INVESTIGATION AND MONITORING OF EMERGING CONTAMINANTS FROM POINT SOURCES ON THE MODDER RIVER CATCHMENT SYSTEM IN THE FREE STATE, SOUTH AFRICA

Report to the
Water Research Commission

by

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EXECUTIVE SUMMARY

BACKGROUND

The existence of emerging pollutants in water sources is largely unregulated by legislation and they do not have to be extremely persistent to cause environmental health effects as their decay is counterbalanced by their incessant introduction. The accumulation and detection of levels of these emerging contaminants in water sources has reduced water quality and made water risky for aquatic and human life. The quantity of these emerging contaminants is likely to upsurge in water sources as a result of the rise in population density, which is a community health problem. Exposure to organic pollutants has been reported to lead to health implications such as endocrine-disruption, immunotoxicity, neurological disorders, reductions in fertility, spontaneous abortions, birth defects, poisoning of genes, sexual organ annoyance, resistance of antibiotics, and congenital disorders, even at low concentrations. Thus this project, which is the first in the Free State province, was undertaken to investigate and monitor emerging contaminants from point sources on the Modder River catchment system in the Free State, South Africa.

AIMS

The following aims were set for the project:

1. To detect the types of emerging contaminants prevalent in the surface water bodies of the Modder River catchment of South Africa, particularly those close to the city of Bloemfontein.
2. To detect the concentration levels of emerging contaminants that may be a health risk.
3. To determine the major sources and pathways of emerging contaminants within the Modder River catchment system.

METHODOLOGY

In order to identify and monitor the presence of emerging contaminants in the Modder River catchment, samples were collected using a grab sampling method from water sources such as rivers (n = 5), dams (n = 5), treated drinking water (n = 2), wastewater influent (n = 3) and wastewater effluent (n = 3) during the spring-, summer-, autumn- and winter seasons. All collected samples (n = 72) were stored in a cooler box filled with ice and transported to the laboratory and then stored in a 4°C fridge prior to extraction. The solid-phase extraction cartridges (Strata C18, 6 mℓ) from Phenomenex (Torrance, LA, US) were used for extraction of the samples. The analysis was performed on a high-performance liquid chromatography linked to a hybrid triple quadrupole ion trap mass spectrometer (ABSCIEX 4000, Framingham, MA, US). Environmental risk assessment of individual compounds were assessed by a risk quotient (RQ) method, while risk mixture (RQmix) and toxic unit sum (TUsum) methods were adopted to assess mixture risks of identified compounds. Moreover, multivariate statistical methods such as the Pearson correlation, principal component analysis and hierarchical cluster analysis were used to determine the sources and pathways of emerging contaminants in the Modder River catchment.

RESULTS AND DISCUSSION

The results of qualitative screening revealed the presence of various classes of emerging contaminants such as stimulants, non-steroidal anti-inflammatory drugs, Illicit drugs, lipid regulators, antiepileptic drugs, antibiotics, antidepressants, antidiabetic drugs, beta-blockers, antivirals, diuretics, herbicides, fungicides, and insecticides in water sources within the Modder River catchment. From these groups of emerging contaminants, herbicides and stimulants were the most commonly detected contaminants. In the quantitative

analysis of targeted compounds such as acetaminophen, carbamazepine, ibuprofen, triclosan, atrazine, metolachlor, simazine, terbuthylazine, 17-alpha-ethinylestradiol, estradiol, progesterone and testosterone, the mean concentrations of 17-alpha-ethinylestradiol showed to be the highest in all water sources in all seasons. Generally, the autumn season recorded the highest mean concentrations of emerging contaminants in all water sources, except in treated drinking water. The results of the ecological risk assessment indicated that the majority of targeted compounds have the possibility to contribute to high ecological risks. The risks of simazine, ibuprofen, 17-alpha-ethinylestradiol, atrazine and carbamazepine were most notable on all aquatic species in all water sources. Moreover, both RQmix and TUsum proved that the mixture of the targeted compounds is likely to contribute to high ecological risks. Multivariate statistical analysis revealed wastewater effluent discharge, illegal dumping, domestic sewage overflow, stormwater runoff and agricultural runoff as the possible sources of emerging contaminants within the Modder River catchment.

CONCLUSIONS

Investigating and monitoring of emerging contaminants for the first time in the Modder River catchment brings to an end the dearth of data on emerging contaminant pollution in the Free State province. The project has shed light that the Modder River catchment is vulnerable to pollution by emerging contaminants as a result of anthropogenic activities, and the aquatic ecosystem may be adversely affected by these contaminants. The outcomes of this study may be relevant for the prioritisation of hazardous substances in order to address suitable monitoring campaigns and any necessary countermeasures to be adopted for environmental protection and sustainability of water resources. This work may also facilitate the management of existing and future sources of emerging contaminant pollution within the Modder River catchment.

RECOMMENDATIONS

The following recommendations can be made:

- Monitoring of emerging contaminants should be expanded to groundwater sources.
- Additional groups of emerging contaminants should be targeted within the Modder River catchment.
- Wastewater treatment managers should conduct individual and mixture risk assessments before discharging effluent into nearby streams.
- Human health risk assessment studies of pesticide exposure through drinking water and vegetables irrigated by wastewater effluents in this study should be assessed.
- Development and implementation of advanced treatment technologies for the removal of broad-spectrum emerging contaminants with different properties is recommended.
- Residents within the Modder River catchment should be educated on segregating wastes at the source.
- Taking back unused or expired medications may help to mitigate their quantities in the aqueous environment and their possible health risks.
- Reducing both intensive farming and the use of livestock drugs could be crucial to warrant the quality of surface water within the Modder River catchment.

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ACRONYMS & ABBREVIATIONS

km	Kilometre
km^2	Square kilometre
ℓ	Litre
m	Metre
mg/ℓ	Milligram per litre
mℓ	Millilitre
ng/ℓ	Nanograms per litre
%	Percentage
ppb	Particle per billion
ppm	Particle per million
psi	Pounds per square inch
µg/ℓ	Micrograms per litre
2,4-D	2,4-Dichlorophenoxyacetic acid
BLD	Below limit of detection
BPA	Bisphenol A
CHE	Collaborative on Health and Environment
DEET	N-diethyl-meta-toluamide
EC_{50}	Effective concentration
FAO	Food and Agriculture Organization of the United Nations
GC	Gas chromatography
HPLC	High-performance liquid chromatography
HPLC-MS	High-performance liquid chromatography-mass spectrometry
HQ	Hazard quotient
LC	Liquid chromatography
LC-MS	Liquid chromatography-mass spectrometry
LC-MS/MS	Liquid chromatography-tandem mass spectrometry
LC_{50}	Lethal concentration
< LOD	Less than limit of detection
< LOQ	Less than limit of quantification
MCPA	2-methyl-4chlorophenoxyacetic acid
MEC	Measured environmental concentration
MMM	Mangaung Metropolitan Municipality
MRA	Mixture Risk Assessment
MRM	Multiple reaction monitoring
MS	Mass spectrometry
ND	Not detected
NOEC	No observed effect concentration
NSAIDs	Non-steroidal anti-inflammatory drugs

PC	Principal component
PCA	Principal component analysis
PCPs	Personal care products
PNEC	Predicted no-effect concentration
PPCPs	Pharmaceuticals and personal care products
RQ	Risk quotient
RQmix	Risk quotient mixture
SPE	Solid-phase extraction
THC-COOH	11-nor-9-carboxy-Δ9-tetrahydrocannabinol
TU	Toxic Unit
TUsum	Toxic Unit Summation
US	United States
V	Voltage
WHO	World Health Organization
WWTP	Wastewater Treatment Plant

GLOSSARY

Acute toxicity: Describes the adverse effects of a substance that result either from a single exposure or from multiple exposures in a short period of time.

Algae: A simple, non-flowering, and typically aquatic plant of a large group that includes seaweed and many single-celled forms.

Catchment: An area of land with a basin-like shape that is bordered by hills or mountains and from which surface and subsurface water flows into rivers, streams, and wetlands.

Chronic toxicity: The development of adverse effects as a result of long-term exposure to a contaminant.

Dam: A wall-like construction placed over a river or creek to stop water from flowing through the surrounding area.

Daphnids: Any member of *Daphnia* or a related genus, many of which are used as feed for aquarium fishes.

Ecological risk assessment: The process for evaluating how likely it is that the environment may be impacted as a result of exposure to one or more environmental stressors, such as chemicals, land-use change, disease, and invasive species.

Emerging contaminants: A man-made or naturally occurring organic compound that are not commonly investigated or regulated by legislation but have the possibility to trigger serious implications to the environment and public health.

Fish: Fish are aquatic, craniate, gill-bearing animals that lack limbs with digits.

Herbicides: Chemical substances widely used in agricultural production and other areas such as in forestry, parks, golf courses, and sports grounds.

Personal care products: Regarded as chemical compounds utilised mostly to increase grooming throughout day-to-day life.

Pharmaceuticals: Considered to be recommended, non-prescription, and beneficial animal medications, utilised to inhibit or treat ailments in humans and mammals.

River: A river is a body of water that resembles a ribbon and moves downward under the influence of gravity.

Steroid hormones: Natural or synthetic compounds widely used as contraceptives and for growth promotion in humans and animals.

Surface water: The water found on the earth's surface is known as surface water. It consists of marshes, lakes, rivers, reservoirs, and streams.

Treated drinking water: Any sort of water that has undergone processing to meet a specified end use is referred to as treated water.

Wastewater treatment plants (also known as wastewater treatment works): Characterised as a facility that combines a number of processes, including physical, biological, and chemical processes, to clean up wastewater and turn it into effluent that can be recycled back into the water cycle.

CHAPTER 1: BACKGROUND

1.1 INTRODUCTION

Urbanisation, industrialisation, rising living standards, and increased consumer demand have all contributed to increased air, soil, and water pollution caused by the release of various chemicals (Thomaidis et al., 2012; Vasilachi et al., 2021). Chemicals are an essential part of everyday life, with over 100 000 different chemicals produced and used by industries (Sanchez and Egea, 2018). Chemicals, according to Bwapwa and Jaiyeola (2019), enable the development of new technologies while also improving living standards and quality of life. Despite their importance in daily life, many chemicals are discharged into the aqueous environment (Sanchez and Egea, 2018). Water, as an indispensable means for life, is most exposed to pollution; as a result, water contamination has grown into a universal source of attention (Vasilachi et al., 2021). This is due to the fact that water is a foremost and important source for organic pollutants to reach the living organisms in the environment and impose their impacts through ingestion (Bwapwa and Jaiyeola, 2019). Chemicals in the water environment exhibit remarkable dynamics in terms of their grouping, which changes over time. However, innovations in detection methods for some chemicals in the aquatic environment have resulted in the documentation of a growing number of chemicals and their conversion products known as emerging contaminants (Vasilachi et al., 2021).

Emerging contaminants are natural or man-made tenacious organic substances that are not typically examined in the environment but have the possibility to cause effects on the environment and human health (Vasilachi et al., 2021). Emerging contaminants consist of an extensive collection of compounds, such as pesticides, cosmetics, personal and domestic care products, pharmaceuticals, hormones, and brominated flame retardants that are used universally and are essential for contemporary civilisation (Odendaal et al., 2015; Thomaidis et al., 2012). These numerous chemical compounds found in the water sources are derived from everyday man-made activities such as domestic, health care, aquaculture, agricultural, and industrial processes (Ramirez-Malule et al., 2020). Several direct and indirect conduits for the introduction of emerging contaminants into the aqueous environment are available (Yazdan et al., 2022), such as runoff or leakage (Ngqwala and Muchesa, 2020). They may occur in wastewater influent due to excretion, bathing, or direct disposal, and wastewater effluent discharge is one of the major conduits for emerging contaminants into rivers, dams and marine waters (Mhuka et al., 2020).

The presence of emerging contaminants in water sources, such as steroid hormones, personal care products, pesticides, and pharmaceuticals, have become widespread and of great concern in recent years due to their high potency and specificity of undesirable ecological effects when interacting with biological systems and human society (Huang et al., 2023). The issue of emerging pollutants is a constant challenge (Vasilachi et al., 2021), because their numbers are increasing all the time (Patel et al., 2019). According to Galindo-Miranda et al. (2019), transformation products of these compounds are frequently more toxic than the original compounds. Exposure to these contaminants may cause acute or chronic effects such as carcinogenic, mutagenic, and teratogenic effects, depending on their concentration and exposure level. Furthermore, chemical mixtures of emerging contaminants in water sources can be extremely hazardous to humans and aquatic life (Visca et al., 2021). Ma et al. (2020) also stated that their presence in water sources not only endangers aquatic and human life, but also impedes public and monetary development.

Given their incessant introduction into the aqueous environment and the impact on aquatic life and human health, qualitative screening and quantification of these compounds is required, particularly in water-stressed countries such as South Africa (Galindo-Miranda et al., 2019). While the number of studies investigating and monitoring the occurrence of emerging contaminants in South African water environments has increased (Madikizela and Ncube, 2021; Madikizela et al., 2020; Mashile et al., 2021; Odendaal et al., 2015; Ojemaye et al., 2022; Rimayi et al., 2019; Vumazonke et al., 2020; Wilkinson et al., 2022), there is still a dearth of studies

monitoring emerging contaminants, as well as their associated risks in the Modder River catchment in the Free State province. Furthermore, water sources faces substantial risks from both point and non-point source pollution, which act as major pathways for the enrichment of emerging contaminants in the Modder River catchment. However, there are no published studies determining the sources of emerging contaminants in the Modder River catchment. Therefore, this study is the first in the Modder River catchment in the Free State province aiming at quantifying the level of emerging contaminants in rivers, dams and treated drinking water. It also aims at assessing the risks and determine the major sources of these contaminants. The outcomes of this research may be very crucial in inhibiting water pollution from emerging contaminants for the protection and sustainability of the Modder River catchment in the Free State province of South Africa.

1.2 PROJECT AIMS

The following were the aims of the project:

1. To detect the types of emerging contaminants prevalent in the surface water bodies of the Modder River catchment of South Africa, particularly those close to the city of Bloemfontein.
2. To detect the concentration levels of emerging contaminants that may be of health risk.
3. To determine the major sources and pathways of emerging contaminants within the Modder River catchment system.

1.3 SCOPE AND LIMITATIONS

The scope of this study entailed:

- To detect the types of emerging contaminants prevalent in water sources within the Modder River catchment system in the Free State province.
- To assess the individual and mixture risks of emerging contaminants.
- To determine the major sources and pathways of emerging contaminants within the Modder River catchment system.

