 29° 00' east (Figure 3.1). Its altitude is between 1 057 and 2 106 m above mean sea level. It is a sizable basin, covering 17 380 km^2 (Oke and Alowo, 2021). The Modder River catchment has very shallow slopes and a propensity for water to pool, which affects how long floods and high-flow conditions last (Pretorius et al., 2005). The Upper Modder, the Middle Modder, and the Lower Modder are its three sub-basins. The Modder River basin is located within the semi-arid Upper Orange Water Management Area to the east and north of the city of Bloemfontein (Woyessa et al., 2006). It has its beginnings close to Dewetsdorp, flows north, and then turns west. The river enters the Riet River, which joins the Oranje–Vaal River, after traveling roughly 340 km. The Modder River was typically a regular stream like the majority of South Africa's inland rivers, but due to the construction of three significant dams, notably the Rustfontein, Mockes, and Krugersdrift Dams, the waterway now resembles a perennial river (Oke and Alowo, 2021).

The city of Bloemfontein, which is under the control of the Mangaung Metropolitan Municipality (MMM), is the only significant developer in the Modder River basin (Pretorius et al., 2005). Geographically, Bloemfontein is situated at 29° 5' 13.9" S and 26° 9' 17.6" E and serves as the provincial capital of the Free State. The estimated 285 385 households in the

MMM have an average household size of 3.1 individuals, and around 65% of all houses are located in Bloemfontein. The population of Bloemfontein is predicted to have expanded from 464 586 to 546 568 between 2011 and 2019, which is a 2% growth of roughly 81 982 people. The water supply of the MMM is made up of a number of dams, rivers, wetlands, and groundwater resources (MMM Integrated Development Plan, 2022).

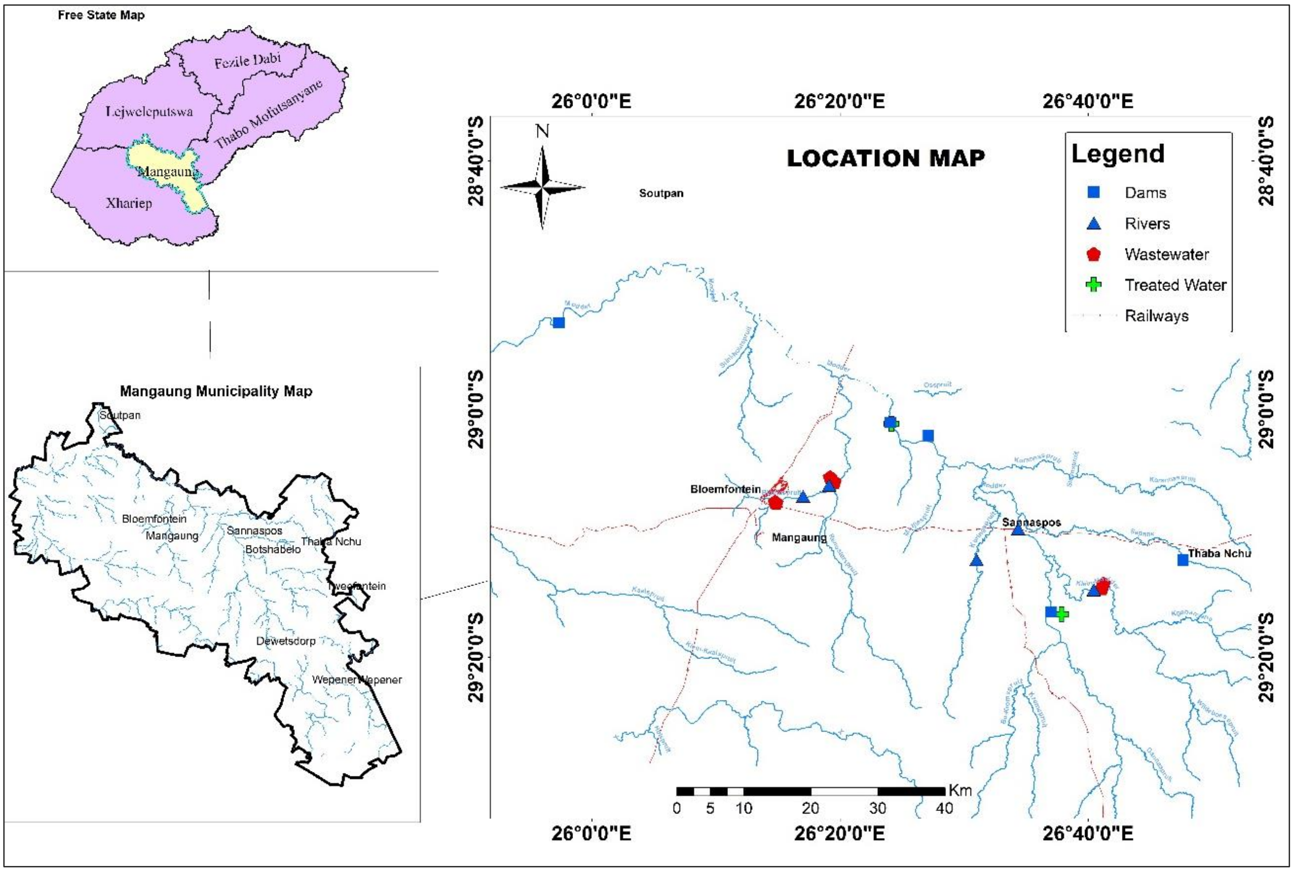


Figure 3.1 Sampling points within the Modder River catchment

The surface water environment is including a number of rivers, including the Modder (Lekatlong), Renosterspruit, Kaalspruit, Korannaspruit, Klein Modder, Koringspruit, and Bloemspruit. Eight dams, with a combined storage capacity of about 300 million cubic metres, provide water to the MMM, including Rustfontein, Welbedacht, Groothoek, Knelpoort, Mockes, Maselspoort, Krugersdrift, and Van Stadensrus. However, only the Welbedacht Dam, Mockes Dam and Maselspoort Dam provide services to the city of Bloemfontein. Water for households, farming, and industrial usage in the Botshabelo and Thaba 'Nchu districts is largely provided by the Rustfontein dam. Furthermore, 84% of households in the MMM is estimated to have access to sanitation facilities above the standard set by the Reconstruction and Development Programme. The municipality has 12 WWTPs (MMM Integrated Development Plan, 2022).

3.3 Material and methods

3.3.1 Sample collection and handling

A total of sixteen (n=16) samples were collected during the spring season, as shown in Table 3.1. Sources of water targeted in this study include rivers (RS03, RBS04, RKOR05, RMOR06 and RKLM07); dams (DMSO1, DMD02, DKD08, DSD09 and DRUSD10); wastewater influent (WWTP01I, WWTP02I and WWTP03I); wastewater treatment effluent (WWTP01E and WWTP02E) and tap water (TWRUS01 and TWMSP02) as presented in Table 3.1.

Table 3.1 Location of sampling points around the study area

Item	Sample ID	Coordinates		Elevation	Site description
		Latitude	Longitude		
			Dams		
1	DMSO1	29° 01' 4.9" S	26° 24' 2.7" E	1 344 m	Collected at Maselspoort Dam
2	DMD02	29° 02' 8.4" S	26° 27' 5.8" E	1 354 m	Collected at Mockes Dam
3	DKD08	28° 53' 03" S	25° 57' 21 E	1 226 m	Collected at Krugersdrift Dam
4	DSD09	29° 12' 10" S	26° 47' 38" E	1 460 m	Collected at Seralo Dam
5	DRUSD10	29° 16' 20" S	26° 37' 00" E	1 370 m	Collected at Rustfontein Dam
			Rivers		
6	RRS03	29° 06' 9.6" S	26° 19' 7.2" E	1 379 m	Collected at Renosterspruit
7	RBS04	29° 07' 2.4" S	26° 17' 1.5" E	1 390 m	Collected at Bloemspruit
8	RKOR05	29° 12' 8.3" S	26° 31' 0.4" E	1 334 m	Collected at Koringspruit
9	RMOR06	29° 09' 39.3" S	26° 34' 20.3" E	1 327 m	Collected at Modder River (Lekatlong)
10	RKLM07	29° 14' 34.3" S	26° 40' 26.2" E	1 373 m	Collected at Klein Modder River
			Wastewater treatment plants (WWTP)		
11	WWTP01I	29° 05' 29" S	26° 19' 12" E	1 386 m	Influent from Bloemfontein north-east WWTP
12	WWTP01E	29° 05' 51" S	26°19' 33" E	1 384 m	Effluent from Bloemfontein north-east WWTP
13	WWTP02I	29° 14' 2.8" S	26° 41' 12.9" E	1 380 m	Influent from Botshabelo WWTP
14	WWTP02E	29° 14' 25.4" S	26° 41' 6.2" E	1 376 m	Effluent from Botshabelo WWTP
			Treated drinking water		
15	TWRUS01	29° 16' 31" S	26° 37' 51" E	1 366 m	Treated water from Rustfontein WWTP
16	TWMSP02	29° 01' 10.3" S	26° 24' 9.2" E	1 339 m	Treated water from Maselspoort WWTP

All water samples in rivers (n=5), dams (n=5), tap water (n=2), wastewater influent (n=2) and wastewater effluent (n=2) were collected in 750 mℓ cleaned bottles (Appendix A) using grab sampling throughout the project. At the site of sampling, the 750 mℓ cleaned bottles were labelled for identification convenience at the laboratory and for data management. Samples from rivers and dams were collected by grab sampling from approximately 30 cm below the water surface (Appendix A). Samples from WWTPs were obtained by submerging the container below the water which were then transferred into sample bottles (Appendix A). To collect water samples from treated water, the tap was allowed to run for a few minutes before collection of the sample. During the sampling campaign, all of the samples that were stored in an ice cube-filled cooler box. The samples were taken to the laboratory following the sampling campaign where they were kept at 4 °C until analysis (Appendix A).

3.3.2 Selection of target compounds

In this investigation, twelve organic pollutants were chosen for monitoring. Ampicillin, atrazine, estradiol, ibuprofen, imidacloprid, lamivudine, progesterone, simazine, terbuthylazine, testosterone, and triclosan were the contaminants that were chosen. Their frequent detection in water sources, partial removal in WWTPs, reagent availability, and potential hazards were the main factors that led to their selection.

3.3.3 Sample preparation

Sigma Aldrich (St. Louis, Missouri, United States) and Dr. Ehrenstorfer (Augsburg, Germany) provided the high purity (>98%) chemical standards for 17-alpha-ethinylestradiol, ampicillin, atrazine, estradiol, ibuprofen, imidacloprid, lamivudine, progesterone, simazine, terbuthylazine, testosterone, and triclosan. Additionally, formic acid, acetonitrile, methanol, and ammonium hydroxide of HPLC grade were acquired from Sigma Aldrich in St. Louis, Missouri, United States. Millipore (Burlington, Massachusetts, United States) provided the ultra-pure water (99%) used in the experiments. Phenomenex (Torrance, Los Angeles, United States) provided the SPE cartridges (Strata C18, 6 mℓ). For each individual standard, stock solutions containing 1 µg/ℓ of methanol were prepared. Following preparation, a temperature of 4 °C was maintained for the stock solutions.

3.3.4 Sample extraction

The method described by Odendaal et al. (2015) and Mugudamani et al. (2023) for sample extraction for the selected compounds, which included 17-alpha-ethinylestradiol, ampicillin, atrazine, estradiol, ibuprofen, imidacloprid, lamivudine, progesterone, simazine, terbuthylazine, testosterone, and triclosan, was adopted. Briefly, in order to remove unwanted particles, the samples were filtered over glass fibre filters. To improve SPE parameters, 99% ultra-pure water was laced with chemical standards of emerging contaminants. Different SPE cartridges with various sorbent properties were examined. Prior to extraction, Milli-Q® water and 6 m methanol were used to equilibrate the SPE cartridges. Samples were then loaded at about a flow rate of 6 mℓ per minute. After being cleaned with 6 mℓ purified water, the sample cartridges were vacuum-dried for 20 minutes. The bound sample was gradually eluted from the dried-up cartridges using 2 mℓ methanol and then 2 mℓ ethyl acetate. A Thermo Scientific Savant Speedvac SC 210A concentrator (Waltham, Massachusetts, United States) was used to hoover dry the eluant until it was almost dry. Reconstituted extract was made with 0.1% formic acid and 1 mℓ purified water.

3.3.5 Sample analysis

Water samples were analysed using a high-performance chromatography system (Agilent 1200) coupled to an ABSCIEX 4000 QTRAP hybrid triple quadrupole ion trap mass spectrometer, with a Shimadzu ultra-fast LC stack serving as the front end. Two different analyses were performed during the analysis: quantitation of the targeted analytes and screening for unknown analytes. The software used for all data processing and acquisition was AB SCIEX Analyst 1.5.

Both positive and negative ionisation modes of analysis were used on the samples. Using a five-minute gradient from 5% solvent A (H_2O/0.1% formic acid) to 95% solvent B (methanol/0.1% formic acid), a total run time of nine minutes was allocated for column re-equilibration. Twenty microlitre of each extracted sample was separated in positive ionisation mode on a C18 (150 mm × 4.6 mm, Gemini NX, Phenomenex) column at a flow rate of 300 µℓ/min. Analytes that were eluted were electrospray ionised in the TurboV ion source at 500 °C to evaporate surplus solvent, along with 40 psi of nebulizer gas, 40 psi of heater gas, and 15 psi of curtain gas. The ion spray voltage was set at 5 500 V.

A C18 (150 mm × 4.6 mm, Gemini NX, Phenomenex) column was used to separate 20 µℓ of each extracted sample in a negative ionisation mode. The column was run at a flow rate of 300 µℓ/min over the course of a two-minute gradient from 5% solvent A (H_2O/0.1% NH_3OH) to 95% solvent B (methanol / 0.1% NH_3OH), with a total run time of 10 minutes to allow for column re-equilibration. Analytes that were eluted were electrospray-ionised in the Turbo V ion source at 500 °C to evaporate surplus solvent, along with 40 psi of nebulizer gas, 40 psi of heater gas, and 15 psi of curtain gas.The ion spray voltage was set at−4 500 V.

For each analyte, several reaction monitoring transitions were used in the analyses. The peak area on the chromatogram produced by the first and most sensitive transition was known as the qualifier, and the peak area produced by the second transition was known as the quantifier. The qualifier acts as an extra layer of assurance that the analyte is present, and both of these transitions require the same retention period. Appendix B of contains detailed information on the list of transitions.

3.3.6 Method verification and quality control

Only quantification limits, selectivity, and linearity were established to verify the operation of the apparatus. Samples were arranged in groups for selectivity, with quality control samples with known values inserted and solvent blank runs in between each sample that was examined. Each compound was given a four-point calibration curve with concentrations ranging from 0.001 ppm to 1 ppm in order to assess linearity. The linearity value (r) of the data was more than 0.98. The instrument's limit of quantification was established for every compound. As shown in Table 3.2, the quantification limits ranged from 0.001 ng/mℓ to 1.00 ng/mℓ for every compound. Laboratory blanks were used for quality assurance. This was done to make sure that all of the equipment had been thoroughly cleaned and that there was no external contamination.

Table 3.2 Measurement of linearity and limit of quantification

Analyte	Linearity (r^2) value	Limit of quantification (LOQ) (ng/mℓ)
Ampicillin	0.99	1.000
Simazine	0.99	0.001
Atrazine	0.99	0.001
Terbuthylazine	0.99	0.001
Imidacloprid	0.99	0.001
Testosterone	0.99	0.001
Progesterone	0.99	0.001
Ibuprofen	0.99	0.010
Estradiol	0.99	0.01
Triclosan	0.99	0.010
17-alpha-ethinyl-estradiol	0.99	0.010
Lamivudine	0.99	0.100

3.3.7 Statistical analysis and source apportionment

Using Microsoft Excel, the descriptive statistics of the data were calculated and displayed as the minimum, maximum, mean, and standard deviation. Furthermore, two statistical techniques – Pearson's correlation coefficients and hierarchical cluster analysis – were used to ascertain the interrelationships and possible sources of particular compounds in the Modder River catchment.

Chapter 4

RESULTS AND DISCUSSION

4.1 Introduction

This chapter provides the presentation and discussion of the analytical results on emerging contaminants along the Modder River catchment. It also covers the presentation and discussion of possible sources of emerging contaminants. The suggested pollution mitigation measures are also discussed.

4.2 Concentration of emerging contaminants along the Modder River catchment

In this study, 12 emerging contaminants, namely 17-alpha-ethinylestradiol, estradiol, progesterone, testosterone, lamivudine, ampicillin, ibuprofen, triclosan, atrazine, simazine, terbuthylazine and imidacloprid were targeted. These contaminants were targeted in rivers, dams, WWTPs and tap drinking water during the spring season along the Modder River catchment. Ampicillin is an antibiotic used to treat and prevent various bacterial infections, including meningitis, endocarditis, respiratory tract infections, and urinary tract infections. The 17-alpha-ethinylestradiol, a synthetic oestrogenic compound, is commonly used as the active ingredient in many oral contraceptives and postmenopausal hormone therapy (Kanama et al., 2018). Estradiol is the most potent oestrogen, and the major female sex hormone useful in regulating female reproductive cycles. The sex hormone testosterone affects many bodily functions, including controlling libido, bone density, fat distribution, muscle mass, and sperm and red blood cell production. While testosterone is a significant androgen compound required for normal spermatogenesis and lowers the risk of osteoporosis, progesterone is a progestogen and is thought to be a female pregnancy hormone (Hu et al., 2010; Prior, 2019). An antiviral medication called lamivudine is used to treat hepatitis B and human immunodeficiency virus infections (Ngumba et al., 2020). Because of its superior antimicrobial and antifungal qualities, triclosan, one of the PCPs found in this study, is widely used in a range of consumer goods. A non-steroidal anti-inflammatory medication called ibuprofen is used to treat inflammation, fever, and pain (Nannou et al., 2022). Pesticides such as atrazine, simazine and terbuthylazine are herbicides used to control various annual and perennial grasses and broadleaf weeds, while imidacloprid is an insecticide used to kill sucking insects and structure crops and soil (Pandey et al., 2019). Their descriptive statistics were summarised as minimum, maximum, mean concentrations and standard deviations, as presented in Table 4.1. The mean concentrations and standard deviations of contaminants detected in one sample were not calculated.

4.2.1 Emerging contaminants in rivers

The concentrations of targeted emerging contaminants, namely 17-alpha-ethinyl-estradiol, estradiol, progesterone, testosterone, lamivudine, ampicillin, ibuprofen, triclosan, atrazine, simazine, terbuthylazine and imidacloprid were as 0.03–4.26 (2.71±1.65), <LOQ, <LOQ, <LOQ, <LOQ, <LOQ, <LOQ, <LOQ–0.07 (0.04±0.03), 0.001–0.05 (0.02±0.02), 0.01–0.25 (0.09±0.10), 0.00–0.17 (0.09±0.06), and <LOQ–0.014 (<LOQ) ng/mℓ, respectively (Table 4.1). The mean concentration of 17-alpha-ethinyl-estradiol was the highest among all the contaminants (Figure 4.1). Their trend was as 17-alpha-ethinylestradiol > simazine =terbuthylazine > triclosan > atrazine > estradiol = progesterone = testosterone = lamivudine = ampicillin = ibuprofen = imidacloprid.

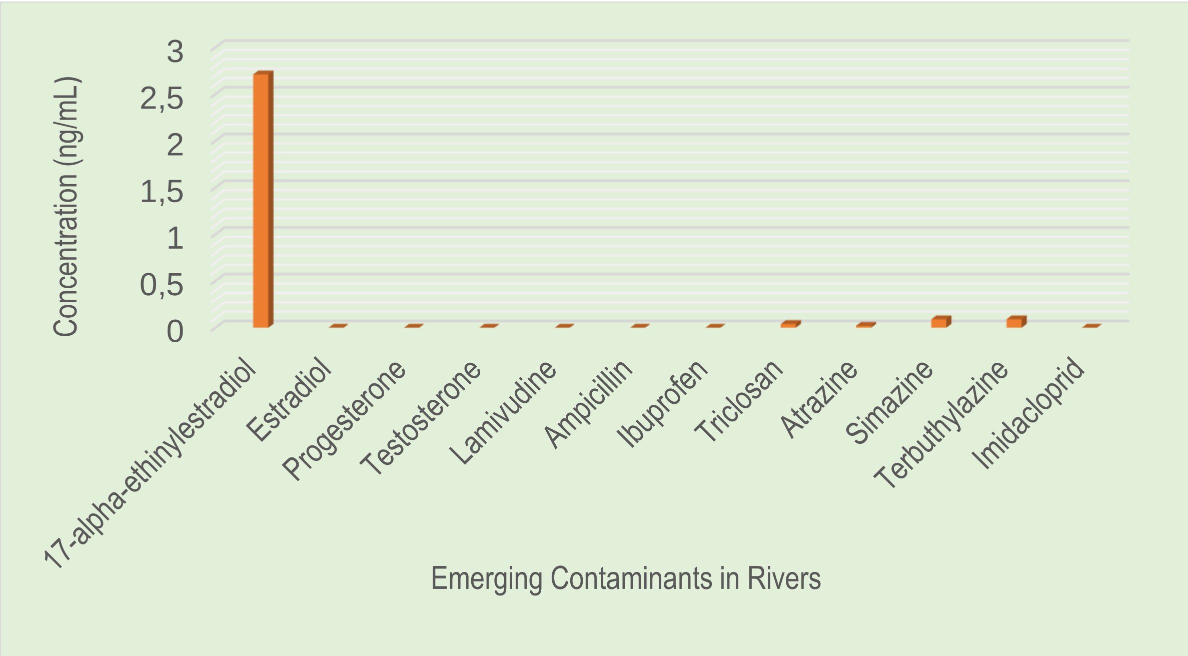


Figure 4.1 Emerging contaminants in rivers

The presence of these compounds in rivers were also reported by other researchers around the world: 17-alpha-ethinyl-estradiol in Pretoria (Van Zijl et al., 2017), ampicillin in KwaZulu-Natal (Agunbiade and Moodley, 2016), triclosan in Gauteng (Madikizela et al., 2014), lamivudine in Gauteng (Mhuka et al., 2020), atrazine and terbuthylazine in Cape Town (Ojemaye, 2020), simazine in the Western Cape (Curchod et al., 2020), estradiol in Mpumalanga (Van Wyk et al., 2014), and ibuprofen in Nigeria (Olarinmoye et al., 2016). The presence of the leading contaminant, 17-alpha-ethinylestradiol, in the rivers along the Modder River catchment may have been influenced by WWTPs that discharge effluent into the streams. This is due to the fact that WWTPs are major sources of these compounds (Forghani et al., 2018). Rivers that passes through townships such as Botshabelo in the Free State are also likely to be contaminated by these compounds as a result of illegal dumping of household waste (e.g. medical drugs) near the rivers. Farming activities such as crop production in the area may necessitate the use of weed control herbicides before, during, and after the production season. Therefore, the presence of atrazine, simazine, and terbuthylazine, which were among the leading contaminants in river samples, may be linked to the runoff from agricultural activities around the selected rivers. Other contaminants detected in this study may be connected to runoff from agricultural activities, stormwater runoff, illegal dumping and discharge of wastewater effluent in rivers.