The limitations of this project included:

- Collecting water samples around the whole province of the Free State was impossible due to financial constraints and period of the study. Therefore, only water sources around the city of Bloemfontein were considered.
- Only a few groups of emerging contaminants were targeted in this study.
- The main challenges in risk assessment included limited occurrence of data about toxicological test assays, chronic and acute toxicity data of some emerging contaminants. The predicted non-effect concentration values were based on currently available data and may change as more reliable data becomes available.
- No human health risk assessment of emerging contaminants was assessed in this project.
- The study did not seek to implement means of mitigation, but only to inform local inhabitants, managers of wastewater treatment plants (WWTPs), farmers and the relevant authorities of the sources of emerging contaminants to their water sources and also the possibilities around reducing the ill-effects of emerging contaminants.

CHAPTER 2: LITERATURE REVIEW

2.1 INTRODUCTION

Environmental pollution has become the symbol of human existence ever since the industrial uprising (Manahil, 2017). Today, humanity regularly uses a wide-ranging group of man-made organic compounds for domestic activities, agricultural applications, industrial manufacturing, as well as human and animal health care (Llamas et al., 2020). The continuous manufacturing of new chemicals and their usages has now led to the type of pollutants recognised as emerging contaminants (Miraji et al., 2016). These are chemicals such as pharmaceuticals, personal care products, pesticides, and endocrine-disrupting compounds, which are utilised globally and crucial for modern society (Gavrilescu et al., 2014).

Many of these emerging contaminants are persistent in the environment as they are resistant to degradation, whereas others may not be persistent. However, their incessant introduction makes them a potential hazard to the environment (Pignotti, 2018). The increasing usage of these chemical compounds in households, hospitals, industries, transport, and agricultural activities leads to their introduction at increasing levels into various aqueous matrices such as surface water, groundwater, WWTP inflows and outflows (Oluwole et al., 2020) as harmful wastes and non-biodegradable substances (Lei et al., 2015). Emerging contaminants enter aqueous matrices due to the inflow of effluents from WWTPs, on-site wastewater disposal systems, street runoffs, agricultural fields, recreational activities, atmospheric deposition, animal feeding activities, sewer line leakages, landfill leachate and septic tank seepage (Daughton, 2009; Hoyett, 2018; Sharma et al., 2018; Wanda et al., 2017).

In South Africa and across many countries, emerging contaminants are of major concern (Gomes et al., 2018) because their presence in water matrices as harmful or non-degradable chemicals creates health risks to both aquatic ecosystems and human beings (Archer, 2018; Prieto-Rodriguez et al., 2012). Their concentration levels may possibly vary from as little as to a hundred micrograms per litre (Prieto-Rodriguez et al., 2012). To measure the concentration of emerging contaminants in micrograms per litre level, highly sensitive and selective instruments are needed. A review of the literature has revealed that gas chromatography (GC) connected to a mass spectrometry (MS) detector, liquid chromatography-mass spectrometry (LC-MS) and high-performance chromatography-mass spectrometry (HPLC-MS are the most efficient analytical techniques (Ojemaye, 2020).

Exposure to emerging contaminants either through ingestion or dermal contact may cause health implications such as endocrine-disruption, immunotoxicity, neurological disorders (Sanchez and Egea, 2018), reductions in fertility, spontaneous abortions, birth defects (Archer, 2018; Robins et al., 2011; Soto and Sonnenschein, 2010), gene toxicity, sex organs imposition, antibiotic resistance (Oluwole et al., 2020), mutagenesis, carcinogenesis, and congenital disorders (Ramírez-Malule et al., 2020). The rise in usage of synthetic compounds in South Africa and Africa as a whole, together with the absence of suitable waste disposal procedures, their level of occurrence in an aqueous environment and possible ecological and health implications highlight the need for constant monitoring and reporting of emerging contaminants in water matrices (Selwe et al., 2022). Therefore, this report provides an overview of emerging contaminants. To achieve this, concepts such as water as crucial natural resources, emerging contaminants, classification of emerging contaminants, and case studies of the occurrence of emerging contaminants in South Africa and other parts of the world have been reviewed. Furthermore, removal mechanisms, analytical procedures, theories of ecological and health risk assessments, possible implications of emerging contaminants, and mitigation measures are discussed.

2.2 WATER AS A CRUCIAL NATURAL RESOURCE

The most crucial resource on earth is water and it represents 70% of the globe (Malewandja, 2018). It is a necessity for existence of all living organisms (Inyinbor et al., 2018). Water offers sustenance and enables the circulation of oxygen within living cells (Moses, 2006). It also serves as a habitation for aquatic organisms and a reproduction home for some terrestrial organisms (Fawell and Nieuwenhuijsen, 2003). According to Adeleye (2016), continuous, safe and clean water supplies are requirements for a decent and healthy living. Rivers, dams, lakes, canals and groundwater are the main sources of required fresh water that are recharged by rainwater (Ojemaye, 2020).

Despite being a crucial natural resource, in most parts of the globe water is poorly managed and experiencing a deterioration in quality as a result of contamination from the discharge of domestic and industrial wastes (Fawell and Nieuwenhuijsen, 2003). The discharge of household and industrial wastewater has contributed to the rise in freshwater contamination and reduction of clean water resources (Edokpayi et al., 2017). According to Tau et al. (2021), water contamination is the condition whereby undesirable materials enter a water body and contaminate it. Today, the main ecological problem distressing the human race universally is the pollution of natural water as a result of industrial and chemical compounds. Most of these pollutants are present at low concentrations that can elevate serious toxicological concerns, especially when such compounds are present as constituents of combined mixtures (Inyinbor et al., 2018).

Numerous micro-pollutants are not completely removed by existing treatment methods and as a result they end up being introduced into the water environment (Luo et al., 2014). Some of these include pharmaceuticals, personal care products, pesticides, endocrine-disrupting compounds and many more emerging contaminants (Inyinbor et al., 2018). Consequently, the release of emerging contaminants into water bodies threatens both the aquatic and human life and are considered a serious danger or threat to sustainable water supply in South Africa (Edokpayi et al., 2017) and other parts of the world. Therefore, the pollution of natural water resources by emerging contaminants is a serious public threat that requires international consideration (Inyinbor et al., 2018).

2.3 EMERGING CONTAMINANTS

Organic compounds that were previously not recognised as important in freshwater are currently being detected due to the improvement of analytical techniques referred to as either contaminants of emerging concern or emerging contaminants (Czech and Ribinowska, 2013; Farre et al., 2012; Miraji et al., 2020; Pignotti, 2018; Sorensen et al., 2015). They are precisely well known as man-made or naturally occurring organic compounds or microorganisms not presently examined in the environment or regulated by legislation; however, they possess the possibility to trigger serious implications to the environment and public health (Miraji et al., 2016). Ojemaye (2020) described emerging contaminants as a subgroup of micro-contaminants occurring in the environment at low concentrations with clear chemical properties, structures, application ranges, and impacts. Furthermore, emerging contaminants are compounds released late into the environment, compounds that were present in the environment for a long time but identified recently due to the development of new analytical methods, and chemical compounds whose adverse health implications are just showing (Ojemaye, 2020).

These compounds are most often discovered in municipal sewage, daily household products, pharmaceutical production plants, wastewater, hospitals, landfills, and the natural water environment (Klamerth et al., 2012). Natural attenuation and conventional treatment processes are unable to remove these contaminants identified mostly in wastewater influent and effluent, surface water and drinking water (Bustos et al., 2015). Most emerging contaminants, predominantly organic ones, are insoluble in the water and are consequently transported as free pollutants or adsorbed on the surfaces of suspended matters or sediments in the direction of moving water (Miraji et al., 2020). Some of them are persistent in the environment, while others can have a fairly short lifecycle within the environment (Barbosa et al., 2016).

Emerging contaminants encompasses numerous compounds and various substances utilised in daily life (Dugas et al., 2016; Pignotti, 2018; Tijani et al., 2016). They are broadly classified as pharmaceuticals, personal care products, pesticides, industrial chemicals, illicit, non-controlled drugs and food additives, nanomaterial and endocrine-disrupting compounds (Gogoi et al., 2018; Ojemaye, 2020). These compounds may be detected at a concentration level ranging from as little as nanograms per litre to a few hundred micrograms per litre (Tran et al., 2013). However, they may have detrimental implications as they are incessantly introduced into water systems, thus exposing aquatic life species throughout their lifespan (Barbosa et al., 2016).

2.3.1 Pharmaceuticals

They are anthropogenic or natural chemical compounds used as a life supplement, to diagnose, treat, or prevent ailments in both people and animals. Pharmaceuticals are known to have dissimilar chemical structures, behaviour, applications and metabolism in both people and animal bodies (Fawell and Ong, 2012; Jiang et al., 2013). They are designed as specific bioactive compounds that interact with receptors in the human body and in animals, or to target specific infectious organisms (Kümmerer 2010) and induce specific biological responses at low doses (Galus et al., 2013a or b).

According to Miraji et al. (2016), pharmaceuticals are used for alteration of physiology and biochemical processes in human and animals in order to treat, diagnose or prevent ailments. They are classified as non-steroidal anti-inflammatory drugs (NSAIDs) (such as acetaminophen); antibiotics (such as ampicillin); β-blockers (such as atenolol); lipid regulators (such as clofibrate); Antiepileptics (such as carbamazepine); antipsychotic (such as thioridazine); antivirals (such as lamivudine); and human indicators or psychomotor stimulant (such as caffeine) (Ademoyegun, 2017; Jiang et al., 2013; Kanakaraju et al., 2014; Kanama et al., 2018).

The extensive use of pharmaceuticals by humans and for animals has contributed to their detection in the environment (Kümmerer, 2010). These pollutants are firm and manufactured to be robust, which make it impossible to be broken down by the current wastewater treatment processes. Furthermore, their polar and non-volatile nature leads to their partial elimination in WWTPs and subsequently in their discharge into the natural water resources (Baker and Kasprzyk-Hordern, 2013). They are regarded as pseudo-persistent contaminants, which frequently enter the water environment at concentrations ranging from nanograms per litre to low micrograms per litre (Gogoi et al., 2018; Kümmerer, 2010). Their frequent release may cause health effects to aquatic organisms and humans (Lindberg et al., 2007).

2.3.2 Personal care products

Personal care products (PCPs) are considered to be chemical compounds found mostly in customer products sold for human body use (Barcelo and Petrovic, 2007). Jiang et al. (2013) indicated that PCPs are manufactured for external human body use and in most cases, not for ingestion. These chemicals are found mostly in cosmetics, skin care, dental products, hair care products, sunscreen agents, soaps, antibacterial products, fragrances, and insect repellents (Barcelo and Petrovic, 2007). They are classified into compounds such as fragrance (e.g. polycyclic musks), preservatives (e.g. parabens), antiseptics (e.g. triclosan) and sunscreen (e.g. benzophenone) (Fawell and Ong, 2012; Miraji et al., 2016; Ojemaye, 2020).

Even though PCPs are non-recommended products, they are overused and directly discharged into the aqueous environment. Their direct discharge into the environment is mainly through consistent usage in showering, spraying, washing of clothes, swimming, sunbathing and improper disposal (Barcelo and Petrovic, 2007; Miraji et al., 2016; Ojemaye, 2020). They are released into wastewater and advanced toward WWTPs in their original or biologically transformed structures (Gogoi et al., 2018). Effluents and surface water have been found to contain concentrations of PCPs and their metabolites as a consequence of their lipophilic nature and non-biodegradability (Jiang et al., 2013; Kasprzyk-Hordern et al., 2008; Ojemaye, 2020).

2.3.3 Pesticides

Pesticides are chemicals or chemical compounds manufactured with the intention to destroy, prevent or control pests, unwanted plants or animals. The Food and Agriculture Organization of the United Nations (FAO, 2003) described pesticides as chemicals used in the production, processing, storage, transport of food, farm produce, animal feedstuffs, wood and wood commodities, or chemicals used to control insects and pests in animals bodies. Generally, pesticides are aimed at controlling the growth of unwanted weeds or the presence of pests, insects and bacterial strains that may interfere with agricultural activity or cause the spread of diseases. They are classified as herbicides, insecticides, and fungicides. More recently, biopesticides have also been identified as those pesticides containing natural active ingredients. The most common type of pesticides is herbicides, which account for approximately 80% of all pesticides in use. The chemical compounds of pesticides have been a topic of concern for surface water quality because of their extensive usage in agricultural activities and industrial discharges. Their exposure may lead to serious health effects to both humans and other organisms (Ojemaye, 2020).

2.3.4 Industrial chemicals

Industrial chemicals are a large group of man-made substances**.** They are often used specifically to produce chemicals, such as flame retardants, plasticisers, perfluorinated compounds, and surfactants (Moritz, 2014).

2.3.4.1 Flame retardants

Flame retardants are defined as substances that can delay or prevent combustion (Roca, 2016). Flame retardants are chemicals added in flammable materials to inhibit fire ignition or slow its blow-out (Chemical Safety Facts 2022). Flame retardants are classified based on their chemical structures and properties (Collaborative on Health and Environment [CHE], 2019). For the flame retardants to work effectively, different chemistries with various properties and molecular structures are regularly mixed (Chemical Safety Facts, 2022). According to Rocca (2016), flame retardants fall into groups such as halogenated organics, phosphorus-based, nitrogen-based, other inorganic compounds and mineral compounds.

Halogenated flame retardants are characterised by chlorinated flame retardants and brominated flame retardants. These types of compounds are mainly used in safeguarding plastics and textiles. The chlorinated organophosphate include tributylphosphate and tris(1,3-dichloro-2-propyl)phosphate as essential agents (CHE, 2019; Ojemaye, 2020). Chlorinated flame retardants are tenacious but more soluble in an aqueous environment than in brominated compounds (Ojemaye, 2020). According to Moritz (2014), the brominated compounds are divided into polybrominated diphenyl ether, tetrabromobisphenol A, hexabromocyclodecane, and decabromodiphenyl ether (Ojemaye, 2020; Roca, 2016). These group of compounds are produced at a high rate because they are cost-efficient. They are applied in plastic casings that cover electric and electronic components (Chemical Safety Facts, 2021). In highly flammable foam, a combination of brominated and non-halogen flame retardants known as Firemaster 550 is used (CHE, 2019).

Phosphorus flame retardants are frequently used in polyurethane foams to make fire-resistant furniture, mattresses, and thermal insulation. It is also used in electronics and high-temperature polymers, which are used to make switches and connectors. Nylons, polyolefins, polyurethane foams, and fire-resistant paints, fabrics, and wallpapers all benefit from nitrogen-based flame retardants. Plastics, foams, textiles, and wood products all contain inorganic and mineral compounds, as well as other elements (Chemical Safety Facts, 2021). These chemicals are not soluble in water environments, they abide to particles, accumulates in river beds and lake sediments (CHE, 2019). As a results of their persistence, bioaccumulation and potential toxicity in animals and humans are regarded as chemicals of environmental concerns (Birnbaum and Staskal, 2004; Moritz, 2014; Roca, 2016).