4.2.2 Emerging contaminants in dams

The concentrations of targeted emerging contaminants namely 17-alpha-ethinylestradiol, estradiol, progesterone, testosterone, lamivudine, ampicillin, ibuprofen, triclosan, atrazine, simazine, terbuthylazine and imidacloprid were 0.04–1.58 (0.61±0.61), <LOQ, <LOQ, <LOQ, <LOQ, <LOQ, <LOQ, <LOQ–0.02 (<LOQ), 0.01–0.09 (0.03±0.03), 0.03–0.12 (0.06±0.04), 0.03–0.12 (0.06±0.04) and <LOQ ng/mℓ, respectively (Table 4.1). The mean concentration of 17-alpha-ethinylestradiol was the highest among all the contaminants (Figure 4.2). Their trend was as 17-alpha-ethinylestradiol >simazine = terbuthylazine >atrazine >estradiol = triclosan = progesterone = testosterone = lamivudine = ampicillin = ibuprofen = imidacloprid. The occurrence of 17-alpha-ethinylestradiol, ibuprofen, triclosan, estradiol, progesterone, and testosterone in dams were also reported in a study conducted around the city of Bloemfontein (Oke et al., 2023). Simazine, terbuthylazine and atrazine were also reported in dams around Mangaung (Mugudamani et al., 2023). In dams, 17-alpha-ethinylestradiol, simazine, terbuthylazine, and atrazine herbicides were among the leading contaminants. Many factors contributed to the detection of steroid hormones in dams, including illegal dumping of household waste containing unused or expired drugs near the dams, and sewage runoff from nearby settlements, which was observed near one of the sampling points. Agricultural areas near some dams, particularly those with livestock production, may also serve as a secondary source of these compounds. Pandey et al. (2019) also mentioned that herbicides can be used to manage intrusive plants in water. Hence, the concentration of these pesticides in dams could be as a result of their application in the management of algae and submerged weeds. High concentrations of pesticides in dams may be pointed to the location of dams which are surrounded by agricultural fields (of which maize crops is common), which necessitate the application of these herbicides to kill weeds. Illegal dumping of household waste containing unused or unfinished medications, as well as sewage runoff from nearby communities observed during a site visit, may have contributed to the concentration of other detected compounds in dam samples.

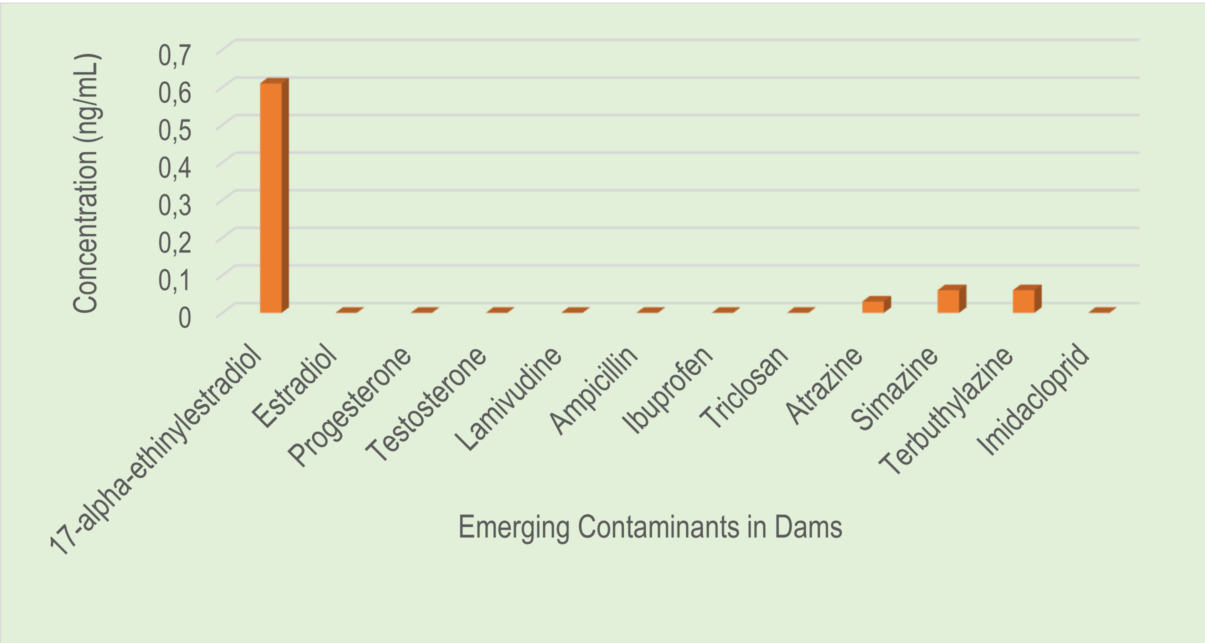


Figure 4.2 Emerging contaminants in dams

4.2.3 Emerging contaminants in tap water

The concentrations of 17-alpha-ethinylestradiol, estradiol, progesterone, testosterone, lamivudine, ampicillin, ibuprofen, triclosan, atrazine, simazine, terbuthylazine and imidacloprid in tap waters were 0.03–2.13 (1.08–1.49), <LOQ, <LOQ, <LOQ, <LOQ, <LOQ, <LOQ, <LOQ, 0.02–0.04 (0.03±0.01), 0.04–0.03 (0.03±0.004), 0.03–0.03 (0.03±0.001) and <LOQ ng/mℓ, respectively (Table 4.1). In tap water, it was 17-alpha-ethinylestradiol that showed the highest mean concentration (Figure 4.4), while imidacloprid had the lowest mean concentration. Their mean concentrations were descending as 17-alpha-ethinylestradiol >atrazine = terbuthylazine = simazine = estradiol = progesterone = testosterone = lamivudine = ampicillin = buprofen = imidacloprid. Van Zijl et al. (2017) reported the occurrence of 17-alpha-ethinylestradiol in treated drinking water around Pretoria, South Africa, which is comparable to the findings of this study. The prevalence of pesticides in treated drinking water within the Modder River catchment is comparable to the findings of other researchers who also detected atrazine, and terbuthylazine in treated drinking water (Machado et al., 2016; Odendaal et al., 2015; Mugudamani et al., 2023). The dominance of herbicides in treated drinking water may be traced back to the polluted dams considered sources of water for water treatment plants in the area. Their occurrence also suggests the incapability to remove them by the methods used to treat water.

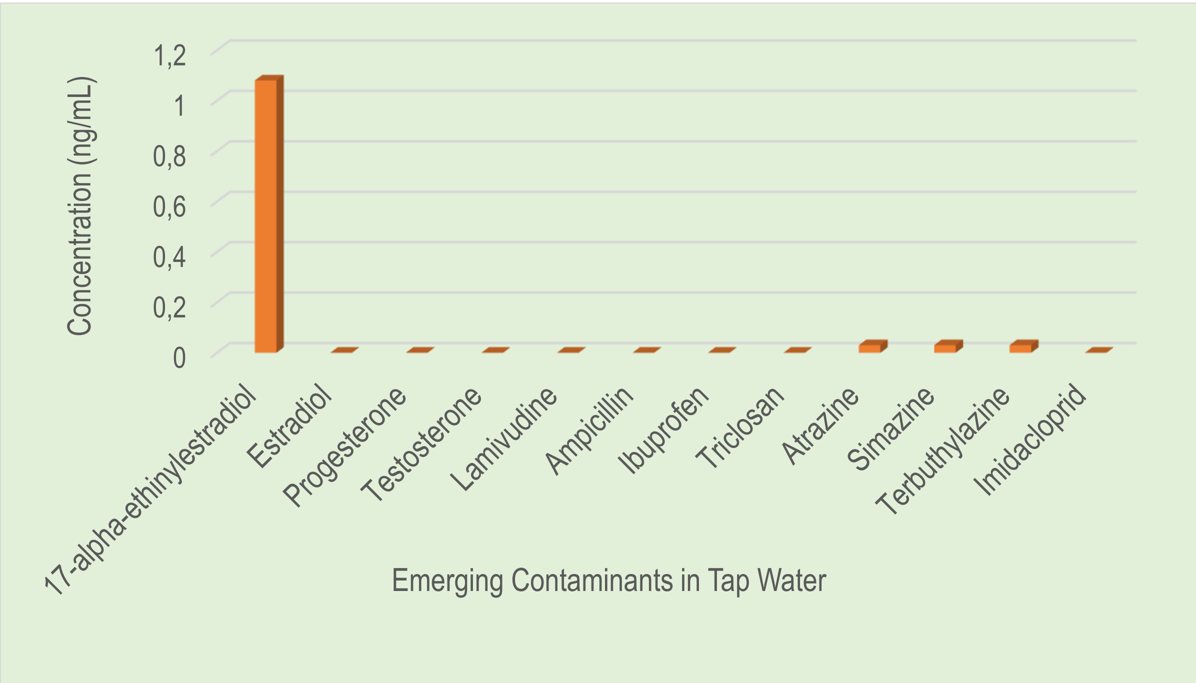


Figure 4.3 Emerging contaminants in tap water

4.2.4 Emerging contaminants in wastewater treatment plants

In wastewater influent, the concentrations of 17-alpha-ethinylestradiol, estradiol, progesterone, testosterone, lamivudine, ampicillin, ibuprofen, triclosan, atrazine, simazine, terbuthylazine and imidacloprid were 2.04–4.57 (3.31±1.79), <LOQ, <LOQ-1.37 (<LOQ), 0.03–1.22 (0.63±0.84), 16.40-20.90 (18.65±3.18), <LOQ–42.30 (<LOQ), 2.14–0.65 (1.40±1.05), 0.04–0.14 (0.09±0.07), 0.05–0.03 (0.04±0.01), 0.10–0.06 (0.08±0.02), 0.04–0.21 (0.12±0.12), and <LOQ–0.40 (<LOQ) ng/mℓ, respectively (Table 4.1). Among all the contaminants in wastewater influent, lamivudine recorded the highest mean concentration (Figure 4.3). Their trend was as follows: lamivudine >17-alpha-ethinylestradiol >ibuprofen >terbuthylazine >testosterone >triclosan >simazine >atrazine = estradiol = progesterone = ampicillin = imidacloprid.

The occurrence of these emerging contaminants in wastewater influent were also reported in other countries: lamivudine in Zambia (Ngumba et al., 2020), 17-alpha-ethinylestradiol in China (Lin et al., 2020), ibuprofen in Cyprus (Hapeshi et al., 2015), atrazine in Brazil (Correia et al., 2020), triclosan in China (Lin et al., 2020), ampicillin in KwaZulu-Natal (Agunbiade and Moodley, 2016) and estradiol in the United States (Glassmeyer et al., 2017). The selected WWTPs receive wastewater from the industry, households and hospitals. Therefore, it is possible that the presence of lamivudine as the primary contaminant is related to the excrement of patients with hepatitis B and HIV. The high level of excretion in humans may be the cause of the presence of 17-alpha-ethinylestradiol in wastewater influent (Kanama et al., 2018). According to Forghani et al. (2018), oestrogens are expelled from men's bodies (1.6 g daily) and women's bodies (2.3 to 259 g daily) without being consumed, which clarifies the presence of influent samples.

The dominance of herbicides in influent samples clearly shows how widely they are used in cities, homes, farms, and industrial facilities that produce pesticides. Other contaminants such as ibuprofen, triclosan, ampicillin, and imidacloprid may be associated with wastewater received from hospitals, households and urban stormwater. Triclosan may be introduced into WWTPs due to its extensive use in a range of customer products due to its exceptional antimicrobial and antifungal properties. Ibuprofen as a non-steroidal anti-inflammatory drug utilised to get rid of pain, fever and inflammation, may also enter WWTPs from household and hospital wastewater (Nannou et al., 2022). Moreover, imidacloprid, an insecticide used to kill sucking insects and to structure crops and soil, may be introduced into WWTPs as a result of runoff from urban gardens and parks (Pandey et al., 2019).

Furthermore, the concentrations of emerging contaminants such as 17-alpha-ethinylestradiol, estradiol, progesterone, testosterone, lamivudine, ampicillin, ibuprofen, triclosan, atrazine, simazine, terbuthylazine and imidacloprid in wastewater effluents were 1.40−4.57 (2.99±2.24), <LOQ, <LOQ, <LOQ, 0.64–10.10 (5.37±6.69), <LOQ, <LOQ–1.45 (<LOQ), 0.04–0.03 (0.03±0.01), 0.12–0.02 (0.07±0.07), 0.19–0.06 (0.12±0.09), 0.20–0.04 (0.12±0.11), and <LOQ–0.04 (<LOQ) ng/mℓ, respectively (Table 4.1). In wastewater effluent, lamivudine also recorded the highest mean concentration as shown in Figure 4.3.

When compared to each other, their mean concentrations were trending as lamivudine >17-alpha-ethinylestradiol >simazine = terbuthylazine >atrazine >triclosan = estrdiol = progesterone = testosterone = ampicillin = ibuprofen imidacloprid. Other researchers also found traces of these compounds in effluent samples in other parts of South Africa, such as lamivudine in KwaZulu-Natal (Späth et al., 2021), 17-alpha-ethinylestradiol in the North West province (Kanama et al., 2018), terbuthylazine in eThekwini (Späth et al., 2021), simazine and atrazine in Amanzimtoti, KwaZulu-Natal (Kunene, 2019), triclosan in Gauteng (Madikizela et al., 2014), ibuprofen in Eastern Cape (Ademoyegun, 2017), ampicillins in KwaZulu-Natal (Agunbiade and Moodley, 2016), testosterone in Gauteng (Mhuka et al., 2020), and progesterone in KwaZulu-Natal (Manickum and John, 2014), as well as estradiol in China (Lin et al., 2020). The occurrence of these contaminants in effluent samples is a confirmation of low elimination efficiency in WWTPs.

All emerging contaminants quantified at low values in the effluent, as compared to influent samples, clearly indicated that these WWTPs have a significant removal efficiency. Therefore, it is safe to conclude that treatment methods in these treatment works are not capable to eliminate some of the selected compounds, and advanced treatment techniques should be put in place.

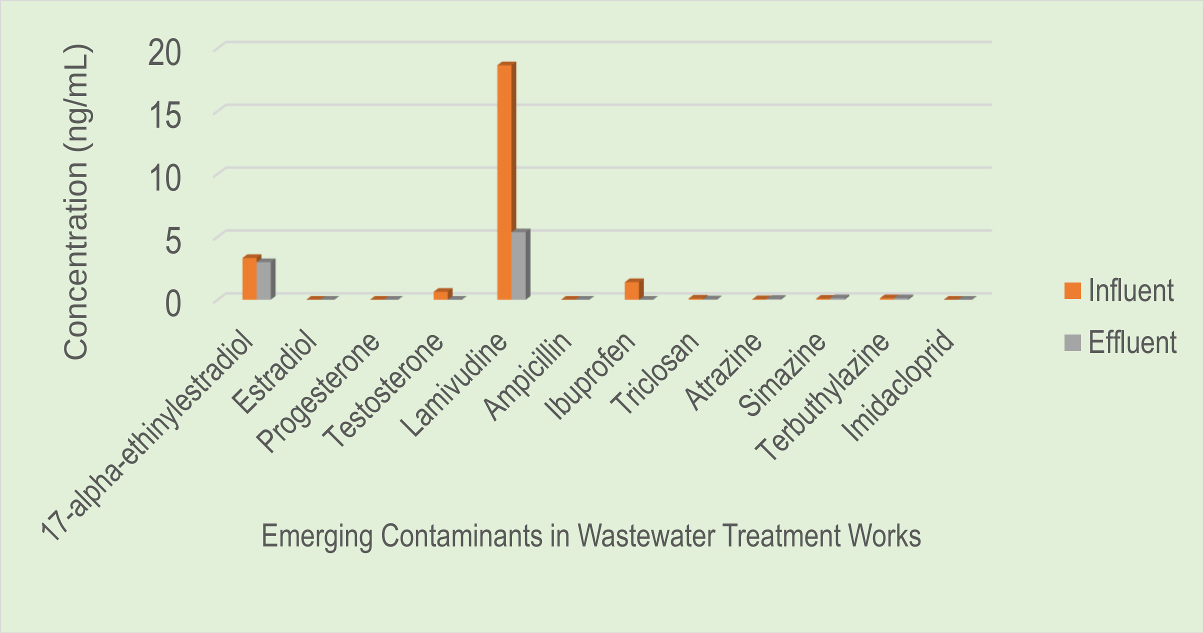


Figure 4.4 Emerging contaminants in wastewater treatment plants

Table 4.1 Concentrations of emerging contaminants in selected water sources

Contaminants	Concentration (ng/mℓ)									
	Rivers (n=5)		Dams (n=5)		Influents (n=2)		Effluents (n=2)		Tap Water (n=2)	
	Min–Max	Mean ±SD	Min–Max	Mean ±SD	Min–Max	Mean ±SD	Min–Max	Mean±SD	Min–Max	Mean±SD
17-alpha-ethinylestradiol	0.03–4.26	2.71±1.65	0.04–1.58	0.61±0.61	2.04±4.57	3.31±1.79	1.40±4.57	2.99–2.24	0.03±2.13	1.08±1.49
Estradiol	–	–	–	–	–	–	–	–	–	–
Progesterone	–	–	–	–	<LOQ–1.37	–	–	–	–	–
Testosterone	–	–	–	–	0.03-1.22	0.63±0.84	–	–	–	–
Lamivudine	–	–	–	–	16.40-±20.90	18.65±3.18	0.64±10.10	5.37±6.69	–	–
Ampicillin	–	–	–	–	<LOQ±42.30	–	–	–	–	–
Ibuprofen	–	–	–	–	2.14±0.65	1.40–1.05	<LOQ±1.45	–	–	–
Triclosan	<LOQ–0.07	0.04±0.03	<LOQ–0.02	–	0.04±0.14	0.09±0.07	0.04±0.03	0.03±0.01	–	–
Atrazine	0.001–0.05	0.02±0.02	0.01–0.09	0.03±0.03	0.05±0.03	0.04±0.01	0.12±0.02	0.07±0.07	0.02±0.04	0.03±0.01
Simazine	0.01–0.25	0.09±0.10	0.03–0.12	0.06±0.04	0.10±0.06	0.08±0.02	0.19±0.06	0.12±0.09	0.04±0.03	0.03±0.004
Terbuthylazine	0.002–0.17	0.09±0.06	0.03–0.12	0.06±0.04	0.04±0.21	0.12±0.12	0.20±0.04	0.12±0.11	0.03±0.03	0.03±0.001
Imidacloprid	<LOQ–0.014	–	–	–	<LOQ±0.40	–	<LOQ±0.04	–	–	–

Notation: n= number of samples; SD= standard deviation; min= minimum concentration; max=maximum concentration; LOQ=limit of quantification.

4.3 Sources of emerging contaminants in the Modder River catchment

4.3.1 Source identification with the Pearson correlation coefficient analysis

The Pearson correlation coefficient analysis was performed to discover the association of emerging contaminants and make inferences on their sources of origin. When the degree of correlation (r) was > 0.7, it was regarded as strong, 0.5 < r < 0.7 connoted moderate correlations, and < 0.5 suggested week correlations (Li et al., 2023). A strong correlation between contaminants suggests a possible common source or similar chemical behaviour (Mugudamani et al., 2022). The outcomes of the Pearson correlation coefficient analysis are presented and discussed in this section as per their sources.

4.3.1.1 Identification of pollution pathways in rivers

Table 4.2 shows the Pearson correlation matrix of the emerging contaminants in rivers during the spring season. The occurrence of emerging contaminants in rivers showed a strong positive correlation between 17-alpha-ethinylestradiol and atrazine, atrazine and simazine, as well as imidacloprid and triclosan. There was also a moderate positive correlation between 17-alpha-ethinylestradiol and imidacloprid, 17-alpha-ethinyl-estradiol and simazine, 17-alpha-ethinylestradiol and terbuthylazine, 17-alpha-ethinyl-estradiol and triclosan as well as atrazine and terbuthylazine.

The strong and moderate positive correlations between emerging contaminants in this study are an indication of the possible similar sources of contamination, possibly from man-made activities. From the findings of the Pearson correlation coefficient analysis, there was a positive correlation between steroid hormones (17-alpha-ethinylestradiol) and pesticides (i.e. atrazine, terbuthylazine, imidacloprid and simazine) indicating similar sources of origin. Some of the rivers run through townships and cities; hence, runoff from clogged sewerage systems, and illegal waste dumping may have introduced these contaminants in rivers. Additionally, because selected WWTPs receive wastewater from households, industries and hospitals, their wastewater effluents discharged into nearby streams may introduce traces of these emerging contaminants, usually categorised as steroid hormones and pesticides. Farming practices and household gardens may also necessitate the use of herbicides (atrazine, simazine, and terbuthylazine) to control unwanted weeds, and insecticides such as imidacloprid to control insects, termites, and fleas on pets, which end up in streams as a result of runoff.

The positive correlation between pesticides such as atrazine and simazine as well as atrazine and terbuthylazine may be linked with agricultural activities, and stormwater runoff. Most of the rivers are surrounded by the agricultural activities producing maize, soybeans, wheat, sorghum, and sunflower, which demand the usage of herbicides such as simazine, atrazine, and terbuthylazine to control weed during the production season. Moreover, the city of Bloemfontein is a developed area with well-built infrastructures, community grounds, business areas, and golf courses. With all these, substantial quantities of pesticides are used to manage unwanted plants and disturbing insects. Therefore, runoff from agricultural fields, and stormwater from the city centre and residential areas may introduce the pesticides detected in rivers within the Modder River catchment. Pesticides may also be introduced into rivers by the discharge of wastewater effluent into nearby streams.

There was also a positive correlation between 17-alpha-ethinylestradiol and triclosan. These contaminants are steroid hormones and PCPs, and their origin can be linked to wastewater effluents and illegal dumping of household waste nearby the streams. WWTPs receive domestic, hospital and industrial waste, which contain loads of various pharmaceutical compounds and PCPs used in our daily lives. As WWTPs are not intended to eradicate these compounds, they may end up in rivers due to wastewater effluent discharge. Illegal dumping of domestic waste containing unused or expired drugs may also introduce traces of these compounds.