2.3.4.2 Plasticisers

Plasticisers are an important group of substances that are mostly combined with materials to increase their plasticity (Moritz, 2014; Roca, 2016). They are classified into various classes such as phthalates acid esters such as di-isononyl-phthalate, di-isodecyl-phthalate, and di-2-propyl-heptyl-phthalate; terephthalate acid ester such as di-ethylhexyl-terephthalate; trimellitates such as trioctyl-trimellitate; citrates such as acetyl-tributyl-citrate; adipates such as diethylhexyl-adipate; and cyclohexanoates such as di-iso-nonyl-cyclohexanoate. All plasticisers have similar functions and properties such as viscous, lipophilic, and low water solubility (Billings et al., 2021).

Plasticisers are commonly used in the manufacturing of plastics, epoxy resins (used to cover food and beverage cans), water pipe lining, thermal printing papers, and medical implants. Mobile phones, CDs and DVDs, plastic food containers, eyeglass lenses, water bottles, food packaging, and dental sealants are all made with them (Wilkinson et al., 2017). Phthalates acid esters are the most utilised group of plasticisers (Billings et al., 2021) mostly in the production of plasticised elastic polyvinyl chloride by mixing resin, phthalate and other additives together. These compounds are not chemically bound and can easily enter various environmental compartments through evaporation, washed out or scraped out of the products. Once introduced into the environment, they become semi-volatile organic compounds and can negatively affect animals and human life (Moritz, 2014).

2.3.4.3 Perfluorinated compounds

These compounds are regarded as organic elements in which fluorine atoms replace all the hydrogens of the hydrocarbon backbones (Moritz, 2014). They have carbon-fluorine bond which is regarded as the strongest chemical bonds (Ojemaye, 2020). Perfluorinated compounds contain hydrophobic alkyl chain and hydrophilic functional groups. They are characterised by compounds such as perfluorooctane sulfonate and perfluorooctanoic acid (Miraji et al., 2016). They are used in manufacturing of paints, adhesives, waxes, polishes, metals, electronics, fire-fighting foams; in the production of polytetrafluoroethylene and teflon non-stick cookware, as well as grease-proof coatings for food packaging (Ojemaye, 2020).

Perfluorinated compounds are extraordinarily stable in the environment and have remarkable characteristics of scattering in the body (Ojemaye, 2020; Richardson, 2009). They are regarded as chemicals of serious concern as they are persistent, toxic and undergo bioaccumulation in biological systems (Miraji et al., 2016; Sturm and Ahrens, 2010). They can be transported for a long distance in the environment, and water environment is the main source and an important medium for their conveyance (Kwadijk et al., 2010; Ojemaye, 2020). Their presence has been detected in various mediums, such treated waters, sewage, biota, and the human body, despite their origins being unclear (Miraji et al., 2016).

2.3.4.4 Surfactants

Surfactants are a group of chemicals universally well-known for their extensive applications in detergents and other cleaning products (Roca, 2016). They are regarded as amphipathic molecules because they possess both hydrophilic and hydrophobic characteristics (Badmus et al., 2021). They are used for different household and industrial applications (Collivignarelli et al., 2019) and are vital for manufacturing of detergents, textiles, paints, polymers, pharmaceuticals, pesticides and personal care products. They are also designed to reduce interfacial tension and stabilise foams or emulsions that make them important for tasks such as oil recovery and mining (Moura et al., 2019). Surfactants such as benzalkonium chloride and alkylbenzene linear sulfonate are used in laundry detergents, personal care and textile softeners, whereas hexadecyltrimethylammonium bromide are used to increase polyelectrolyte multilayer films to maximise its antimicrobial effectiveness and buffer constituents for complete DNA removal (Badmus et al., 2021). These chemical compounds are frequently introduced into the environment through the discharge of WWTPs as a result of their high usage in

industrial and urban environments (Roca, 2016), thus posing health risks to humans, animals and aquatic lives (Badmus et al., 2021).

2.3.4.5 Organic solvents

They are the type of volatile organic compounds likely to evaporate at room temperature. Organic solvents are carbon-based compounds that can dissolve or disperse one or more other compounds. They include compounds such as aromatic compounds, (benzene and toluene); alcohols (methanol); esters and ethers, ketones (acetone); amines; nitrated and halogenated hydrocarbons. Most of organic solvents are utilised in the manufacturing of paints, varnishes, lacquers, adhesives, glues, and in degreasing and cleaning agents, and in the production of dyes, polymers, plastics, textiles, printing inks, agricultural products and pharmaceuticals (National Institute for Occupational Safety and Health, 2018).

The ethers are oxygen-rich chemicals synthesised from feedstock such as methanol, bioethanol and isobutylene. These may be added to unleaded gasoline to increase fuel octane number, improve combustion efficiency, and reduce vehicle emission of carbon monoxide, ozone, nitrogen oxides and unburned hydrocarbons (Concawe 2018). The organic solvents methyl tertiary butyl ether and ethyl tertiary butyl ether are used as petroleum additive to improve ignition, lessen outflows, and as antiknock agent. Ethyl tertiary butyl ether has superior properties as an octane enhancer in promoting gasoline combustion and reducing vehicle emissions compared to methyl tertiary butyl ether (Thornton et al., 2020).

The widespread use of ether oxygenated compounds has led to their increased detection in surface water bodies and groundwater. In the environment, methyl tertiary butyl ether and ethyl tertiary butyl ether are recognised to disseminate rapidly due to their high solvency and low biodegradability characteristics. In drinking water purifications they are not effectively degraded (Ojemaye, 2020), while in surface water are detected at low microgram per litre concentrations (Thornton et al., 2020; Van der Waals et al., 2018). Hence, their presence can cause significant water pollution and potential health effects (National Institute for Occupational Safety and Health, 2018).

2.3.5 Illicit drugs, non-controlled drugs and food additives

Illicit and non-controlled drugs include drugs such as cocaine, heroin, cannabinoids, and amphetamine-like stimulants. These drugs are now considered emerging contaminants because of their high level of production and usage (Kasprzyk-Hordern et al., 2008; Miraji et al., 2016). Excreted as either the parent compound or as metabolites, they have been reported to persist into the wider environment (Paciuszkiewicz et al., 2019) and their concentration level in wastewater and surface water has been detected mostly ranging from a nanogram to a low microgram per litre concentration (Kasprzyk-Hordern et al., 2008). Although they occur at low concentrations and their effects are less known, they are presumed as being toxic to aquatic organisms (Miraji et al., 2016; Zuccato and Castiglioni, 2009).

Food additives have also been considered as important emerging contaminants as a result of their possible negative impact on the environment and human health (Moritz, 2014). Artificial sweeteners, which are included in thousands of food products, are the most widely used food ingredient. Saccharin, cyclamate, aspartame, acesulfame, sucralose, alitame, neotame, and dihydrochalcone are the most common artificial sweeteners. Among the sulfamates, cyclamate is the most advanced artificial sweetener, followed by saccharin. Foods, beverages, desserts, chewing gums, pastries, and breads all include artificial sweeteners (Naik et al., 2021).

Furthermore, drugs, sanitary products, personal care and pharmaceutical products also contain certain amounts of artificial sweeteners. They are regarded as contaminants of emerging concern due to their persistent occurrence and world-wide presence in various water matrices. Artificial sweeteners may cause serious toxic effects in the ecosystem, plant growth, and aquatic organisms due to the inability of current wastewater treatment processes to completely remove them. Depending on their concentration level,

persistence, and bioaccumulation potential, artificial sweeteners may cause serious toxic effects in the ecosystem, plant growth, and aquatic organisms (Naik et al., 2021).

2.3.6 Nanomaterials

The United States Environmental Protection Agency (2008), defined nanomaterials as a miscellaneous group of minor substances characterised by structural components with less than one micrometre in at least one dimension. Fillers, catalysts, semiconductors, textiles, microelectronics, energy storage, and antifriction coatings are some of the applications of nanomaterials. Furthermore, they are applied in cosmetics, pharmaceuticals, and drug carriers (Moritz, 2014). The size of a nanomaterial ranges typically between one and a hundred nanometre (United States Environmental Protection Agency, 2008). Nanomaterials are made up of several diverse base materials with different structures such as carbon, silicon and metals such as gold, cadmium and selenium (Moritz, 2014).

The European Commission (2022) categorised nanomaterials as natural, incidental or engineered. Engineered nanoparticles consist of carbon-based and inorganic forms, partly with a functionalised surface (Bundschuh et al., 2018). Inorganic compounds such as titanium dioxide, nano-silver and organic compounds such as carbon nanotubes are classified as nanoparticles (Lin et al., 2010). Carbon nanotubes are employed in the manufacturing of tennis racquets, whereas titanium dioxides are used as a sunscreen in cosmetics. Silver nanoparticles are used to decrease smell in outfits such as socks, underwear, and sports clothes. In bandages, silver nanoparticles are used to inhibit bacterial infections (Wilson, 2018).

Because of their high usage, nanoparticles end up polluting the water environment (Benn and Westerhoff, 2008). Compared to bulk materials, nanoparticles can have totally different physical, chemical, or biological reactions in different environmental compartments based on their class, form, size, and surface. They can penetrate the body and cell more easily compared to bigger particles, consequently causing serious medical effects (Lin et al., 2010).

2.3.7 Endocrine-disrupting compounds

According to La Merrill et al. (2020), the endocrine system is made up of glands that release hormones that assist the human body in interacting with specific targets or receptors. Hormones released in the body stimulate functions such as growth, development, fertility, and reproduction (Ojemaye, 2020). Endocrine-disrupting compounds are chemicals with the ability to mimic or hinder hormones, altering normal bodily functions (Gogoi et al., 2018), consequently causing serious medical implications such as cancer, reproductive impairment, cognitive deficits and obesity (La Merrill et al., 2020). They are made up of a variety of chemical molecules, both natural and manufactured. However, most of them are synthetic organic compounds such as alkylphenols, alkylphenols-ethoxylates, and polychlorinated biphenyls. Others include polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans, organochlor pesticides, dichlorodiphenyl, dichloroethylene, nonylphenols, steroid hormones and phthalates cells (Olujimi et al., 2010).

These chemical compounds interrupt normal functioning of the body in three different ways: They can bind to the receptors and imitate or provoke the effects of the endocrine hormones; they can affect the concentration of hormones by changing their synthesis or natural metabolism; and, they can interfere with signals between the various mechanisms of the hypothalamus-pituitary-endocrine gland axes (Olujimi et al., 2010). According to Pignotti (2018), endocrine-disrupting compounds interfere mostly with nuclear receptors. These include receptors such as estrogen, androgen, mineralocorticoid, progesterone, glucocorticoid, thyroid, as well as peroxisome proliferator-activated. These compounds are mainly detected in WWTPs than in the natural environment. Current wastewater treatment processes cannot completely remove all the emerging contaminants, and the release of effluent has contaminated several receiving water bodies, thus making water unsafe for aquatic animals and for human consumption (Tijani et al., 2013). There is still no complete of list of

endocrine-disrupting compounds as massive quantities of new chemicals are being manufactured regularly (Ojemaye, 2020).

2.4 SOURCES AND PATHWAYS OF EMERGING CONTAMINANTS

Emerging contaminants are introduced into the water environment through various sources and pathways (Janna, 2011). They can be discharged into the water environment either from a point source or non-point source (Ojemaye, 2020), as depicted in Figure 2.1.

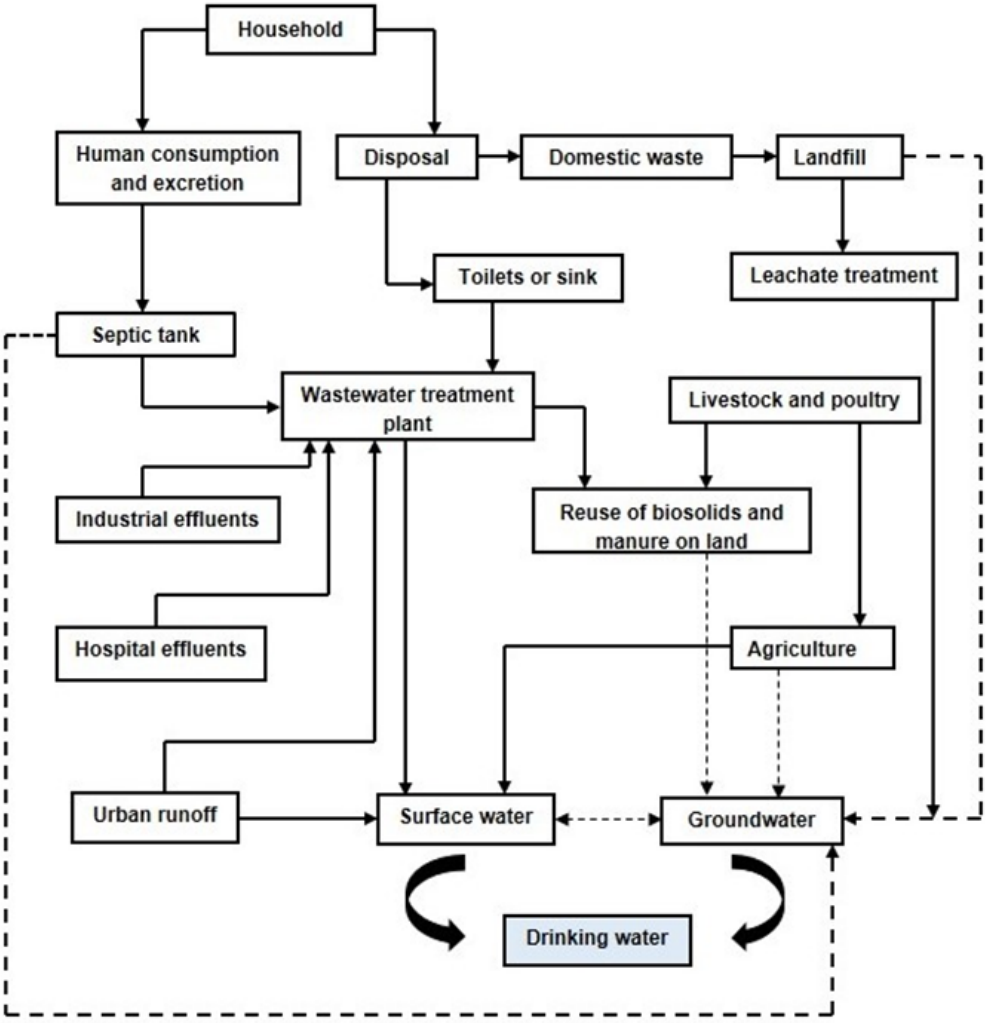


Figure 2.1 Sources and pathways of emerging contaminants in the environment (Adopted and modified from Stefanakis and Becker, 2016)

2.4.1 Point source of emerging contaminants

The point source of contamination signifies any particular detectable source of contamination from which contaminants are released (Mandarić, 2018). Household waste, hospital wastewater outflows, industrial activities, agricultural activities, and wastewater effluents, which are frequently being released into streams and rivers, are some of the examples of point source pollution (Janna, 2011; Ojemaye, 2020; Roca, 2016; Stefanakis and Becker, 2016). Emerging contaminants are classified as either natural or man-made chemical compounds (Janna, 2011). Natural chemical compounds such as hormones are emitted from excretion of vertebrates and invertebrates (Oehlmann and Schulte-Oehlmann, 2003), whereas man-made chemical compounds are produced by manufacturing industries (Janna, 2011). In factories or manufacturing industries

such as pharmaceuticals and personal care products (PPCPs) industries, mining, rubber industries, corrosion inhibitors and pesticides industries, contaminants of emerging concern are manufactured regularly or used as raw materials to produce other products (Moon et al., 2007). Furthermore, effluents are also discharged into the environment from these manufacturers or industries. These effluents can contain various chemicals such as pharmaceuticals, personal care products, flame retardants (Peng et al., 2009), alkylphenols and polycyclic aromatic hydrocarbons, phthalates and pesticides (Janna, 2011; Kahle et al., 2008).

Agricultural runoff and leachates are also regarded as a point source of some of the emerging pollutants (Janna, 2011). Crop production improvement, especially with the use of pesticides, may contribute to loading of chemicals such as endosulfan, atrazine, or fluopicolide (Snow et al., 2010). Animal farms are considered as good point sources of high levels of estrogens such as E1, E2, oestrone, testosterone, and androstenedione (Furuichi et al., 2006). Stefanakis and Becker (2016) also suggested that production of waste, storing of waste in lagoons and using of waste in concentrated animal feeding activities could lead to seepage of veterinary antibiotics into underground aquifers. Irrigation of fields with treated wastewater also introduces various emerging pollutants and their metabolites to the receiving water bodies. Some of these emerging contaminants may be released into the environment again if wastewater is reused for agricultural activities (Gros et al., 2010; Janna, 2011).

Another significant point source of various emerging contaminants is households. Many PPCPs such as trimethoprim, ibuprofen, diazepam, metoprolol, polycyclic and macrocyclic musks or benzophenone are frequently discarded from household solid waste or flushed down in the toilet (Stefanakis and Becker, 2016). Dumping of pharmaceuticals with household solid waste consequently leads to the introduction of these chemical compounds in landfill leachates, which also pollute groundwater. Moreover, in regions where the water table is near the surface, water pollution with PPCPs from onsite wastewater disposal systems, such as septic tanks, may occur (Pal et al., 2010; Stefanakis and Becker, 2016).

Wastewater discharged from hospitals are a potential source of emerging contaminants. Hospital wastewater discharges contain remaining quantities of medical drugs, together with pharmaceutical substances and X-ray contrast media. Although the volume of hospital wastewater discharges is low, they comprise larger quantities of pharmaceutical compounds than municipal wastewater (Stefanakis and Becker, 2016). Many emerging pollutants reach sewage treatment plants through households, hospitals, industrial use, and occasionally storm water, making WWTPs a noteworthy source of contaminants of emerging concern. These chemical compounds are not completely eliminated by the chemical, physical, and biological treatment techniques (Bolong et al., 2009; Koh et al., 2008), and as a result, they end up being discharged into the aquatic environment in a substantial quantity (Janna, 2011; Gerber, 2019).

Furthermore, landfill sites are regarded as a noteworthy sources of emerging pollutants. Wrong selection of the location or poor design of the landfill may pollute groundwater (Stefanakis and Becker, 2016). Other pathways through which emerging contaminants may be introduced into the environment are burning of solid waste, metal production, brick and cement production, tobacco smoking, illegal waste dumping, production of textiles and cleaning agents (Dougherty et al., 2010; Ojemaye, 2020).

2.4.2 Non-point source of emerging contaminants

According to Darradi et al. (2012) a non-point source contamination can be defined as a diffuse pollution in nature which occurs over wide geographic scales. They are not connected to a particular source (Darradi et al., 2012) and cannot be readily defined in a specially or temporally obvious way (Ncube, 2009). Although non-point sources are associated with lighter loads of contaminants (Lapworth et al., 2012), they are responsible for the majority of surface contamination and hence a serious threat to the aquatic ecosystems (Darradi et al., 2012). Urban runoff may be regarded as a non-point source of emerging contaminants. Urban runoff occurs as a result of impermeable surfaces such as roads, housing and construction sites, which are typical features of urbanisation. It carries contaminants straight into surface water, particularly during rainy seasons (Gerber,

2019). Other examples of non-point sources are sediments from mining activities, loose river banks, poorly managed construction sites and forestry. Livestock bacteria and nutrients, atmospheric deposition, and hydro-modifications are also regarded as non-point sources of pollution. Furthermore, farming and forestry activities may contribute to diffusion of micro-pollutants in the surface water and groundwater through leakages from manures used as fertilisers and wash-away of pesticides used in agriculture and forestry (Mandarić, 2018). Discharge of non-point source contaminants into the water environment is a serious threat to the entire biosphere of an aquatic environment (Mandarić, 2018; Wu and Chen, 2013).

2.5 OCCURRENCE OF EMERGING CONTAMINANTS IN THE WATER ENVIRONMENT

There is a large quantity of emerging pollutants that is being released into the water environment, and because of their continued introduction and possible damage to aquatic creatures and human health, they have become a centre of attention in many countries across the world (Yang et al., 2014), including South Africa. Most of these contaminants are detected in various water matrices such as hospital discharges, wastewater influents and effluents, surface water, groundwater, and drinking water, and are traceable in every continent due to human activities (Patel et al., 2019). Manufacturing plants, hospitals, sewerage deterioration, rainfall, sampling uncertainties, and analytical procedures all have a role in the production of these chemical compounds. Depending on consumption patterns and places, their concentration can vary hourly, daily, seasonally, geographically, chronologically, and socio-economically (Ort et al., 2010; Patel et al., 2019). Emerging pollutants in water matrices are detected differently in different nations and even different locations of the same country (Ebele et al., 2017). One of the goals of this project was to give an overview of emerging contaminants in various water matrices focussing specifically on pharmaceuticals, personal care products, pesticides (specifically herbicides) and endocrine-disrupting compounds. In order to provide useful and valued information, an international and South African case studies of the occurrence of such compounds were reviewed.

2.5.1 Occurrences of emerging contaminants internationally

2.5.1.1 Pharmaceuticals and personal care products in surface water, groundwater and drinking water

Pharmaceuticals are a broad category of chemical pollutants that come from human consumption, excretion, and veterinary use. Most of the pharmaceuticals detected in surface water, groundwater and drinking water are classified as non-steroidal anti-inflammatory drugs, antibiotics, beta-blockers, antiepileptics, antipsychotic, lipid regulators, antivirals, and psychomotor stimulants (Comerton et al., 2009; Ngqwala and Muchesa, 2020). The primary classes of PCPs are antiseptics, fragrances, insect repellents, preservatives and ultraviolet fillers. Several studies have detected the concentration of PPCPs in various water matrices in different concentrations (Petersen, 2016), and some of the scenarios of the occurrence of PPCPs in international surface water, groundwater and drinking water are discussed below and summarised in Table 2.1.

Non-steroidal anti-inflammatory drugs

NSAIDs are drugs used as antipyretic, anti-inflammatory, and analgesic agents. Muscle soreness, dysmenorrhea, rheumatic diseases, pyrexia, gout, and migraines are all routinely treated with these drugs. Additionally, in some cases of acute trauma, they are employed as opioid-sparing medicines. Aspirin, diflunisal, salsalate, naproxen, ibuprofen, diclofenac, indomethacin, meloxicam, piroxicam, meclofenamate, and mefenamic acid are some of the medications that are included under NSAIDs (Ghlichloo and Gerriets, 2022). The occurrence of these drugs has been detected in surface water, groundwater, and drinking water in many countries. In Lagos Nigeria, Ogah et al. (2020) conducted a study on pharmaceuticals in the environment focusing on levels of selected drugs in several water matrices and reported concentrations of NSAIDs such as diclofenac in borehole water as 0.39 mg/ℓ, treated tap water as 0.17 mg/ℓ, and well water as 0.73 mg/ℓ. In Montana United States (US), a study was conducted in the Helena valley groundwater to detect pharmaceuticals, personal care products, endocrine-disruptors and microbial indicators of faecal

contamination, and reported the maximum concentration of diclofenac in groundwater as 46 ng/ℓ (Miller and Meek, 2006).

In Germany, Ferrari et al. (2004), in their study on the environmental risk assessment of six human pharmaceuticals, reported the occurrence of diclofenac in surface water at a mean concentration of 1.2 µg/ℓ. A pilot study was done on the assessment of trace organic contaminants, including PPCPs from on-site wastewater treatment systems along Skaneateles Lake in New York State, US, where ibuprofen was reported at a concentration ranging from not detected (ND) to 1.16 ng/ℓ in tap water (Subedi et al., 2015). Wilkinson et al. (2017) conducted a study on spatial distribution of organic contaminants in three rivers of southern England, which were bound to suspended particulate matter and dissolved in water. They recorded the concentration of acetaminophen and diclofenac in an upper stream at mean concentrations of 20.8 and 11.4 ng/ℓ, respectively. A study of the Mississippi River in New Orleans, Louisiana, revealed contamination by ibuprofen (<1 to 34 ng/ℓ), acetaminophen (25 to 65 ng/ℓ), and naproxen (<1 to 135 ng/ℓ) (Zhang et al., 2006).

Choi et al. (2008) examined the concentrations of several pharmaceutical residues in surface water of the Han River, Korea, and detected the concentration of acetaminophen at 34.8 ng/ℓ. In a nationwide reconnaissance of contaminants of emerging concern in source and treated drinking waters of the US, conducted in two phases, a maximum concentration of tramadol was detected in source water as 23.04 ng/ℓ during Phase 2 (Glassmeyer et al., 2017). Fairbairn et al. (2015) conducted a study in the US focusing on sediment-water distribution of contaminants of emerging concern in a mixed use watershed, and detected acetaminophen in surface water with a concentration ranging from 0.99 to 7.0 ng/ℓ. Another study detected several pharmaceuticals such as mefenamic acid (ND to 326 ng/ℓ) and indomethacin (ND to 33.5 ng/ℓ) in surface water from the Mankyung River in South Korea (Kim et al., 2009).

A preliminary study on the occurrence of pharmaceutically active compounds in the river basins and their removal in two conventional drinking water treatment plants in Chongqing, China, detected diclofenac (ND to 1.5 ng/ℓ), ibuprofen (0.86 to 115.8 ng/ℓ) and acetaminophen (0.5 to 445.6 ng/ℓ) among the NAISDs in river water (Yan et al., 2015). Lin et al. (2015) conducted a study on the occurrence of pharmaceuticals, hormones, and perfluorinated compounds in groundwater in Taiwan and reported the concentrations of NSAIDs such as acetaminophen, ibuprofen, naproxen, and diclofenac as 0.9 to 1 036, 17.4 to 836.7, 128.0, and 2.1 to 33.2 ng/ℓ, respectively (Lin et al., 2015).

An investigation study on PPCPs and endocrine-disrupting chemicals in a tropical urban catchment of Singapore, reported concentrations of acetaminophen (< 4 to 159 ng/ℓ), and naproxen (< 1 to 10.85 ng/ℓ) among the NSAIDs in river water (You et al., 2015). In mangrove ecosystems in Singapore, a study was conducted to determine pharmaceutically active compounds and endocrine-disrupting chemicals in water, sediments and molluscs. This study detected concentrations of diclofenac ranging from 0.04 to 1.7 ng/ℓ in surface water (Bayen et al., 2016). In a preliminary study of the occurrence of pharmaceutically active compounds in hospital wastewater and surface water in Hanoi, Vietnam, ibuprofen (0.10 to 0.58 ng/ℓ), fenoprofen (< 0.04 to 0.41 ng/ℓ), ketoprofen (< 0.04 to 0.45 ng/ℓ), naproxen (0.08 to 0.38 ng/ℓ), diclofenac (0.41 to 0.31 ng/ℓ), indomethacin (< 0.02 to 0.27 ng/ℓ), and propyphenazone (< 0.06 ng/ℓ) were detected among NSAIDs in surface water (Tran et al., 2014).

Hsin et al. (2008) conducted a study using LC ion trap MS to determine pharmaceutical residues in Taiwanese rivers and wastewaters and reported a concentration of ketoprofen (110 to 620 ng/ℓ), ibuprofen (< 12 to 30 ng/ℓ), and diclofenac (24 to 62 ng/ℓ) in Taiwanese rivers. Another study in Lagos, Nigeria, conducted to quantify pharmaceutical residues in wastewater, impacted surface waters and sewage sludge detected a range of different pharmaceuticals in surface water samples from six locations (Olarinmoye et al., 2016). The maximum concentration of acetylsalicylic acid was recorded at 0.13 µg/ℓ, diclofenac at 0.27 µg/ℓ, fenoprofen at < 0.02 µg/ℓ, ibuprofen at 8.84 µg/ℓ and ketoprofen at < 0.02 µg/ℓ, while naproxen was recorded at 0.03 µg/ℓ in surface water (Olarinmoye et al., 2016).

In an investigation study of the presence of emerging contaminants in urban water bodies in southern Brazil, the mean concentrations of various steroid hormones and NSAIDs were detected in the Cancela-Tamandaí and João Goulart catchments (Pivetta and Gastaldini, 2019). Among the NSAIDs, diclofenac, ibuprofen, and paracetamol were detected in the Cancela-Tamandaí at mean concentrations of 0.060, 1.266, and 2.975 µg/ℓ, respectively. In the João Goulart catchments their respective mean concentrations were 0.069, 0.515, and 0.426 µg/ℓ (Pivetta and Gastaldini, 2019). In Hanoi, Vietman, a preliminary study on the occurrence of pharmaceutically active compounds in hospital wastewater and surface water detected concentrations of ketoprofen (< 40 to 330 ng/ℓ), ibuprofen (100 to 1 100 ng/ℓ), diclofenac (< 140 to 310 ng/ℓ), and naproxen (80 to 380 ng/ℓ) in surface water (Tran et al., 2014).

Furthermore, a study was conducted to determine selected pharmaceuticals in tap water and drinking water treatment plants in Beijing, China, and detected concentrations of ibuprofen (Less than limit of detection [< LOD] to 17.17 ng/ℓ), antipyrine (0.15 to 0.22 ng/ℓ), and aminopyrine (0.17 to 0.64 ng/ℓ) among the NSAIDs in drinking water (Cai et al., 2015). The study also detected concentrations of naproxen (< LOD to 3.12 ng/ℓ), and diclofenac (< LOD to 2.37 ng/ℓ) in tap water (Cai et al., 2015). In a study of spatiotemporal distributions and ecological risk assessment of PPCPs in groundwater conducted in North China, maximum concentrations of ibuprofen in unconfined aquifers was detected as 24.50 and 42.99 ng/ℓ during the wet and dry season, respectively (Wu et al., 2020).