Moreover, pesticides (imidacloprid) and PCPs (triclosan) also showed a positive correlations, which is an indication of the same source, possibly urban stormwater and wastewater effluent. The incapability of WWTPs to entirely eliminate emerging contaminants may contribute to river contamination by these compounds as their effluents are mostly discharged in streams. The application of insecticides such as imidacloprid to control insects, and termites, from households and city centres may also lead to the detection of traces of these compounds in rivers as a result of stormwater runoff.

Table 4.2 Correlation matrix of emerging contaminants in rivers

Contaminants	*17a-ethinylestradiol*	*Ampicillin*	*Atrazine*	*Estradiol*	*Ibuprofen*	*Imidacloprid*	*Lamivudine*	*Progesterone*	*Simazine*	*Terbuthylazine*	*Testosterone*	*Triclosan*
17a-ethinylestradiol	1											
Ampicillin	0.00	1										
Atrazine	**0.74**	0.00	1									
Estradiol	0.00	0.00	0.00	1								
Ibuprofen	0.00	0.00	0.00	0.00	1							
Imidacloprid	**0.52**	0.00	0.10	0.00	0.00	1						
Lamivudine	0.00	0.00	0.00	0.00	0.00	0.00	1					
Progesterone	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1				
Simazine	**0.62**	0.00	**0.98**	0.00	0.00	0.05	0.00	0.00	1			
Terbuthylazine	**0.62**	0.00	**0.56**	0.00	0.00	–0.27	0.00	0.00	0.45	1		
Testosterone	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1	
Triclosan	**0.64**	0.00	0.21	0.00	0.00	**0.98**	0.00	0.00	0.14	–0.09	0.00	1

Notation: Numbers in bold represent positive strong and moderate correlations.

4.3.1.2 Identification of pollution pathways in dams

In dams, only a strong positive correlation matrix between the emerging contaminants atrazine and simazine, atrazine and terbuthylazine as well as simazine and terbuthylazine was witnessed (Table 4.3). Generally, the strong positive degree of correlations between these pesticides, specifically classified as herbicides, indicate a similar source of origin. Herbicides can be applied to manage weeds in agricultural fields (Wang et al., 2022). Therefore, runoff from agricultural practices around the selected dams may have introduced these compounds. Some dams are surrounded by a well-managed turf which may need herbicides for its management. Hence, runoff from these large turfs may introduce traces of herbicides in dams. Moreover, their strong positive correlations may be linked to sources such as agricultural runoff, and wastewater effluent discharged in rivers that recharge these dams.

4.3.1.3 Identification of pollution pathways in tap water

The correlation matrix of the emerging contaminants in tap water showed a positive strong correlation between 17-alpha-ethinylestradiol and atrazine and simazine and terbuthylazine as presented in Table 4.4. Generally, there is a strong positive relationship between pairs of steroid hormones (17-alpha-ethinylestradiol) and herbicides (atrazine) which clearly suggest the same sources of origin that may possibly be illegal dumping of medical dugs during conferences, fishing and other aquatic sports in dams used as a source of water by WWTPs. Rivers that receive effluents from WWTPs may introduce traces of emerging contaminants in dams, which eventually can be traced in treated drinking water. Another strong positive correlation in treated drinking water was between herbicides (simazine and terbuthylazine) which indicate that they were probably derived from the same anthropogenic sources. Use of herbicides in surrounding farming areas, in lawns around the dams, and paved areas for management of weeds may lead to their introduction in reservoirs or dams used as a source of water for WWTPs as a result of agricultural runoff and stormwater runoff from lawns used for picnics or paved areas around the dams. Consequently, they are detected in treated drinking water.

Table 4.3 Correlation matrix of emerging contaminants in dams

Contaminants	*17a-ethinylestradiol*	*Ampicillin*	*Atrazine*	*Estradiol*	*Ibuprofen*	*Imidacloprid*	*Lamivudine*	*Progesterone*	*Simazine*	*Terbuthylazine*	*Testosterone*	*Triclosan*
17a-ethinylestradiol	1											
Ampicillin	0.00	1										
Atrazine	–0.24	0.00	1									
Estradiol	0.00	0.00	0.00	1								
Ibuprofen	0.00	0.00	0.00	0.00	1							
Imidacloprid	0.00	0.00	0.00	0.00	0.00	1						
Lamivudine	0.00	0.00	0.00	0.00	0.00	0.00	1					
Progesterone	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1				
Simazine	–0.29	0.00	**0.97**	0.00	0.00	0.00	0.00	0.00	1			
Terbuthylazine	–0.11	0.00	**0.93**	0.00	0.00	0.00	0.00	0.00	**0.98**	1		
Testosterone	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1	
Triclosan	–0.53	0.00	–0.13	0.00	0.00	0.00	0.00	0.00	–0.27	–0.46	0.00	1

Notation: Numbers in bold represent positive strong and moderate correlations.

Table 4.4 Correlation matrix of emerging contaminants in tap water

Contaminants	*17a-ethinylestradiol*	*Ampicillin*	*Atrazine*	*Estradiol*	*Ibuprofen*	*Imidacloprid*	*Lamivudine*	*Progesterone*	*Simazine*	*Terbuthylazine*	*Testosterone*	*Triclosan*
17a-ethinylestradiol	1											
Ampicillin	0.00	1										
Atrazine	**1.00**	0.00	1									
Estradiol	0.00	0.00	0.00	1								
Ibuprofen	0.00	0.00	0.00	0.00	1							
Imidacloprid	0.00	0.00	0.00	0.00	0.00	1						
Lamivudine	0.00	0.00	0.00	0.00	0.00	0.00	1					
Progesterone	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1				
Simazine	-1.00	0.00	-1.00	0.00	0.00	0.00	0.00	0.00	1			
Terbuthylazine	-1.00	0.00	-1.00	0.00	0.00	0.00	0.00	0.00	**1.00**	1		
Testosterone	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1	
Triclosan	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1

Notation: Numbers in bold represent positive strong and moderate correlations.

4.3.1.4 Identification of pollution pathways in wastewater treatment plants

In wastewater influents, the majority of contaminants showed positive strong correlations. These strong correlations were of 17-alpha-ethinylestradiol/ampicillin, 17-alpha-ethinylestradiol/imidacloprid, 17-alpha-ethinylestradiol/progesterone, 17-alpha-ethinylestradiol/terbuthylazine, 17-alpha-ethinylestradiol/testosterone, 17-alpha-ethinylestradiol/triclosan, ampicillin/imidacloprid, ampicillin/lamivudine, ampicillin/ progesterone, ampicillin/terbuthylazine, ampicillin/testosterone, ampicillin/triclosan, atrazine/ibuprofen, atrazine/simazine, ibuprofen/simazine, imidacloprid/lamivudine, imidacloprid/progesterone, imidacloprid/terbuthylazine, imidacloprid/testosterone, imidacloprid/triclosan, lamivudine/progesterone, lamivudine/terbuthylazine, lamivudine/testosterone, lamivudine/triclosan, progesterone/terbuthylazine, progesterone/testosterone, terbuthylazine/testosterone, terbuthylazine/triclosan, and progesterone/triclosan (Table 4.4).

Generally, in wastewater influent, there was strong positive correlations among compounds such as terbuthylazine/testosterone; progesterone and terbuthylazine, lamidacloprid/testosterone, and imidacloprid/progesterone that falls under pesticides, and steroid hormones which is an indication of similar man-made sources. Their strong positive correlations are an indication of similar sources such as stormwater, domestic, industrial, and hospital wastewater. There were also strong positive correlations between atrazine and simazine, and imidacloprid and terbuthylazine. These contaminants are pesticides mostly used in industrial areas, households, roadsides, and public squares to control weeds and insects. WWTPs in this area receive wastewater from all residents, industrial areas as well as fruit and vegetable cleaning areas. Therefore, their sources may be linked to industrial wastewater, and stormwater runoff from roadsides, industrial, residential, and public squares. Strong positive correlations between steroid hormones, namely 17-alpha-ethinylestradiol and progesterone, 17-alpha-ethinylestradiol and testosterone, as well as testosterone and progesterone, were witnessed in wastewater influent. Steroid hormones also showed a close relationship with antibiotics as 17-alpha-ethinylestradiol/ampicillin, ampicillin/progesterone, and ampicillin/testosterone. A strong positive correlation matrix of steroid hormones and antivirals was witnessed as lamivudine/progesterone and lamivudine/testosterone. These compounds are medical drugs mostly used by individuals at homes and hospitals to manage various diseases. Therefore, their relationships in wastewater influent may be linked to the wastewater from hospitals, industrial areas and households that are received by these WWTPs. Additionally, steroid hormones (17-alpha-ethinylestradiol and progesterone) were positively related to PCPs (triclosan) in wastewater influent suggesting a similar source of origin. The association of these contaminants may also be linked to hospital and domestic wastewater that are received by these WWTPs.

Moreover, wastewater effluent also showed strong positive correlations among various emerging contaminants (Figure 4.5). First and foremost, the amount of contaminants in wastewater influent may be a result of inability of WWTPs in removing them. Effluent samples showed strong positive correlations of atrazine/imidacloprid, atrazine/ simazine, atrazine/terbuthylazine, imidacloprid/simazine, imidacloprid/ terbuthylazine and simazine/terbuthylazine. which clearly suggest the same source of origin. These contaminants may be traced back to the stormwater runoff, and domestic wastewater.

The results of the correlation matrix in effluent samples showed strong positive correlations of contaminants such as 17-alpha-ethinylestradiol/ibuprofen, 17-alpha-ethinylestradiol/lamivudine and ibuprofen/lamivudine, which are medical drugs likely to be introduced into WWTPs by domestic and hospital wastewater. The correlation of other emerging contaminants such as imidacloprid/triclosan, and simazine/triclosan as well as testosterone/triclosan may also be linked to stormwater runoff, hospital, domestic and industrial wastewater entering these treatment works.

Table 4.5 Correlation matrix of emerging contaminants in wastewater treatment plants

Contaminants	*17a-ethinylestradiol*	*Ampicillin*	*Atrazine*	*Estradiol*	*Ibuprofen*	*Imidacloprid*	*Lamivudine*	*Progesterone*	*Simazine*	*Terbuthylazine*	*Testosterone*	*Triclosan*
					Wastewater influent							
17a-ethinylestradiol	1											
Ampicillin	**1.00**	1										
Atrazine	-1.00	-1.00	1									
Estradiol	0.00	0.00	0.00	1								
Ibuprofen	-1.00	-1.00	**1.00**	0.00	1							
Imidacloprid	**1.00**	**1.00**	-1.00	0.00	-1.00	1						
Lamivudine	**1.00**	**1.00**	-1.00	0.00	-1.00	**1.00**	1					
Progesterone	**1.00**	**1.00**	-1.00	0.00	-1.00	**1.00**	**1.00**	1				
Simazine	-1.00	-1.00	**1.00**	0.00	**1.00**	-1.00	-1.00	-1.00	1			
Terbuthylazine	**1.00**	**1.00**	-1.00	0.00	-1.00	**1.00**	**1.00**	**1.00**	-1.00	1		
Testosterone	**1.00**	**1.00**	-1.00	0.00	-1.00	**1.00**	**1.00**	**1.00**	-1.00	**1.00**	1	
Triclosan	**1.00**	**1.00**	-1.00	0.00	-1.00	**1.00**	**1.00**	**1.00**	-1.00	**1.00**	**1.00**	1
					Wastewater effluent							
17a-ethinylestradiol	1											
Ampicillin	0.00	1										
Atrazine	-1.00	0.00	1									
Estradiol	0.00	0.00	0.00	1								
Ibuprofen	**1.00**	0.00	-1.00	0.00	1							
Imidacloprid	-1.00	0.00	**1.00**	0.00	-1.00	1						
Lamivudine	**1.00**	0.00	-1.00	0.00	**1.00**	-1.00	1					
Progesterone	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1				
Simazine	-1.00	0.00	**1.00**	0.00	-1.00	**1.00**	-1.00	0.00	1			
Terbuthylazine	-1.00	0.00	**1.00**	0.00	-1.00	**1.00**	-1.00	0.00	**1.00**	1		
Testosterone	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1	
Triclosan	-1.00	0.00	**1.00**	0.00	-1.00	**1.00**	-1.00	0.00	**1.00**	**1.00**	0.00	1

Notation: Numbers in bold represent positive strong and moderate correlations.