Antibiotics

Both human and animal health depend heavily on antibiotics. They are produced to treat pathogen-caused illnesses (Viana et al., 2021). They include compounds such as amoxicillin, erythromycin, fluoroquinolones, sulfamethoxazole, tetracycline, trimethoprim, doxycycline, ciprofloxacin, ofloxacin, lincomycin, norfloxacin, azithromycin, oxytetracycline and florfenicol. As the current sewage treatment works are unable to completely eliminate these compounds, they end up entering natural surface water, groundwater and drinking water (Viana et al., 2021). Choi et al. (2008) examined the concentrations of several pharmaceutical residues in surface water of the Han River in Korea and detected sulfamethoxazole in the surface water at a concentration of 26.9 ng/ℓ. In Germany, a study on environmental risk assessment of six human pharmaceuticals reported a mean concentration of sulfamethoxazole in surface water as 0.48 µ/ℓ (Ferrari et al., 2004).

In Cape Cod in Massachusetts, US, a study was conducted to investigate pharmaceuticals, perfluorosurfactants, and other organic wastewater compounds in public drinking water wells in a shallow sand and gravel aquifer, and a maximum concentration of sulfamethoxazole was reported as 113 ng/ℓ in well water (Schaider et al., 2014). In their study in Helena valley groundwater in Montana, US, to determine PPCPs, endocrine disruptors, and microbial indicators of faecal contamination, Miller and Meek (2006) reported a maximum concentration of sulfamethoxazole in groundwater as 490 ng/ℓ. In surface water from the Mankyung River, South Korea, pharmaceuticals such as clarithromycin and erythromycin were detected at concentrations ranging from ND to 443 and ND to 137 ng/ℓ, respectively (Kim et al., 2009).

A nationwide reconnaissance of contaminants of emerging concern in source and treated drinking waters of the US conducted in two phases, reported the concentrations of sulfamethoxazole in source water at a maximum concentration of 161.1 ng/ℓ and in treated drinking water at a maximum concentration of 8.2 ng/ℓ during Phase 2 (Glassmeyer et al., 2017). A study conducted on the occurrence of antibiotics and antivirals in the Nairobi River basin in Kenya, reported the maximum concentrations of sulfamethoxazole, trimethoprim, and ciprofloxacin, as 13.8, 2.6, and 0.5 mg/ℓ, respectively (Ngumba et al., 2016). In Beijing, China, a study was conducted to determine selected pharmaceuticals in a tap water and drinking water treatment plant, and detected a concentration of sulfamethoxazole ranging from < LOD to 1.81 ng/ℓ among antibiotics in tap water (Cai et al., 2015).

Lin et al. (2015) conducted a study on the occurrence of pharmaceuticals, hormones, and perfluorinated compounds in groundwater in Taiwan and reported concentrations of various antibiotics such as sulfadiazine

(0.1 to 14.4 ng/ℓ), sulfamethoxazole (0.2 to 1 820 ng/ℓ), sulfathiazole (0.7 to 3.0 ng/ℓ), sulfamethazine (1.6 to 28.9 ng/ℓ), sulfamonomethoxine (0.6 to 1.8 ng/ℓ), sulfadimethoxine (0.8 to 4.3 ng/ℓ), erythromycin-H_2O (54.8 ng/ℓ), clarithromycin (6.9 ng/ℓ), nalidixic acid (1.6 to 16.4 ng/ℓ), flumequine (2.4 to 6.6 ng/ℓ), pipemidic acid (10.2 ng/ℓ), norfloxacin (9.3 ng/ℓ), ofloxacin (0.9 to 11.8 ng/ℓ), dimetridazole (1.8 ng/ℓ), and metronidazole (26.2 ng/ℓ) in groundwater.

In Bangladesh, Hossain et al. (2018) in their study of the occurrence and ecological risk of pharmaceuticals in river surface water, reported concentrations of sulfadiazine (< LOD to 0.58 ng/ℓ), sulfamethazine (< LOD to 4.19 ng/ℓ), sulfamethoxazole (< LOD to 7.24 ng/ℓ), sulfamethizole (< LOD to 11.35 ng/ℓ), trimethoprim (Less than limit of quantification [< LOQ] to 17.20 ng/ℓ), erythromycin (< LOD to 6.46 ng/ℓ), tylosin (< LOD to 16.68 ng/ℓ), and metronidazole (0.05 to 13.51 ng/ℓ). In Chongqing, China, a preliminary study on the occurrence of pharmaceutically active compounds in the river basins and their removal in two conventional drinking water treatment plants, detected antibiotics such as erythromycin-H_2O (1.41 to 156 ng/ℓ), roxithromycin (0.6 to 88.4 ng/ℓ), azithromycin (2.6 to 166.5 ng/ℓ), sulfamethazine (ND to 3.7 ng/ℓ), sulfamethoxazole (0.44 to 115.3 ng/ℓ), sulfadiazine (0.36 to 26.7 ng/ℓ), trimethoprim (0.4 to 20.5 ng/ℓ), ofloxacin (3.1 to 114.1 ng/ℓ), norfloxacin (ND to 92.4 ng/ℓ), moxifloxacin (ND to 6.4 ng/ℓ) in river water (Yan et al., 2015).

A study of the PPCPs and endocrine-disrupting chemicals in a tropical urban catchment of Singapore, reported concentrations of antibiotic chloramphenicol ranging from <0.07 to 1.53 ng/ℓ in river water (You et al., 2015). Another study on pharmaceutical active compounds and endocrine-disrupting chemicals in water, sediments and molluscs in the mangrove ecosystems of Singapore, detected concentrations of lincomycin (0.04 to 1.36 ng/ℓ), chloramphenicol (0.003 to 0.70 ng/ℓ), sulfadiazine (0.04 to 0.80 ng/ℓ), sulfamerazine (0.03 to 0.24 ng/ℓ), and sulfamethazine (06 to 6.26 ng/ℓ) in surface water (Bayen et al., 2016). A pilot study conducted on the assessment of trace organic contaminants including PPCPs from on-site wastewater treatment systems along Skaneateles Lake in New York, reported a sulfamethoxazole concentration of ND to 0.39 ng/ℓ among the antibiotics in tap water (Subedi et al., 2015).

Ngumba et al. (2020) determined the occurrence of antibiotics and antiretroviral drugs in source-separated urine, groundwater, surface water and wastewater in the peri-urban area of Chunga in Lusaka, Zambia. Among the antibiotics, trimethoprim, sulfamethoxole, ciprofloxacin, tetracycline, doxycycline, and amoxicillin, were detected at mean concentrations of 2 410, 11 800, 400, 2 200, 2 730, and 2 500 ng/ℓ, respectively. In Kenya, Kairigo et al. (2020), in their study of the contamination of surface water and river sediments by antibiotic and antiretroviral drug cocktails in low and middle-income countries, with the focus on occurrence, risk and mitigation strategies, reported the mean concentration of norfloxacin, trimethoprim, ciprofloxacin, sulfamethoxole in upstream surface water as 1.6, 3.8, 2.5, and 96.9, respectively.

A study by Ogah et al. (2020), conducted in Lagos, Nigeria, on the pharmaceuticals in the environment, focusing on levels of selected drugs in water, detected concentrations of ofloxacin in borehole water and treated tap water as 0.24 and 0.08 mg/ℓ, respectively. Another study in Lagos, Nigeria, conducted to quantify pharmaceutical residues in wastewater impacted surface waters and sewage sludge detected the maximum concentration of microgram per litre antibiotics such as chloramphenicol (0.36 µg/ℓ), chlortetracycline (< 0.05 µg/ℓ), clarithromycin (< 0.05 µg/ℓ), doxycycline (< 0.05 µg/ℓ), erythromycin (1.00 µg/ℓ), sulfadiazine (0.04 µg/ℓ), sulfadimidine (< 0.01 µg/ℓ), sulfamethoxazole (1.50 µg/ℓ), tetracycline (< 0.05 µg/ℓ), and trimethoprim (0.40 µg/ℓ) in surface water (Olarinmoye et al., 2016).

Lin et al. (2020), conducted a study on the occurrence and risk assessment of emerging contaminants in a water reclamation and ecological reuse project in China, and reported the concentration of the antibiotics sulfamethoxole, enrofloxacin, oxytetracycline, and florfenicol in river samples as ranging from ND to 39.6, ND to 45.8, 85.0 to 375.9, and ND to 287.5 ng/ℓ, respectively. In a spatiotemporal distribution and ecological risk assessment study of PPCPs in groundwater in North China, Wu et al. (2020) reported the respective maximum concentrations of various antibiotics in unconfined aquifers during the wet and dry season as follows:

erythromycin (1.55 and 1.71 ng/ℓ); sulfamonomethoxine (3.43 and 12.39 ng/ℓ); sufathiozole (3.86 and 2.24 ng/ℓ); sufisoxazole (1.51 and 16.73 ng/ℓ); sulfamerazine (2.49 and 0.69 ng/ℓ); sulfamethazine (0.49 and 0.83 ng/ℓ); sulfamethoxazole (19.29 and 11.01 ng/ℓ); chloramphenicol (0.55 and 0.16 ng/ℓ); and trimethoprim (1.03 and 3.23 ng/ℓ).

Beta-blockers

Beta-blockers are frequently used for the treatment of cardiovascular illnesses such hypertension, cardiac arrhythmias, tachycardia, thyrotoxicosis, hypertrophic subaortic stenosis, or ischemic heart disease. Additionally, they are used to treat acute panic feelings in anxious circumstances, as well as ocular pressure in glaucoma treatment and migraine prophylaxis. The WWTPs does not completely remove these chemicals and, as a result, they are found in surface water, groundwater, and drinking water in many different nations. Atenolol, propranolol, metoprolol, bisoprolol, and betaxolol are the most used beta-blockers (Iancu et al., 2020). A nationwide reconnaissance study of contaminants of emerging concern in source and treated drinking water of the US conducted in two phases, reported metoprolol in source water and treated drinking water during Phase 2 at a maximum concentration of 35.7 and 18.4 ng/ℓ, respectively (Glassmeyer et al., 2017).

In Germany, a study by Ferrari et al. (2004) on environmental risk assessment of six human pharmaceuticals, reported propranolol at mean concentrations of 0.59 µg/ℓ in surface water. A study conducted to determine the occurrence of pharmaceuticals, hormones, and perfluorinated compounds in groundwater in Taiwan, detected concentrations of β-blockers such as atenolol (3.6 ng/ℓ), and acebutolol (0.7 ng/ℓ) (Lin et al., 2015). Another study aimed at the occurrence of PPCPs in surface water of the Mankyung River in South Korea, detected beta-blockers such as atenolol (ND to 690 ng/ℓ) and propranolol (ND to 40.1 ng/ℓ) (Kim et al., 2009). A preliminary study conducted on the occurrence of pharmaceutically active compounds in river basins and their removal in two conventional drinking water treatment plants in Chongqing, China, detected a beta-blocker metoprolol at a concentration ranging from 0.46 to 17.3 ng/ℓ in river water (Yan et al., 2015). A pilot study was conducted to assess the trace organic contaminants including PPCPs from on-site wastewater treatment systems along the Skaneateles Lake in New York, US, and detected atenolol at a concentration ranging from ND to 19.5 ng/ℓ among the beta-blockers in tap water (Subedi et al., 2015).

Antiepileptics

Patients with epilepsy are treated with antiepileptic drugs. Carbamazepine is the most popular and commonly used antiepileptic medication. Pharmaceuticals are not effectively removed from wastewater, thus they are released into rivers together with wastewater effluent, where they may seep into groundwater or be absorbed by water treatment facilities. There have been instances of carbamazepine in drinking water, despite the use of sophisticated water treatment techniques (Rezka et al., 2015). In Cape Cod in Massachusetts, Schaider et al. (2014) conducted a study targeting pharmaceuticals, perfluorosurfactants, and other organic wastewater compounds in public drinking water wells in a shallow sand and gravel aquifer, and detected anticonvulsants such as phenytoin and carbamazepine in well water at maximum concentrations of 66 and 72 ng/ℓ, respectively. A study in Montana, US, conducted in the Helena valley groundwater to detect PPCPs, endocrine disruptors, and microbial indicators of faecal contamination, Miller and Meek (2006) reported detection of carbamazepine and dilantin in groundwater with maximum concentrations of 22 and 420 ng/ℓ, respectively.

In a study conducted in Germany on environmental risk assessment of six human pharmaceuticals in an aquatic environment, Ferrari et al. (2004), detected carbamazepine at mean concentrations of 1.1 µg/ℓ. Lin et al. (2015) conducted a study targeting the occurrence of pharmaceuticals, hormones, and perfluorinated compounds in groundwater in Taiwan, and detected carbamazepine with a concentration ranging from 0.4 to 37.9 ng/ℓ. A nationwide reconnaissance of contaminants of emerging concern in source and treated drinking water in the US, conducted in two phases, reported maximum concentrations of carbamazepine as 269 ng/ℓ in source water and 586 ng/ℓ in treated drinking water during Phase 1. During Phase 2, carbamazepine was

detected in source water at a maximum concentration of 35.7 ng/ℓ, and in treated drinking water at a maximum concentration of 26.50 ng/ℓ (Glassmeyer et al., 2017).

A study conducted in the Mississippi River in New Orleans, Louisiana, US, to simultaneously quantify polycyclic aromatic hydrocarbons, polychlorinated biphenyls and PPCPs, revealed contamination by carbamazepine at a concentration ranging from 43 to 114 ng/ℓ (Zhang et al., 2006). Another study targeting occurrence of PPCPs in surface water of the Mankyung River, South Korea, reported carbamazepine at a concentration ranging from ND to 595 ng/ℓ (Kim et al., 2009). In Bangladesh, Hossain et al. (2018), in their study on the occurrence and ecological risk of pharmaceuticals in river surface water, detected the concentration of carbamazepine ranging from < LOD to 8.80 ng/ℓ among the antiepileptic drugs in the Old Brahamaputra River. A preliminary study conducted on the occurrence of pharmaceutically active compounds in the river basins, and their removal in two conventional drinking water treatment plants in Chongqing, China, detected the antiepileptic drug carbamazepine at concentration ranging from 0.41 to 10.3 ng/ℓ (Yan et al., 2015).

In the mangrove ecosystems of Singapore, a study targeting pharmaceutically active compounds and endocrine-disrupting chemicals in water, sediments and molluscs, reported concentrations of carbamazepine ranging from 0.06 to 4.63 ng/ℓ in surface water (Bayen et al., 2016). Tran et al. (2014), in their preliminary study on the occurrence of pharmaceutically active compounds in hospital wastewater and surface water in Hanoi, Vietnam, detected carbamazepine ranging from < 0.144 to 0.53 ng/ℓ in surface water. In Lagos, Nigeria, a study conducted to quantify pharmaceutical residues in wastewater, impacted surface waters and sewage sludge from six locations, detected maximum concentrations of carbamazepine in surface water as < 0.01 µg/ℓ (Olarinmoye et al., 2016). Furthermore, a study targeting selected pharmaceuticals in a tap water and drinking water treatment plant in Beijing, China, detected concentrations of carbamazepine ranging from 0.37 to 1.15 ng/ℓ in drinking water and 0.51 to 38.24 ng/ℓ in tap water (Cai et al., 2015).

Antipsychotics

Because antipsychotics are used to treat a variety of illnesses and patients of various ages, including schizophrenia, bipolar disorder, depression, autism, attention deficit hyperactivity disorder, and behavioural and psychological signs of dementia, their use is continually expanding (Escudero et al., 2021). They may include chemical compounds such as thioridazine, quetiapine, bromazepam, clonazepam, diazepam, sulpiride, and aripiprazole. Antipsychotics remain in the environment once excreted by patient's urine or faeces and are transferred to WWTPs. As WWTPs are not designed to remove drugs and their metabolites, a variable part of the administered dose ends up in the rivers, lakes, the sea and even drinking water (Escudero et al., 2021).

A study by Ferreira (2014) investigated psychiatric pharmaceuticals in the Guandu River, Rio de Janeiro, Brazil, and revealed the presence of bromazepam, clonazepam and diazepam in all samples of surface water at maximum concentrations of 42, 198, and 335 ng/ℓ, respectively. A study conducted to investigate pharmaceuticals, PCPs and endocrine-disrupting chemicals in a tropical urban catchment of Singapore, reported concentrations of antipsychotic drugs such as sulpiride ranging from < 0.1 to 1.23 ng/ℓ in river water (You et al., 2015).

Another study in the Singapore mangrove ecosystems aiming at pharmaceutically active compounds and endocrine-disrupting chemicals in water, sediments and molluscs, detected concentrations of antipsychotics such as risperidone (03 to 0.21 ng/ℓ) in surface water (Bayen et al., 2016). In Lagos, Nigeria, a study was conducted to quantify pharmaceutical residues in wastewater-impacted surface waters and sewage sludge from six locations, and detected a maximum concentration of antipsychotic drugs such as diazepam (< 0.01 µg/ℓ) in surface water (Olarinmoye et al., 2016).

Lipid regulators

The high usage of blood lipid regulators has led to the introduction of chemical compounds such as bezafibrate, clofibric acid, gemfibrozil, fenofibric acid, simvastatin, etofibrate, and atorvastatin in aquatic environments. The majority of fibrates are excreted unaltered (Rosal et al., 2010). Lipid-lowering agents such as bezafibrate (ND to 31.4 ng/ℓ), clofibric acid (ND to 17.2 ng/ℓ), gemfibrozil (ND to 1.4 ng/ℓ), simvastatin (2.3 to 16.7 ng/ℓ), and atorvastatin (ND to 0.6 ng/ℓ) were detected in river water in a preliminary study conducted with the aim of determining the occurrence of pharmaceutically active compounds in the river basins and their removal in two conventional drinking water treatment plants in Chongqing, China (Yan et al., 2015).

In a study conducted with the aim of determining the occurrence of pharmaceuticals, hormones, and perfluorinated compounds in groundwater in Taiwan, Lin et al. (2015) reported concentrations of lipid regulators and cholesterol-lowering drugs such as clofibric acid and bezafibrate, ranging from 0.1 to 1.0, and 0.1 to 256.7 ng/ℓ, respectively. Another study conducted in the urban riverine water of the Pearl River Delta at Guangzhou, South China, revealed the presence of acidic pharmaceuticals such as clofibric acid in water samples with maximum concentrations of 248 ng/ℓ (Peng et al., 2009).

In the mangrove ecosystems of Singapore, a study was conducted to determine pharmaceutically active compounds and endocrine-disrupting chemicals in water, sediments and molluscs and detected concentrations of lipid regulators such as gemfibrozil ranging from 0.77 to 17.7 ng/ℓ in surface water (Bayen et al., 2016). A simultaneous quantification of polycyclic aromatic hydrocarbons, polychlorinated biphenyls, and PPCPs in a study conducted in the Mississippi River in New Orleans, Louisiana, revealed the prevalence of clofibric acid at a concentration ranging from 3 to 27 ng/ℓ (Zhang et al., 2006). A preliminary study on the occurrence of pharmaceutically active compounds in hospital wastewater and surface water in Hanoi, Vietnam, detected lipid regulators such as clofibric acid (< 0.05 ng/ℓ), and gemfibrozil (< 0.05 ng/ℓ) in surface water (Tran et al., 2014).

Olarinmoye et al. (2016) conducted a study in Lagos, Nigeria, with the aim of quantifying pharmaceutical residues in wastewater, impacted surface waters and sewage sludge and detected a maximum concentration of lipid regulators such as bezafibrate (< 0.02 µg/ℓ), clofibric acid (0.04 µg/ℓ), etofibrate (< 0.02 µg/ℓ), fenofibrate (< 0.04 µg/ℓ), and gemfibrozil (< 0.02 µg/ℓ) in surface water. In Beijing, China, a study was conducted targeting selected pharmaceuticals in tap water and a drinking water treatment plant. In tap water, a concentration of bezafibrate (< LOD to 0.16 ng/ℓ), and clofibric acid (< LOD to 1.37 ng/ℓ) were detected among the lipid regulators, whereas in drinking water, only bezafibrate was detected ranging from 0.31 to 0.85 ng/ℓ (Cai et al., 2015).

Human indicators or psychomotor stimulants

As one of the most common psychoactive chemicals taken globally, caffeine is a human indicator or psychomotor stimulant that is found in coffee, tea, soft drinks, and chocolate. Because it stimulates the central nervous system and has the short-term effect of revitalising the body and regaining attention, caffeine is widely ingested. Numerous countries have reported the occurrence of caffeine in natural water (Edwards et al., 2015). A nationwide reconnaissance study was conducted in two phases to determine contaminants of emerging concern in source and treated drinking water of the US and detected the maximum concentration of caffeine in source water and treated drinking water during Phase 1 as 124 and 88 ng/ℓ, respectively. Furthermore, caffeine was detected in source water at a maximum concentration of 90.89 ng/ℓ during Phase 2 (Glassmeyer et al., 2017).

In a study conducted to examine the concentrations of several pharmaceutical residues in the surface water of the Han River in Korea, a concentration of 268.7 ng/ℓ caffeine was detected (Choi et al., 2008). In a study conducted to detect several emerging contaminants in urban groundwater sources in Africa, a maximum concentration of caffeine (1.7 ng/ℓ) was detected during the wet season in Zambia (Sorensen et al., 2015). In

Taiwan, Lin et al. (2015) conducted a study on groundwater targeting the occurrence of pharmaceuticals, hormones, and perfluorinated compounds and reported caffeine as the only psychostimulant at a concentration ranging from 1.2 to 930.7 ng/ℓ. A study conducted in the US focusing on sediment-water distribution of contaminants of emerging concern in a mixed use watershed detected caffeine in surface water at concentrations ranging from 0.84 to 250 ng/ℓ (Fairbairn et al., 2015).

An investigation of PPCPs and endocrine-disrupting chemicals in a tropical urban catchment of Singapore, reported concentrations of caffeine ranging from 33.9 to 644.5 ng/ℓ in river water (You et al., 2015). Another study in the Singapore mangogrove ecosystems was conducted with the aim of detecting pharmaceutically active compounds and endocrine-disrupting chemicals in water, sediments and molluscs, and reported concentrations of caffeine ranging from 5 to 1 389 ng/ℓ in surface water (Bayen et al., 2016). A simultaneous quantification of polycyclic aromatic hydrocarbons, polychlorinated biphenyls, and PPCPs conducted in the Mississippi River in New Orleans, Louisiana, revealed the concentration of caffeine ranging from <1 to 38 ng/ℓ (Zhang et al., 2006).

In the Skaneateles Lake in New York, the results of a pilot study on the assessment of trace organic contaminants including PPCPs from on-site wastewater treatment systems reported caffeine at concentrations ranging from ND to 11.1 ng/ℓ in tap water (Subedi et al., 2015). In a study of spatiotemporal distributions and ecological risk assessment of PPCPs in groundwater conducted in North China, human indicators such as caffeine was detected in an unconfined aquifer at a maximum concentration of 782.62 and 461.87 ng/ℓ during the wet and dry season, respectively (Wu et al., 2020).

Antivirals

Antivirals are medications that are primarily used to treat HIV, including abacavir, nevirapine, zidovudine, lamivudine, and stavudine. Acyclovir and penciclovir for the treatment of herpes infections were also included, as are medications such as ribavirin for the treatment of Hepatitis C, and oseltamivir for the treatment of influenza A and B. Similar to other medications, these substances are partially digested in patients and then eliminated through the urine or faeces. Therefore, they can pollute the environment through discharges from WWTPs (Prasse et al., 2010). As a result of probable ecosystem changes and the emergence of antiviral resistance, the environmental release of antiviral medications is highly concerning (Nannou et al., 2020). In the Nairobi River basin in Kenya, a study was conducted to determine the occurrence of antibiotics and antivirals and reported the maximum concentrations of lamivudine, nevirapine, and zidovudine in river water as 5.4, 4.8, and 7.7 mg/ℓ, respectively (Ngumba et al., 2016).

In Lusaka in Zambia, Ngumba et al. (2020) also determined the occurrence of antibiotics and antiretroviral drugs in source-separated urine, groundwater, surface water and wastewater in the peri-urban area of Chunga, and reported among the antiretroviral drugs nevirapine, zidovidine, and lamivudine in the Chunga River at mean concentrations of 210, 1 280 and 49 700 ng/ℓ, respectively. In Kenya, a study on contamination of surface water and river sediments by antibiotic and antiretroviral drug cocktails in low and middle-income countries focusing on occurrence, risk and mitigation strategies, reported the mean concentration of lamivudine, zidovidine, and nevirapine in upstream surface water as 219.6, 2.1 and 0.9 µg/ℓ, respectively (Kairigo et al., 2020).

Antiseptics

An antiseptic is a chemical that inhibits or retards microbial growth. In hospitals and other health care facilities, antiseptics are widely utilised for a variety of topical and hard-surface applications (Mcdonnell and Russell, 1999). Even in tiny amounts, the release of these chemicals into aquatic environments may have harmful consequences on aquatic organisms and human health (Das et al., 2014). Lin et al. (2020) conducted a study on the occurrence and risk assessment of emerging contaminants in a water reclamation and ecological reuse

project in China, and detected triclosan in river samples at concentrations ranging from 61 to 660 ng/ℓ. A study conducted in North China on spatiotemporal distribution and ecological risk assessment of PPCPs in groundwater reported maximum concentration of triclosan in unconfined aquifers in the wet and dry season as 18.05 and 109.90 ng/ℓ, respectively (Wu et al., 2020).

A pilot study conducted to assess trace organic contaminants including PPCPs from on-site wastewater treatment systems along the Skaneateles Lake in New York, reported antiseptics such as triclosan and triclocarbanin in tap water at concentrations ranging from ND to 1.93, and ND to 20.2 ng/ℓ, respectively (Subedi et al., 2015). Another study on the simultaneous quantification of polycyclic aromatic hydrocarbons, polychlorinated biphenyls, and PPCPs in the Mississippi River in New Orleans, Louisiana, revealed a concentration of triclosan ranging from 9 to 26 ng/ℓ (Zhang et al., 2006). A study conducted to detect several emerging contaminants in urban groundwater sources in Africa, reported the maximum concentration of triclosan during the dry and wet season in Zambia as 0.02 and 0.03 ng/ℓ, respectively (Sorensen et al., 2015).

Insect repellent

To ward off mosquitoes, ticks, flies, and other biting insects, people use insect repellents. An insect repellent that is rinsed off the skin during recreation, bathing, and during washing of laundry, is one of the emerging contaminants that puts a lot of strain on stream ecosystems (Campos et al., 2016). Fairbairn et al. (2015) conducted a study on sediment-water distribution of contaminants of emerging concern in a mixed use watershed in the South Fork Zumbro River in south-eastern Minnesota and detected N, N-diethyl-meta-toluamide (DEET) with a concentration ranging from 7.2 to 110 ng/ℓ and a mean concentration of 27 ng/ℓ in surface water. In China, a study conducted with the aim of determining the occurrences of pharmaceuticals in drinking water sources of major river watersheds, reported DEET in surface water at concentrations ranging from 0.8 to 10.2 ng/ℓ (Sun et al., 2015).

Table 2.1 Occurrence and concentration levels of pharmaceuticals and personal care products in international surface water, groundwater and drinking water

Pharmaceuticals and personal care products	Country	Concentration in various water matrices						References
		Surface water		Groundwater		Drinking water		
		Range	Mean	Range	Mean	Range	Mean	
Non-steroidal anti-inflammatory drugs (NSAIDs)								
Acetaminophen	United States	0.99-7.0 ng/ℓ	3.5 ng/ℓ					[Fairbairn et al., 2015]
	United States	25-65 ng/ℓ						[Zhang et al., 2006]
	China	0.5-445.6 ng/ℓ						[Yan et al., 2015]
	Singapore	<4-159 ng/ℓ						[You et al., 2015]
	Taiwan			0.9-1 036 ng/ℓ				[Lin et al., 2015]
	Korea		34.8 ng/ℓ					[Choi et al., 2008]
	England		20.8 ng/ℓ					[Wilkinson et al., 2017]
Antipyrine	China					0.15-0.22 ng/ℓ		[Cai et al., 2015]
Aminopyrine	China					0.17-0.64 ng/ℓ		[Cai et al., 2015]
Diclofenac	Germany		1.2 µg/ℓ					[Ferrari et al., 2004]
	United States			46 ng/ℓ				[Miller and Meek, 2006]
	England		11.4 ng/ℓ					[Wilkinson et al., 2017]
	China	ND-1.5 ng/ℓ						[Yan et al., 2015]
	Taiwan			2.1-33.2 ng/ℓ				[Lin et al., 2015]
	Singapore	0.04-1.7 ng/ℓ						[Bayen et al., 2016]
	Nigeria				0.39 mg/ℓ		0.17 mg/ℓ	[Ogah et al., 2020]
	Nigeria				0.73 mg/ℓ			[Ogah et al., 2020]
	Vietnam	0.41-0.31 ng/ℓ						[Tran et al., 2014]
	Nigeria	0.27 µg/ℓ						[Olarinmoye et al., 2016]
	Brazil		0.060 µg/ℓ					[Pivetta and Gastaldini, 2019]
	Brazil		0.069 µg/ℓ					[Pivetta and Gastaldini, 2019]