4.3.2 Source identification with the hierarchical cluster analysis

The hierarchical cluster analysis technique was also used to determine the sources of emerging contaminants in the Modder River catchment during the spring season. According to the hierarchical cluster method, the most possible observations fell within the same cluster (Rashid et al., 2022). In this study, emerging contaminants within the same clusters were considered as emanating from the homogenous pollution sources. Table 4.6 provides a simplified analysis of the clusters identified in this study.

Table 4.6 Simplified analysis of clusters identified for emerging contaminants in water sources within the Modder River catchment

Water sources	Cluster group	Nodes	Contaminants cluster	Possible pollution sources
Rivers	C1	1	17-alpha-ethinylestradiol	Wastewater effluent, illegal dumping, stormwater runoff, and domestic sewage
	C2	1	Simazine	Agricultural runoff, stormwater runoff, wastewater effluent
	C3	2	Atrazine and terbuthylazine	Stormwater runoff, agricultural runoff, wastewater effluent
	C4	8	Ampicillin, testosterone, progesterone, lamivudine, estradiol, ibuprofen, imidacloprid and triclosan	Wastewater effluent, agricultural runoff, illegal dumping, stormwater runoff, and domestic sewage
Dams	C1	7	Progesterone, lamivudine, imidacloprid, ibuprofen, estradiol, testosterone, and ampicillin	Wastewater effluent, sewage runoff, illegal dumping, and stormwater runoff
	C2	2	Atrazine and triclosan	Agricultural runoff, stormwater runoff, wastewater effluent
	C3	2	Simazine and terbuthylazine	Agricultural runoff, stormwater runoff, wastewater effluent
	C4	1	17-alpha-ethinylestradiol	Wastewater effluent, illegal dumping, stormwater runoff, and domestic sewage
Influent	C1	1	Lamivudine	Domestic, industrial, and hospital wastewater
	C2	2	Ibuprofen and 17-alpha-ethinylestradiol	Domestic, industrial, and hospital wastewater, urban stormwater
	C3	8	Progesterone, testosterone, imidacloprid, estradiol, triclosan, terbuthylazine, atrazine and simazine	Domestic, industrial, and hospital wastewater, urban stormwater
	C4	1	Ampicillin	Domestic, industrial, and hospital wastewater
Effluent	C1	1	17-alpha-ethinylestradiol	As a result of inefficient removal, contaminants end up in effluent; thus, they can be linked to received domestic, industrial, and hospital wastewater as well as urban stormwater
	C2	1	Lamivudine	
	C3	7	Imidacloprid, triclosan, estradiol, progesterone, testosterone, ampicillin, and ibuprofen	
	C4	3	Atrazine, simazine and terbuthylazine	
Treated water	C1	8	Ampicillin, triclosan, testosterone, estradiol, ibuprofen, imidacloprid, lamivudine and progesterone	Reservoirs used as a source of water for water treatment plants are polluted by wastewater effluent, agricultural runoff, illegal dumping, urban surface runoff and domestic sewage, thus leading to detection
	C2	2	Atrazine, and terbuthylazine	
	C3	1	Simazine	

C4	1	17-alpha-ethinylestradiol	of this contaminants in treated drinking water

4.3.2.1 Identification of pollution ways in rivers

The hierarchical cluster analysis in rivers clustered the 12 targeted emerging contaminants into four clusters, as highlighted in Figure 4.5 and presented in Table 4.6. Cluster 1 is characterised by one contaminant (17-alpha-ethinylestradiol) that may be linked to wastewater effluent, illegal dumping, stormwater runoff, and domestic sewage. Cluster 2 is characterised by one contaminant (simazine) that may be linked to agricultural runoff, stormwater runoff, and wastewater effluent. Cluster 2 is characterised by two contaminants (atrazine and terbuthylazine) that may be linked to stormwater runoff, agricultural runoff, and wastewater effluent, while Cluster 4 is characterised by eight contaminants (ampicillin, testosterone, progesterone, lamivudine, estradiol, ibuprofen, imidacloprid and triclosan), which may be linked to wastewater effluent, agricultural runoff, illegal dumping, stormwater runoff, and domestic sewage.

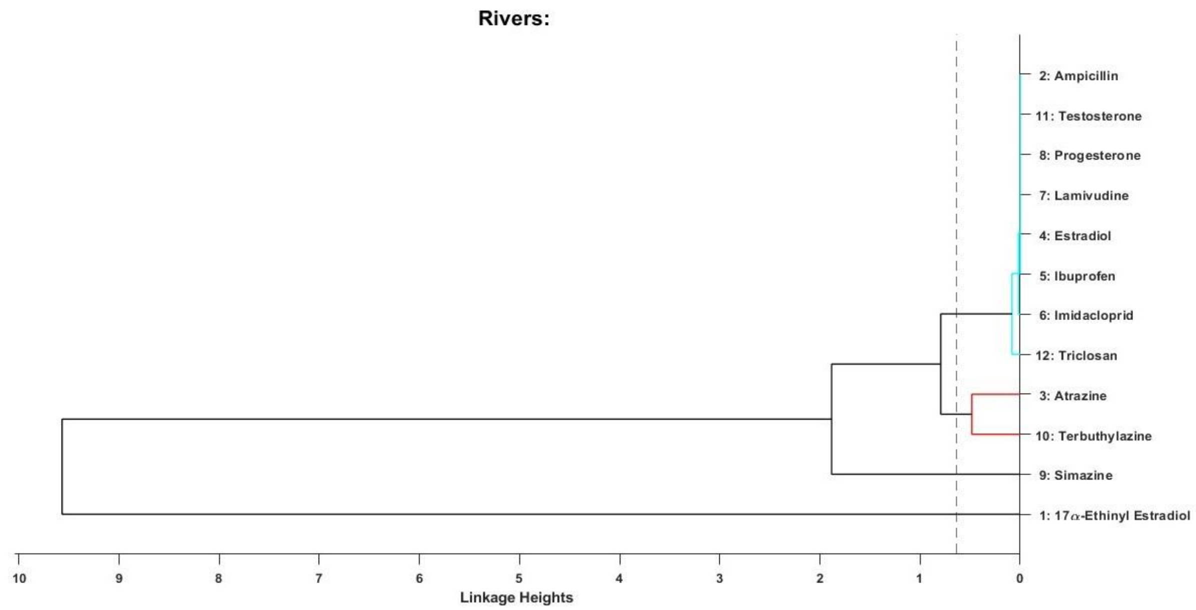


Figure 4.5 Cluster diagram showing similarities of emerging contaminants in rivers

Agricultural activities that surround most of the rivers within the Modder River catchment may influence the occurrence of pesticides in rivers as a result of agricultural runoff. The application of herbicides to manage weeds and insecticides to manage insects in households, around the city centres, public parks, and industrial areas in the city of Bloemfontein may also lead to the detection of traces of pesticides due to urban stormwater runoff. In other studies, agricultural runoff and urban surface runoff were also identified as the potential sources of pesticides in natural water sources (Hou et al., 2022). Moreover, it was also observed during field sampling that some farmhouses had septic tanks, rivers received effluent from WWTPs, surrounded by activities such as animal husbandry, and polluted by household waste from nearby settlements. Therefore, it is reasonable to link emerging contaminants such as ibuprofen, estradiol, triclosan, progesterone, testosterone and 17-alpha-ethinylestradiol to domestic sewage leakage (from septic tanks at farmhouses), discharge of wastewater effluents in streams, runoff from animal husbandry, and illegal dumping of household waste (containing unused or expired drugs) nearby the streams. In many parts of the world, human activities such as crop production, animal husbandry, illegal dumping, and wastewater effluents have been pinpointed as main potential sources of many organic chemical pollutants in water sources (Bella-Atangana et al., 2023; Rashid et al., 2022).

4.3.2.2 Identification of pollution ways in dams

The hierarchical cluster analysis in dams also clustered the 12 targeted emerging contaminants into four clusters, as highlighted in Figure 4.6 and presented in Table 4.6. Cluster 1 is made up of seven nodes characterised by contaminants such as progesterone, lamivudine, imidacloprid, ibuprofen, estradiol, testosterone, and ampicillin, which linked very well to wastewater effluent, sewage runoff, illegal dumping, and stormwater runoff. Cluster 2, made up of two nodes characterised by contaminants, atrazine and triclosan, linked very well to agricultural runoff, stormwater runoff, and wastewater effluent. Cluster 3, made up of two nodes with two contaminants, simazine and terbuthylazine, linked to wastewater effluent, illegal dumping, stormwater runoff, and domestic sewage, while Cluster 4 was made up of only one node, 17-alpha-ethinylestradiol, linked to domestic, industrial, and hospital wastewater.

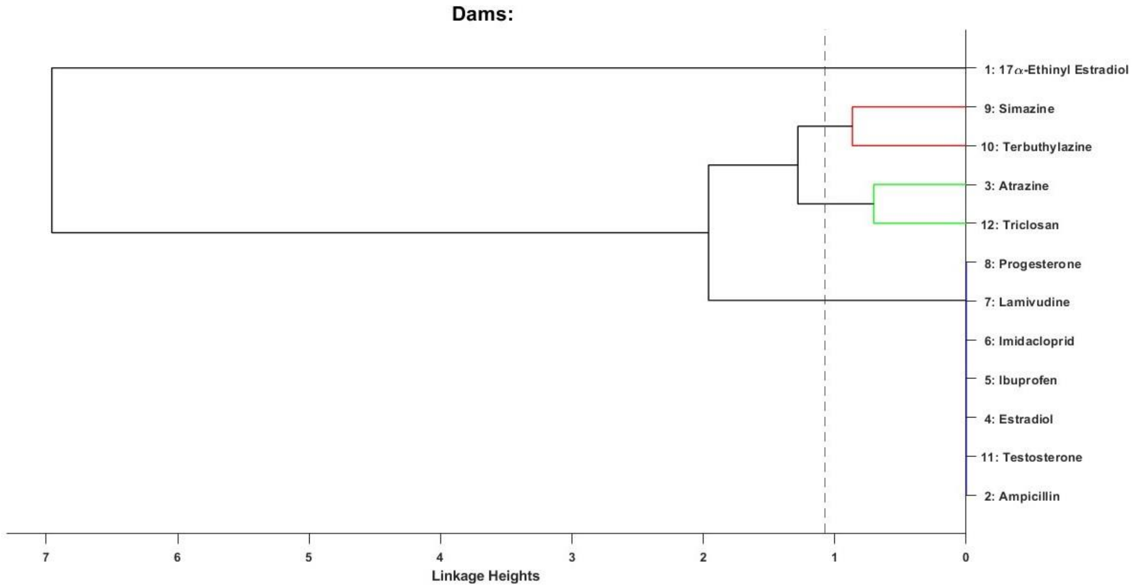


Figure 4.6 Cluster diagram showing similarities of emerging contaminants in dams

Agricultural activities, namely crop production and animal husbandry, are the most prominent around the Modder River catchment. Therefore, agricultural runoff may be a contributing factor to the existence of some contaminants in surface water such as dams. Hou et al. (2022) also reported agricultural runoff as the potential source of organic substances in surface water sources. Illegal dumping of domestic waste may also introduce traces of emerging contaminants in local reservoirs or dams as some of them are open to the public for picnics, aquatic sports activities and events at conference centres. Illegal dumping of domestic waste was also cited by other authors as the potential pathways of chemical water contamination (Rashid et al., 2019).