Pharmaceuticals and personal care products	Country	Concentration in various water matrices						References
		Surface water		Groundwater		Drinking water		
		Range	Mean	Range	Mean	Range	Mean	
	Taiwan	24-62 ng/ℓ						[Hsin et al., 2008]
	Vietnam	<140-310 ng/ℓ						[Tran et al., 2014]
	China					< LOD-2.37 ng/ℓ		[Cai et al., 2015]
Paracetamol	Brazil		2.975 µg/ℓ					[Pivetta and Gastaldini, 2019]
	Brazil		0.426 µg/ℓ					[Pivetta and Gastaldini, 2019]
Ibuprofen	United States	<1-34 ng/ℓ						[Zhang et al., 2006]
	South Korea	ND-414 ng/ℓ						[Kim et al., 2009]
	China	0.86-115.8 ng/ℓ						[Yan et al., 2015]
	Taiwan			17.4-836.7 ng/ℓ				[Lin et al., 2015]
	China	1 417 ng/ℓ						[Peng et al., 2009]
	Vietnam	0.10-0.58 ng/ℓ						[Tran et al., 2014]
	United States					ND-1.16 ng/ℓ		[Subedi et al., 2015]
	Nigeria	8.84 µg/ℓ						[Olarinmoye et al., 2016]
	Brazil		1.266 µg/ℓ					[Pivetta and Gastaldini, 2019]
	Brazil		0.515 µg/ℓ					[(Pivetta and Gastaldini, 2019]
	Taiwan	<12-30 ng/ℓ						[Hsin et al., 2008]
	Vietnam	100-1 100 ng/ℓ						[Tran et al., 2014]
	China					< LOD-17.17 ng/ℓ		[Cai et al., 2015]
	China			24.50 ng/ℓ				[Wu et al., 2020]
	China			42.99 ng/ℓ				[Wu et al., 2020]
	Vietnam	< 0.04-0.45 ng/ℓ						[Tran et al., 2014]
	Nigeria	<0.02 µg/ℓ						[Olarinmoye et al., 2016]
	United States	<1-135 ng/ℓ						[Zhang et al., 2006]
	Taiwan	110-620 ng/ℓ						[Hsin et al., 2008]

Pharmaceuticals and personal care products	Country	Concentration in various water matrices						References
		Surface water		Groundwater		Drinking water		
		Range	Mean	Range	Mean	Range	Mean	
	Vietnam	<40-330 ng/ℓ						[Tran et al., 2014]
Naproxen	Taiwan				128.0 ng/ℓ			[Lin et al., 2015]
	Singapore	< 1-10.85 ng/ℓ						[You et al., 2015]
	Vietnam	0.08-0.38 ng/ℓ						[Tran et al., 2014]
	Nigeria	0.03 µg/ℓ						[Olarinmoye et al., 2016]
	Vietnam	80-380 ng/ℓ						[Tran et al., 2014]
Fenoprofen	Vietnam	< 0.04-0.41 ng/ℓ						[Tran et al., 2014]
	Nigeria	< 0.02 µg/ℓ						[Olarinmoye et al., 2016]
	South Korea	ND-326 ng/ℓ						[Kim et al., 2009]
	South Korea	ND-33.5 ng/ℓ						[Kim et al., 2009]
	Vietnam	< 0.02-0.27 ng/ℓ						[Tran et al., 2014]
Propyphenazone	Vietnam	< 0.06 ng/ℓ						[Tran et al., 2014]
Acetylsalicylic acid	Nigeria	0.13 µg/ℓ						[Olarinmoye et al., 2016]
Antibiotics								
Amoxicillin	Zambia		2 500 ng/ℓ					[Ngumba et al., 2020]
Chloramphenicol	Singapore	< 0.07-1.53 ng/ℓ						[You et al., 2015]
	Singapore	0.003-0.70 ng/ℓ						[Bayen et al., 2016]
	Nigeria	0.36 µg/ℓ						[Olarinmoye et al., 2016]
	China			0.55 ng/ℓ				[Wu et al., 2020]
	China			0.16 ng/ℓ				[Wu et al., 2020]
Chlortetracycline	Nigeria	< 0.05 µg/ℓ						[Olarinmoye et al., 2016]
Erythromycin	South Korea	ND-137 ng/ℓ						[Kim et al., 2009]
	Taiwan				54.8 ng/ℓ			[Lin et al., 2015]
	Bangladesh	< LOD-6.46 ng/ℓ						[Hossain et al., 2018]
	China	1.41-156 ng/ℓ						[Yan et al., 2015]
	Nigeria	1.00 µg/ℓ						[Olarinmoye et al., 2016]

Pharmaceuticals and personal care products	Country	Concentration in various water matrices						References
		Surface water		Groundwater		Drinking water		
		Range	Mean	Range	Mean	Range	Mean	
	China			1.55 ng/ℓ				[Wu et al., 2020]
	China			1.71 ng/ℓ				[Wu et al., 2020]
Clarithromycin	Taiwan				6.9 ng/ℓ			[Lin et al., 2015]
	Nigeria	< 0.05 ng/ℓ						[Olarinmoye et al., 2016]
Fluoroquinolones	China	N-45.8 ng/ℓ	15.4 ng/ℓ					[Lin et al., 2020]
Sulfadimidine	Nigeria	< 0.01 µg/ℓ						[Olarinmoye et al., 2016]
Nalidixic acid	Taiwan			1.6-16.4 ng/ℓ				[Lin et al., 2015]
Sulfamethoxazole	Germany		0.48 µ/L					[Ferrari et al., 2004]
	Taiwan			0.2-1 820 ng/ℓ				[Lin et al., 2015]
	United States			490 ng/ℓ				[Miller and Meek, 2006]
	United States			113 ng/ℓ				[Schaider et al., 2014]
	Korea		26.9 ng/ℓ					[Choi et al., 2008]
	United States					8.2 ng/ℓ		[Glassmeyer et al., 2017]
	Kenya	13.8 mg/ℓ						[Ngumba et al., 2016]
	China	0.44-115.3 ng/ℓ						[Yan et al., 2015]
	Bangladesh	< LOD-7.24 ng/ℓ						[Hossain et al., 2018]
	United States					ND-0.39 ng/ℓ		[Subedi et al., 2015]
	Nigeria	1.50 µg/ℓ						[Olarinmoye et al., 2016]
	China	ND-39.6 ng/ℓ	20 ng/ℓ					[Lin et al., 2020]
	China					< LOD-1.81 ng/ℓ		[Cai et al., 2015]
	China			19.29 ng/ℓ				[Wu et al., 2020]
	China			11.01 ng/ℓ				[Wu et al., 2020]
	Zambia		11 800 ng/ℓ					[Ngumba et al., 2020]
	Kenya		96.9 µg/ℓ					[Kairigo et al., 2020]
Tetracycline	Kenya	2.6 mg/ℓ						[Ngumba et al., 2016]
	Zambia		2 200 ng/ℓ					[Ngumba et al., 2020]

Pharmaceuticals and personal care products	Country	Concentration in various water matrices						References
		Surface water		Groundwater		Drinking water		
		Range	Mean	Range	Mean	Range	Mean	
	Nigeria	< 0.05 µg/ℓ						[Olarinmoye et al., 2016]
Trimethoprim	Bangladesh	< LOQ-17.20 ng/ℓ						[Hossain et al., 2018]
	China	0.4-20.5 ng/ℓ						[Yan et al., 2015]
	Zambia		2 410 ng/ℓ					[Ngumba et al., 2020]
	Kenya		3.8 µg/ℓ					[Kairigo et al., 2020]
	Nigeria	0.40 µg/ℓ						[Olarinmoye et al., 2016]
	China			1.03 ng/ℓ				[Wu et al., 2020]
	China			3.23 ng/ℓ				[Wu et al., 2020]
	India							[Subedi et al., 2017]
Doxycycline	Zambia		2 730 ng/ℓ					[Ngumba et al., 2020]
	Nigeria		< 0.05 µg/ℓ					[Olarinmoye et al., 2016]
Tylosin	Bangladesh	< LOD-16.68 ng/ℓ						[Hossain et al., 2018]
Clarithromycin	South Korea	ND-443 ng/ℓ						[Kim et al., 2009]
Ciprofloxacin	Kenya	0.5 mg/ℓ						[Ngumba et al., 2016]
	Zambia		400 ng/ℓ					[Ngumba et al., 2020]
	Kenya		2.5 µg/ℓ					[Kairigo et al., 2020]
Ofloxacin	Taiwan					0.9-11.8 ng/ℓ		[Lin et al., 2015]
	China	3.1-114.1 ng/ℓ						[Yan et al., 2015]
	Nigeria				0.24 mg/ℓ		0.08 mg/ℓ	[Ogah et al., 2020]
Sulfadiazine	Taiwan			0.1-14.4 ng/ℓ				[Lin et al., 2015]
	China	0.36-26.7 ng/ℓ						[Yan et al., 2015]
	Singapore	0.04-0.80 ng/ℓ						[Bayen et al., 2016]
	Nigeria	0.04 µg/ℓ						[Olarinmoye et al., 2016]
Sulfamonomethoxine	Taiwan			0.6-1.8 ng/ℓ				[Lin et al., 2015]
	China			3.43 ng/ℓ				[Wu et al., 2020]
	China			12.39 ng/ℓ				[Wu et al., 2020]

Pharmaceuticals and personal care products	Country	Concentration in various water matrices						References
		Surface water		Groundwater		Drinking water		
		Range	Mean	Range	Mean	Range	Mean	
Sulfathiazole	Taiwan			0.7-3.0 ng/ℓ				[Lin et al., 2015]
	China			3.86 ng/ℓ				[Wu et al., 2020]
	China			2.24 ng/ℓ				[Wu et al., 2020]
Sulfamethizole	Bangladesh	< LOD to 11.35 ng/ℓ						[Hossain et al., 2018]
Sufisoxazole	China			1.51 ng/ℓ				[Wu et al., 2020]
	China			16.73 ng/ℓ				[Wu et al., 2020]
Sulfamethazine	Taiwan			1.6 to 28.9 ng/ℓ				[Lin et al., 2015]
	Bangladesh	< LOD to 4.19 ng/ℓ						[Hossain et al., 2018]
	China	ND to 3.7 ng/ℓ						[Yan et al., 2015]
	Singapore	06 to 6.26 ng/ℓ						[Bayen et al., 2016]
	China			0.49 ng/ℓ				[Wu et al., 2020]
	China			0.83 ng/ℓ				[Wu et al., 2020]
Sulfadimethoxine	Taiwan			0.8 to 4.3 ng/ℓ				[Lin et al., 2015]
Flumequine	Taiwan			2.4 to 6.6 ng/ℓ				[Lin et al., 2015]
Pipemidic acid	Taiwan				10.2 ng/ℓ			[Lin et al., 2015]
Lincomycin	Singapore	0.04 to 1.36 ng/ℓ						[Bayen et al., 2016]
Dimetridazole	Taiwan				1.8 ng/ℓ			[Lin et al., 2015]
Norfloxacin	Taiwan				9.3 ng/ℓ			[Lin et al., 2015]
	China	ND to 92.4 ng/ℓ						[Yan et al., 2015]
	Kenya		1.6 µg/ℓ					[Kairigo et al., 2020]
Moxifloxacin	China	ND to 6.4 ng/ℓ						[Yan et al., 2015]
Metronidazole	Taiwan				26.2 ng/ℓ			[Lin et al., 2015]
	Bangladesh	0.05 to 13.51 ng/ℓ						[Hossain et al., 2018]
Roxithromycin	China	0.6 to 88.4 ng/ℓ						[Yan et al., 2015]
Sulfamerazine	Singapore	0.03 to 0.24 ng/ℓ						[Bayen et al., 2016]
	China			2.49 ng/ℓ				[Wu et al., 2020]
	China			0.69 ng/ℓ				[Wu et al., 2020]

Pharmaceuticals and personal care products	Country	Concentration in various water matrices						References
		Surface water		Groundwater		Drinking water		
		Range	Mean	Range	Mean	Range	Mean	
Azithromycin	China	2.6 to 166.5 ng/ℓ						[Yan et al., 2015]
Oxytetiacycline	China	85.0 to 375.9 ng/ℓ	213.1 ng/ℓ					[Lin et al., 2020]
Florfenicol	China	ND to 287.5 ng/ℓ	153.1 ng/ℓ					[Lin et al., 2020]
Antiseptic								
Triclosan	United States	9 to 26 ng/ℓ						[Zhang et al., 2006]
	Kenya			0.02 ng/ℓ				[Sorensen et al., 2015]
	China	61 to 660 ng/ℓ	189 ng/ℓ					[Lin et al., 2020]
	Kenya			0.03 ng/ℓ				[Sorensen et al., 2015]
	United States					ND to 1.93 ng/ℓ		[Subedi et al., 2015]
	China			18.05 ng/ℓ				[Wu et al., 2020]
	China			109.90 ng/ℓ				[Wu et al., 2020]
Triclocarban	United States					ND to 20.2 ng/ℓ		[Subedi et al., 2015]
N,N-Diethyltoluamide (DEET)	United States	7.2 to 110 ng/ℓ						[Fairbairn et al., 2015]
	China	0.8 to 10.2 ng/ℓ						[Sun et al., 2015]
Antihypertensives/Beta-blockers								
Atenolol	South Korea	ND to 690 ng/ℓ						[Kim et al., 2009]
	Taiwan				3.6 ng/ℓ			[Lin et al., 2015]
	United States					ND to 19.5 ng/ℓ		[Subedi et al., 2015]
Acebutolol	Taiwan				0.7 ng/ℓ			[Lin et al., 2015]
Metoprolol	United States					18.4 ng/ℓ		[Glassmeyer et al., 2017]
	China	0.46 to 17.3 ng/ℓ						[Yan et al., 2015]
Propranolol	Germany		0.59 µg/ℓ					[Ferrari et al., 2004]
	South Korea	ND to 40.1 ng/ℓ						[Kim et al., 2009]
Antiepileptics								
Carbamazepine	Bangladesh	< LOD to 8.8 ng/ℓ						[Hossain et al., 2018]
	United States					586 ng/ℓ		[Glassmeyer et al., 2017]
	United States					26.50 ng/ℓ		[Glassmeyer et al., 2017]