There was a sewage runoff from a nearby settlement flowing into one of the dams during field work, which may contribute to traces of some antiviral, antibiotics, steroid hormones and PCPs detected in this study. Other studies have also identified urban sewage and domestic wastewater discharge as main potential sources of many chemical pollutants in water sources (Das, 2022). Emerging contaminants are continuously released in trace amounts into receiving streams due to inefficiency of WWTPs to remove those contaminants (Gosset et al., 2021). Considering this case, these contaminants ended up being introduced into local reservoirs or dams during the recharging period.

4.3.2.3 Identification of pollution ways in tap waters

The hierarchical cluster analysis in tap water also generated four clusters as highlighted in Figure 4.7 and presented in Table 4.6. In Cluster 1, eight contaminants – ampicillin, triclosan, testosterone, estradiol, ibuprofen, imidacloprid, lamivudine and progesterone – were clustered together. In Cluster 2, two contaminants – atrazine and terbuthylazine – were clustered together. In Cluster 3, one contaminant, namely simazine, was observed, while in Cluster 4, one contaminant, namely 17-alpha-ethinylestradiol, was observed.

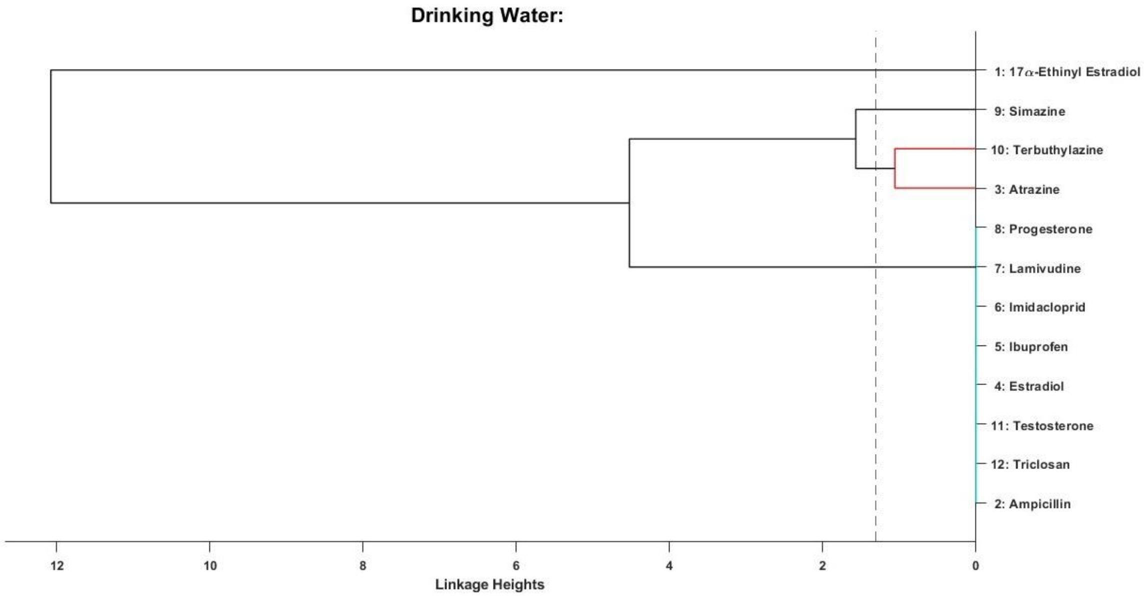


Figure 4.7 Cluster diagram showing similarities of emerging contaminants in tap water

It is reasonable to conclude that dams that are regarded as a source of water for water treatment plants are polluted by wastewater effluent, agricultural runoff, illegal dumping, urban surface runoff and domestic sewage. This status quo lead to the detection of these contaminants in treated drinking water as a result of inefficient removal by the treatment method currently used in water treatment plants. Therefore, managers of water treatment plants should continuously monitor their reservoirs in order to implement innovative treatment techniques that can remove the selected contaminants in this study.

4.3.2.4 Identification of pollution ways in wastewater treatment plants

Sources of emerging contaminants in wastewater treatment influent were determined as shown in Figure 4.8 and summarised in Table 4.6. Cluster 1 is a host of one contaminant (lamivudine) linked to domestic, industrial, and hospital wastewater. Cluster 2 is a host of two contaminants – ibuprofen and 17-alpha-ethinylestradiol – linked to domestic, industrial, hospital wastewater and urban stormwater. Cluster 3 is a host of eight contaminants – progesterone, testosterone, imidacloprid, estradiol, triclosan, terbuthylazine, atrazine, and simazine – linked to domestic, industrial, and hospital wastewater, as well as urban stormwater. Moreover, Cluster 4 is a host of one contaminant – ampicillin – linked very well to domestic, industrial, and hospital wastewater.

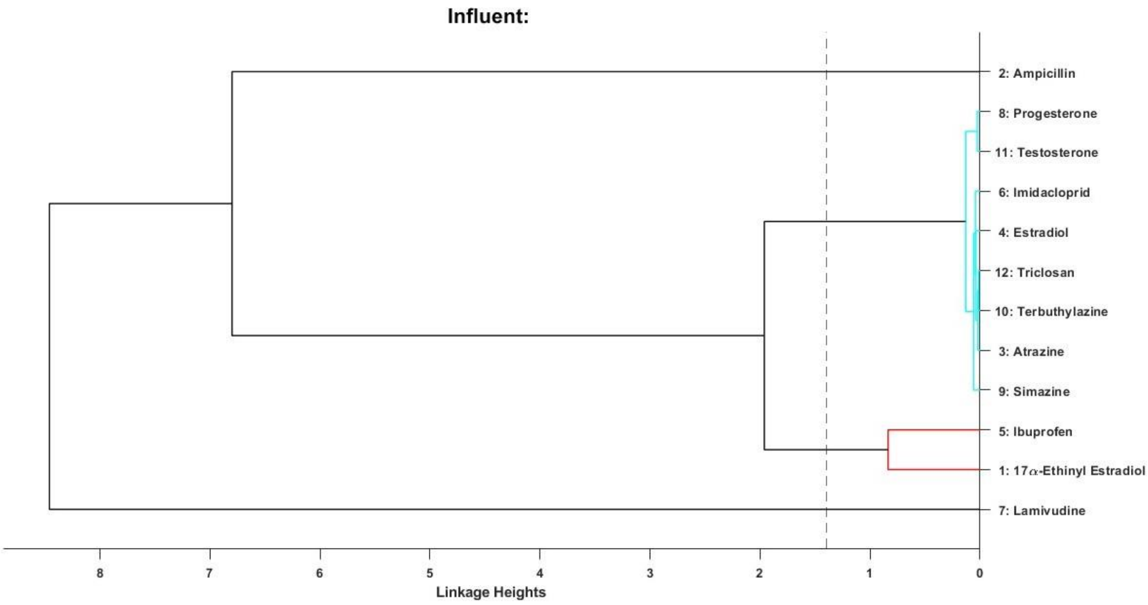


Figure 4.8 Cluster diagram showing similarities of emerging contaminants in wastewater influents

In this area, WWTPs received all sorts of wastewater such as domestic, industrial, and hospital wastewater. Lim et al. (2017) also indicated that WWTPs receive wastewater from various areas containing various chemical pollutants, which support the situation in this study. Therefore, it is rational to deduce domestic wastewater, industrial wastewater, hospital wastewater and urban stormwater as carriers of these contaminants in wastewater influents in this study. Domestic and hospital wastewater are considered as the major sources of medical drugs (Khan et al., 2021; Ulvi et al., 2022). Urban stormwater may also introduce emerging contaminants such as medical drugs as a result of illegal dumping of unwanted medications in residential and industrial areas (Rodriguez-Mozaz et al., 2015). Moreover, urban stormwater may introduce traces of pesticides in WWTPs due to the use of sewage sludge to ensure soil fertility in community gardens, recreational parks, and other public areas in this study area (Čelić et al., 2019).

Moreover, in wastewater effluent during the spring season, Cluster 1 contained one contaminants (17-alpha-ethinylestradiol); Cluster 2 contained one contaminant (lamivudine); Cluster 3 contained seven contaminants (imidacloprid, triclosan, estradiol, progesterone, testosterone, ampicillin, and ibuprofen), and Cluster 4 contained three contaminants (atrazine, simazine and terbuthylazine) as shown in Figure 4.9 and summarised in Table 4.6. As a result of inefficient removal, contaminants end up in effluent. Thus, they can be linked to received domestic, industrial, and hospital wastewater as well as urban stormwater.

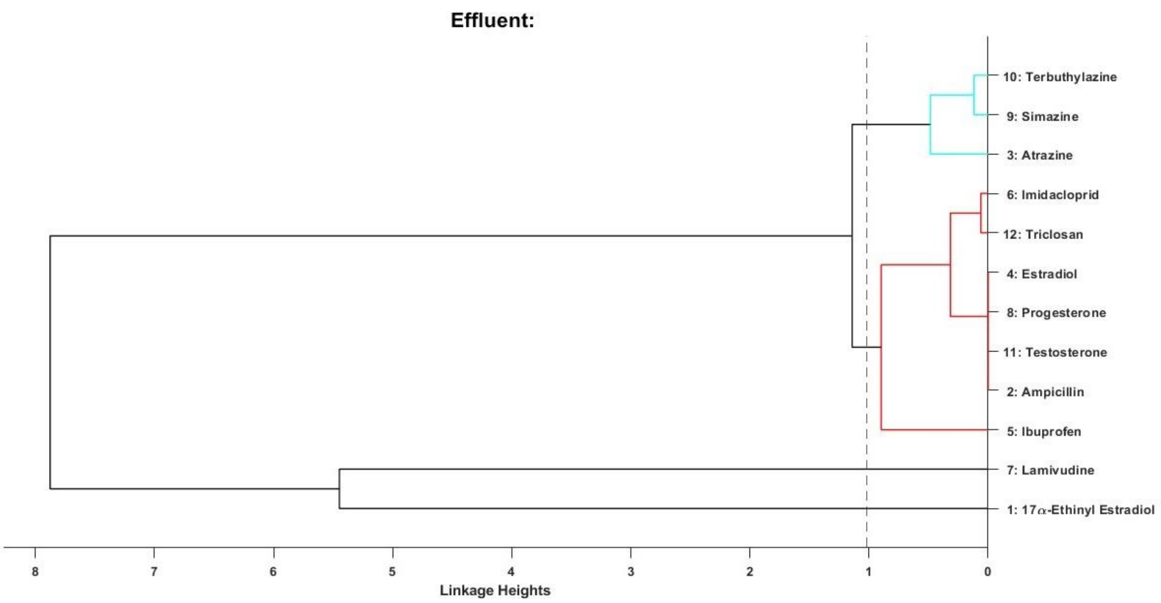


Figure 4.9 Cluster diagram showing similarities of emerging contaminants in wastewater effluents

The amount of emerging contaminants in effluent samples may be first defined as the inability of WWTPs to remove them. According to Kuroda et al. (2021), frequently used conventional WWTPs are not intended to remove emerging contaminants, which was also the case in this area. Therefore, many emerging contaminants go over conventional WWTPs without sufficient treatment. Thus, their occurrence in effluents may be linked to received domestic, industrial, and hospital wastewater as well as urban stormwater. Most of the wastewater effluents are released into rivers that introduce emerging contaminants in surface water receiving rivers (Lim et al., 2017).

4.4 Emerging contaminant pollution control measures along the Modder River catchment

From the results of source apportionment in this study, emerging contaminants are introduced in water sources mainly as a result of wastewater effluents, domestic sewage, urban surface runoff, agricultural runoff, and illegal dumping. Therefore, the following mitigation measures are suggested to limit their further introduction.

4.4.1 Agricultural runoff

The Modder River catchment is surrounded by various agricultural activities such as crop production and animal husbandry. These activities may necessitate the use of herbicides for maintenance of various crops, while animal husbandry may require the use of medical drugs (i.e. estradiol) for the health of livestock. Consequently, these contaminants may end up in water sources. According to Gozzo et al. (2023), one of the leading reasons of emerging contaminant pollution is rigorous agriculture, excretion through faeces, urine during the free grazing of animals, manure spreading on land, and contamination via runoff; therefore, decreasing both rigorous farming and the usage of animal drugs are vital in protecting the Modder River catchment. Furthermore, improvements in agricultural practices may protect water resources and also contribute to the reduction of threats related to the occurrence of emerging contaminants (Topp et al., 2008).

4.4.2 Urban stormwater runoff

Emerging contaminants in stormwater can be caused by overflow in combined sewer systems, runoff, and unlawful dumping of wastewater and unsealed systems. Furthermore, a number of practices, including the use of solid waste from WWTPs as soil amendments, the irrigation of reclaimed wastewater, the use of slurry and liquid manure as fertilisers, and the urination and defecation of pets and grazing animals, are linked to the contamination of surface runoff by emerging contaminants. Pesticides from parks, golf courses, and residential buildings may find their way into stormwater drains, rivers, and nearby water reservoirs via rainwater. In the Modder River watershed, improving non-point source pollution control strategies should also be given top priority. This includes installing infrastructure upgrades such as rainwater and sewage separation systems. These actions can successfully prevent emerging contaminants from the land from entering water sources in the Modder River catchment (Caban and Stepnowski, 2021).

4.4.3 Improper domestic waste disposal

Illegal dumping of domestic waste containing unused or expired medical drugs near some of the dams and rivers was witnessed. This situation may be a result of absence of information about the effect that organic contaminants may have on the environment. Therefore, educating people to segregate wastes at the source and provide incentives to facilitate waste segregation may reduce illegal dumping in the area (Kihila et al., 2021). Local communities should be educated on the proper waste disposal methods and the environmental implications of illegal dumping.

4.4.4 Domestic sewage overflow

Domestic sewage overflows were considered to be the most important sources for the release of emerging contaminants into water sources. From the field observations, some of the raw domestic sewage water overflows were channelled towards surface water. This situation means that the majority of contaminants enter the water sources without the necessary treatment. Considering the increase in intensity and frequency of rainfall as a result of climate change, technical measures in the design of the sewerage system are required in this area in order to reduce emission from these sources (Bourgin et al., 2018).

4.4.5 Wastewater effluent discharge

According to Wang et al. (2015), no conventional WWTPs were constructed to eliminate emerging contaminants. The inability of WWTPs to remove emerging contaminants creates major points of release of emerging contaminants into the water environment as they are mostly discharged in the nearby streams. Governments should financially support current WWTPs in developing and implementing advanced treatment technologies (i.e. ozonation) for the removal of emerging contaminants (Gozzo et al., 2023). This should be followed by setting up performance indicators to assess the performance of a WWTPs towards the removal of emerging contaminants.

Chapter 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The aim of the project was to investigate emerging contaminants along the Modder River catchment in the Free State province of South Africa. Therefore, the following are conclusions and recommendations from this study.

5.2 Investigation of emerging contaminants along the Modder River catchment

Investigating emerging contaminants in the Modder River catchment add to the existing database of the occurrence of emerging contaminants around the region and country. The quantification of targeted compounds such as 17-alpha-ethinylestradiol, ampicillin, atrazine, estradiol, ibuprofen, imidacloprid, lamivudine, progesterone, testosterone, simazine, terbuthylazine and triclosan along the Modder River catchment provided a much-needed initial measurement of these contaminants. The majority of these contaminants have been detected in measurable concentrations in all water sources. Most notably were the concentrations of 17-alpha-ethinylestradiol, which showed the highest concentrations in rivers, dams, and tap water. Lamivudine showed the highest average concentrations in wastewater influent and effluent.

These contaminants should be listed as priority pollutants in future pollution monitoring studies along the Modder River catchment. WWTPs along the Modder River catchment are unable to completely eliminate the majority of emerging contaminants. In addition, tap water was also found to have traces of emerging contaminants which is a public health concern. It can be concluded that the Modder River catchment is exposed to emerging contaminant pollution. In South Africa, effluent is normally released into nearby water sources, introducing contaminants into water sources. These situations may impair the ecosystem in the long run. Detection of traces of emerging contaminants in drinking water may lead to serious health risks such as cancer among the consumers in the long run. The outcomes of this study will raise awareness on the existence of emerging contaminants in the Modder River catchment. It may also facilitate the need to develop regulations aimed at reducing the spread of emerging contaminants in the Modder River catchment and other parts of the country.

5.3 Sources and pathways of emerging contaminants along the Modder River catchment

The multivariate statistical analysis put forward that the Modder River catchment is vulnerable to pollution by emerging contaminants as a result of man-made activities such as wastewater effluents, domestic sewage, urban surface runoff, agricultural runoff, and illegal dumping. The outcomes of the study will help in developing the necessary countermeasures for environmental protection and the sustainability of water resources. This work may also facilitate the management of existing and future sources of pollution by emerging contaminants within the Modder River catchment. Moreover, the adoption of the suggested mitigation measures in this study may be helpful in reducing pollution of emerging contaminants in the Modder River catchment.

5.4 Recommendations

From the findings of the study, the following recommendations can be made:

- Investigation and monitoring of emerging contaminants in groundwater should be prioritised in the future.
- Future studies should focus on individual and a mixture of ecological risks of emerging contaminants in the area.
- Application of advanced treatment methods for complete elimination of emerging contaminants is recommended.
- Residents within the Modder River catchment should be educated on segregating waste at the source.
- Decreasing both rigorous farming and the use of animal drugs could be crucial to guarantee the quality of surface water within the Modder River catchment.
- New WWTPs that receive and discriminate industrial, domestic, and hospital wastewater should be constructed.

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APPENDIX A

Collection of Water Samples

Collection of water samples at (A) Renosterspruit, (B) Bloemspruit, (C) Koringspruit, (D) Modder River, and (E) Klein Modder River

Collection of water samples at (A) Maselspoort, (B) Mockes Dam, (C) Krugersdrift Dam, (D) Seroalo Dam, and (E) Rustfontein Dam


A (in)
A (ef)
B (in)
B (ef)

APPENDIX B

Target Analytes Multiple Reaction Monitoring, Transition Values

Positive ionization mode		
Q1 (m/z)	**Q3 (m/z)**	**ANALYTE**
202.0	132.1	Simazine 1
202.0	104.1	Simazine 2
216.1	104.0	Atrazine 1
216.1	174.0	Atrazine 2
230.0	95.2	Lamivudine 1
230.0	69.0	Lamivudine 2
230.0	174.0	Terbuthylazine 1
230.0	68.0	Terbuthylazine 2
256.0	209.2	Imidacloprid 1
256.0	175.1	Imidacloprid 2
289.2	97.0	Testosterone 1
289.2	109.0	Testosterone 2
315.3	97.0	Progesterone 1
315.3	79.0	Progesterone 2
350.1	160.0	Ampicillin 1
350.1	114.1	Ampicillin 2

Negative ionization mode		
Q1 (m/z)	**Q3 (m/z)**	**ANALYTE**
205.0	161.1	Ibuprofen 1
205.0	159.0	Ibuprofen 2
271.2	145.0	Estradiol 1
271.2	182.9	Estradiol 2
286.9	35.0	Triclosan 1
286.9	33.9	Triclosan 2
295.2	144.9	17α ethynylestradiol 1
295.2	159.0	17 α ethynylestradiol 2

APPENDIX C

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RESEARCH TRENDS ON ENDOCRINE DISRUPTORS COMPOUNDS AND PERSONAL CARE PRODUCTS AS EMERGING CONTAMINANT IN SOUTH AFRICAN WATER SYSTEMS

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GRAPHICAL ABSTRACT

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ABSTRACT

The presence of pharmaceuticals, herbicides, endocrine disruptors and personal care products have recently attracted the interest of researchers due to their concern with regards to a wide variety of human health risk arising from their prevalence in surface waters resulting from inadequate waste water treatment processes. In this study, a recent trend in the fate and occurrence of personal care products such as (triclosan, nitro, polycyclic, macrocyclic musk, surfactants, Alkyl-phenol, Ethylates, 4-nonylphenol carboxylates, octylphenol) and endocrine disrupting compounds such as (17B-estradiol, estriol, estrone, alkylphenols, bisphenols A) will be reviewed for South Africa. These compounds are found at wastewater treatment plants, domestic and industrial pathways, agricultural sources and surface waters of South Africa. Sample analysis includes extraction with solid phase process of chemical compounds, with techniques such as liquid chromatography, Gas chromatography (GM), Mass spectrometry (MS) and high performance Liquid chromatography (HPLC). The identification and quantification of these emerging chemical compounds in surface waters and wastewaters has become a major scientific responsibility which is lacking regulation currently in South Africa especially when endocrine disruptors' compounds and personal care products have been detected to impact pregnant women and hormones of human adversely.

Keywords: emerging contaminants, endocrine disrupting compounds (EDCs), personal care product (PCPs), environmental waters

1. INTRODUCTION

Fresh water is one of the essential resources for the support of all life on earth. It is well recognized that anthropogenic activities are creating a huge amount of pressure on the water quality, and through such human activities, pollutants are entering fresh water systems [1]. There has recently been an exponentially growing concern regarding synthetic chemical pollutants that reach our aquatic environment [2]. Emerging contaminants (EC) are pervasive in environmental waters and are raising a concern due to their potential risks on human health and the environment [3]. Emerging contaminants are part of environmental pollutions which were linked to ancient times with the main focus then on the regulated pollutants that impacted human health with antecedent ecological effects [4].

[5] pointed out the history of emerging contaminants since it was discovered in water and aquatic environment due to the improvement in science and technology. Since the discovery of ECs, around 1970's in the USA, leading countries in studies of emerging contaminants are Canada, Japan, USA and China and Germany [5]. Africa is reported to lack behind in the study of EC even though there have been recent improvements and developments [6, 5, 7, 8, 9,]. However, countries like South Africa, Tanzania and Zambia has contributed into studying the extent of emerging contaminants in their water systems [1, 2, 6, 9, 10, 11].

Types of ECs that has adverse effects on human health and the environment are antibiotics, pharmaceuticals, personal care products (PCPs), hormones, artificial sweeteners and illicit drugs. These are recognised class of water contaminants in surface waters and underground waters due to their unregulated state. Globally, these contaminants are known as emerging because they lacked standards and guidelines for their environmental monitoring [5, 12]. The attention these emerging contaminants are receiving is due to recent development of

APPENDIX D

Technical Editing Letter

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CONFIRMATION OF EDITING AND PROOFREADING

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Yours sincerely

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