Pharmaceuticals and personal care products	Country	Concentration in various water matrices						References
		Surface water		Groundwater		Drinking water		
		Range	Mean	Range	Mean	Range	Mean	
	Germany		1.1 µg/ℓ					[Ferrari et al., 2004]
	United States			72 ng/ℓ				[Schaider et al., 2014]
	United States	43 to 114 ng/ℓ						[Zhang et al., 2006]
	United States			420 ng/ℓ				[Miller and Meek, 2006]
	Singapore	0.06 to 4.63 ng/ℓ						[Bayen et al., 2016]
	Taiwan			0.4 to 37.9 ng/ℓ				[Lin et al., 2015]
	China	0.41 to 10.3 ng/ℓ						[Yan et al., 2015]
	South Korea	ND to 595 ng/ℓ						[Kim et al., 2009]
	Vietnam	< 0.144 to 0.53 ng/ℓ						[Tran et al., 2014]
	Nigeria	< 0.01 ng/ℓ						[Olarinmoye et al., 2016]
	China					0.37 to 1.15 ng/ℓ		[Cai et al., 2015]
	China					0.51 to 38.24 ng/ℓ		[Cai et al., 2015]
Dilantin	United States			22 ng/ℓ				[Miller and Meek, 2006]
Phenytoin	United States			66 ng/ℓ				[Schaider et al., 2014]
Antipsychotic								
Bromazepam	United States	42 ng/ℓ						[Ferreira, 2014]
Clonazepam	United States	198 ng/ℓ						[Ferreira, 2014]
Sulpiride	Singapore	< 0.1 to1.23 ng/ℓ						[You et al., 2015).
Risperidone	Singapore	03 to 0.21 ng/ℓ						[Bayen et al., 2016]
Diazepam	United States	335 ng/ℓ						[Ferreira, 2014]
	Nigeria	< 0.01 µg/ℓ						[Olarinmoye et al., 2016]
Lipid regulators								
Bezafibrate	China	ND to 31.4 ng/ℓ						[Yan et al., 2015]
	Taiwan			0.1 to 256.7 ng/ℓ				[Lin et al., 2015]
	Nigeria	< 0.02 µg/ℓ						[Olarinmoye et al., 2016]
	China					0.31 to 0.85 ng/ℓ		[Cai et al., 2015]
	China					< LOD to 0.16 ng/ℓ		[Cai et al., 2015]
Clofibrac acid	Germany		0.55 µg/ℓ					[Ferrari et al., 2004]

Pharmaceuticals and personal care products	Country	Concentration in various water matrices						References
		Surface water		Groundwater		Drinking water		
		Range	Mean	Range	Mean	Range	Mean	
	China	ND to 17.2 ng/ℓ						[Yan et al., 2015]
	United States	3 to 27 ng/ℓ						[Zhang et al., 2006]
	China	248 ng/ℓ						[Peng et al., 2009]
	Taiwan			0.1 to 1.0 ng/ℓ				[Lin et al., 2015]
	Vietnam	< 0.05 ng/ℓ						[Tran et al., 2014]
	Nigeria	0.04 µg/ℓ						[Olarinmoye et al., 2016]
	China					< LOD to 1.37 ng/ℓ		[Cai et al., 2015]
Gemfibrozil	China	ND to 1.4 ng/ℓ						[Yan et al., 2015]
	Singapore	0.77 to 17.7 ng/ℓ						[Bayen et al., 2016]
	Vietnam	< 0.05 ng/ℓ						[Tran et al., 2014]
	Nigeria	< 0.02 µg/ℓ						[Olarinmoye et al., 2016]
Simvastatin	China	2.3 to 16.7 ng/ℓ						[Yan et al., 2015]
Atorvastatin	China	ND to 0.6 ng/ℓ						[Yan et al., 2015]
Etofibrate	Nigeria	< 0.02 µg/ℓ						[Olarinmoye et al., 2016]
Fenofibrate	Nigeria	< 0.04 µg/ℓ						[Olarinmoye et al., 2016]
Antivirals								
Lamivudine	Kenya	5.4 mg/ℓ						[Ngumba et al., 2016]
	Zambia		49 700 ng/ℓ					[Ngumba et al., 2020]
	Kenya		219.6 µg/ℓ					[Kairigo et al., 2020]
Zidovudine	Kenya	7.7 mg/ℓ						[Ngumba et al., 2016]
	Zambia		1 280 ng/ℓ					[Ngumba et al., 2020]
	Kenya		2.1 µg/ℓ					[Kairigo et al., 2020]
Nevirapine	Kenya	4.8 mg/ℓ						[Ngumba et al., 2016]
	Zambia		210 ng/ℓ					[Ngumba et al., 2020]
	Kenya		0.9 µg/ℓ					[Kairigo et al., 2020]
Human indicators								
Caffeine	United States	0.84 to 250 ng/ℓ	44 ng/ℓ					[Fairbairn et al., 2015]
	United States	<1 to 38 ng/ℓ						[Zhang et al., 2006]
	Singapore	33.9 to 644.5 ng/ℓ						[You et al., 2015]
	Korea		268.7 ng/ℓ					[Choi et al., 2008]

Pharmaceuticals and personal care products	Country	Concentration in various water matrices						References
		Surface water		Groundwater		Drinking water		
		Range	Mean	Range	Mean	Range	Mean	
	Zambia			1.7 ng/ℓ				[Sorensen et al., 2015]
	United States					88 ng/ℓ		[Glassmeyer et al., 2017]
	Taiwan			1.2 to 930.7 ng/ℓ				[Lin et al., 2015]
	Singapore	5 to 1 389 ng/ℓ						[Bayen et al., 2016]
	United States					ND to 11.1 ng/ℓ		[Subedi et al., 2015]
	China			782.62 ng/ℓ				[Wu et al., 2020]
	China			461.87 ng/ℓ				[Wu et al., 2020]

2.5.1.2 Pharmaceuticals and personal care products in wastewater influents and effluents

The international prevalent of PPCPs in wastewater influent and effluent is well researched as discussed below and summarised in Table 2.2.

Non-steroidal anti-inflammatory drugs

Subedi et al. (2017) conducted a study on mass loading and removal of PPCPs, including psycho-actives, antihypertensive, and antibiotics, in two sewage treatment plants in Southern India and detected among the NSAIDs, acetaminophen (5 400 to 11 000 ng/ℓ) in influent samples. In effluent samples, ibuprofen (270 to 1 940 ng/ℓ), acetaminophen (330 to 1 200 ng/ℓ), and mefenamic acid (320 to 750 ng/ℓ) were also detected (Subedi et al., 2017). A study on human pharmaceuticals conducted in Jordanian wastewater samples reported the concentration of ibuprofen (ND to 5.7 ng/ℓ), naproxen (0.7 to 5.2 ng/ℓ) and diclofenac (0.8 to 3.3 ng/ℓ) in influent, while in effluent they were reported as ibuprofen (ND to 2.2 ng/ℓ), naproxen (ND to 1.3 ng/ℓ), and diclofenac (ND to 1.1 ng/ℓ) (Al-Tarawneh et al., 2014).

In Cyprus, Hapeshi et al. (2015), conducted a study on licit and illicit drugs in urban wastewater, and detected acetaminophen (7 871 to 232 300 ng/ℓ) with a mean concentration of 115 004 ng/ℓ; diclofenac (1 202 to 3 457 ng/ℓ), with a mean concentration of 2 339 ng/ℓ; ibuprofen (1 680 to 5 315 ng/ℓ), with a mean concentration of 2 801 ng/ℓ; indomethacin (19-120 ng/ℓ), with a mean concentration of 73 ng/ℓ; ketoprofen (below limit of detection [BLD] to 956 ng/ℓ), with a mean concentration of 900 ng/ℓ; mefenamic acid (1 040 to 2 040 ng/ℓ), with a mean concentration of 1 411 ng/ℓ; propyphenazone (BLD to 10 ng/ℓ), with a mean concentration of 10 ng/ℓ; and naproxen (BLD to 210 ng/ℓ), with a mean concentration of 90 ng/ℓ in influent samples. The study also detected concentrations of acetaminophen (BLD to 650 ng/ℓ), with a mean concentration of 553 ng/ℓ; diclofenac (BLD to 2 950 ng/ℓ), with a mean concentration of 804 ng/ℓ; ibuprofen (BLD to 82 ng/ℓ), with a mean concentration of 43 ng/ℓ; indomethacin (BLD to 110 ng/ℓ), with a mean concentration of 23 ng/ℓ; ketoprofen (BLD to 120 ng/ℓ), with a mean concentration of 89 ng/ℓ; and mefenamic acid (BLD to 310 ng/ℓ), with a mean concentration of 68 ng/ℓ in effluent samples (Hapeshi et al., 2015).

Another study, conducted in Northern Taiwan by Fang et al. (2012) to determine the occurrence and distribution of pharmaceutical compounds in the effluents of a major sewage treatment plant and the receiving coastal waters, reported the concentration of diclofenac (152 to 185 ng/ℓ); ibuprofen (724 to 2 200 ng/ℓ); and ketoprofen (128 to 184 ng/ℓ) in influent. Their corresponding concentrations in effluent ranged from 100 to 131, 552 to 1 600, and 68 to 128 ng/ℓ, respectively (Fang et al., 2012). Wilkinson et al. (2017) conducted a study on spatial distribution of organic contaminants in three rivers of southern England bound to suspended particulate material dissolved in water, and recorded the concentration of acetaminophen and diclofenac in upper stream and sewage treatment effluent. In effluent, the concentration of acetaminophen and diclofenac were recorded as 47.5 and 86.5 ng/ℓ, respectively (Wilkinson et al., 2017).

Antibiotics

A study conducted in Lusaka, Zambia, to determine the occurrence of antibiotics and antiretroviral drugs in source-separated urine, groundwater, surface water and wastewater in the peri-urban area of Chunga, reported mean concentrations of trimethoprim (32 670 ng/ℓ), sulfamethoxole (33 300 ng/ℓ), ciprofloxacin (740 ng/ℓ), norfloxacin (100 ng/ℓ), tetracycline (220 ng/ℓ), doxycycline (4 490 ng/ℓ), and amoxicillin (3 270 ng/ℓ) in influent samples. The study also detected trimethoprim, sulfamethoxole, ciprofloxacin, norfloxacin, tetracycline, doxycycline, amoxicillin, in effluent at mean concentrations of 1 770, 30 040, 230, 80, 4 590, 5 280, and 5 580 ng/ℓ, respectively (Ngumba et al., 2020). In a study aimed at assessing the contamination of surface water and river sediments by antibiotic and antiretroviral drug cocktails in low and middle-income countries with specific reference to the occurrence, risk and mitigation strategies, the mean concentrations of norfloxacin, trimethoprim, ciprofloxacin, and sulfamethoxole were reported in effluent samples as 4.2, 15.8, 5.3, and 956.4 µg/ℓ, respectively (Kairigo et al., 2020).

A study on human pharmaceuticals in Jordanian wastewater samples reported concentrations of sulfamethoxazole (ND to 0.9 ng/ℓ) and erythromycin (0.5 to 1.1 ng/ℓ) in influent samples. Furthermore, sulfamethoxazole (ND to 0.3 ng/ℓ) and erythromycin (ND to 0.5 ng/ℓ) were detected in effluent samples (Al-Tarawneh et al., 2014). A study investigating the occurrence and risk assessment of emerging contaminants in a water reclamation and ecological reuse project in China, reported the concentrations of sulfamethoxole, enrofloxacin, oxytetracycline, and florfenicol in influent samples ranging from 2.7 to 40.8, 50.1 to 135.2, 203.6 to 348.5, and ND to 297.3 ng/ℓ, respectively. In effluent, sulfamethoxole, enrofloxacin, oxytetracycline, florfenicol, were also detected as ND to 14.0, ND to 100.6, 32.5 to 381.0, and ND to 219.6 ng/ℓ, respectively (Lin et al., 2020).

In Southern India, a study was conducted that aimed on mass loading and removal of PPCPs, including psychoactives, antihypertensives, and antibiotics in two sewage treatment plants, and detected antibiotics such as trimethoprim (68 to 400 ng/ℓ), sulfamethoxazole (55 to 690 ng/ℓ), and clindamycin (25 to 790 ng/ℓ) in influent samples. In effluent samples, the same study detected the concentration of sulfamethoxazole ranging from 120 to 420 ng/ℓ and lincomycin ranging from 280 to 510 ng/ℓ (Subedi et al., 2017).

In Cyprus, a study was conducted targeting licit and illicit drugs in urban wastewater and detected antibiotics such as erythromycin (BLD to 428 ng/ℓ), with a mean concentration of 97 ng/ℓ; ofloxacin (220 to 2 360 ng/ℓ) with a mean concentration of 615 ng/ℓ; sulfamethoxazole (178 to 350 ng/ℓ), with a mean concentration of 305 ng/ℓ; and trimethoprim (30 to 130 ng/ℓ), with a mean concentration of 71 ng/ℓ in influent samples. The same study also detected a concentration of erythromycin (BLD to 140 ng/ℓ), with a mean concentration of 32 ng/ℓ; ofloxacin (BLD to 353 ng/ℓ), with a mean concentration of 218 ng/ℓ; sulfamethoxazole (BLD to 290 ng/ℓ), with a mean concentration of 76 ng/ℓ; trimethoprim (BLD to 4 ng/ℓ), with a mean concentration of 4 ng/ℓ; and azythromycin (BLD to 70 ng/ℓ), with a mean concentration of 38 ng/ℓ in effluent (Hapeshi et al., 2015).

Beta-blockers

In a study aimed at mass loading and removal of PPCPs, including psychoactives, antihypertensives, and antibiotics in two sewage treatment plants in Southern India, concentrations of antihypertensives and beta-blockers such as propranolol (42 to 62 ng/ℓ), atenolol (2 100 to 3 800 ng/ℓ), nordiazepam (5 to 17 ng/ℓ), diltiazem (23 to 120 ng/ℓ), desacetyl diltiazem (20 to 64 ng/ℓ), verapamil (16 to 103 ng/ℓ), norverapamil (65 to 550 ng/ℓ), venlafaxine (11 to 77 ng/ℓ), and bupropion (13 to 32 ng/ℓ) were detected in influent samples. Furthermore, diazepam (6 to 100 ng/ℓ), nordiazepam (13 to 20 ng/ℓ), venlafaxine (12 to 18 ng/ℓ), bupropion (13 to 16 ng/ℓ), sertraline (8 to 21 ng/ℓ), propranolol (36 to 52 ng/ℓ), diltiazem (3 to 7 ng/ℓ), and desacetyl diltiazem (28 to 65 ng/ℓ) were detected in effluent samples Subedi et al., 2017).

Another study conducted to determine licit and illicit drugs in urban wastewater in Cyprus reported the concentrations of beta-blockers such as atenolol (2 750 to 4 740 ng/ℓ) with a mean concentration of 3 733 ng/ℓ, metoprolol (196 to 610 ng/ℓ) with a mean concentration of 340 ng/ℓ, propranolol (BLD to 270 ng/ℓ), with a mean concentration of 45 ng/ℓ, and sotalol (336 to 950 ng/ℓ) with a mean concentration of 597 ng/ℓ in influent samples. In the same study, effluent samples were found to have concentrations of atenolol (10 to 900 ng/ℓ) with a mean concentration of 466 ng/ℓ, metoprolol (20 to 210 ng/ℓ) with a mean concentration of 92 ng/ℓ, propranolol (BLD to 90 ng/ℓ) with a mean concentration of 40 ng/ℓ, and sotalol (BLD to 330 ng/ℓ) with a mean concentration of 121 ng/ℓ. The study also detected famotidine (490 to 2 320 ng/ℓ) with a mean concentration of 1 181 ng/ℓ, and ranitidine (28 to 640 ng/ℓ with a mean concentration of 207 ng/ℓ in influent samples, while in effluent samples, famotidine (BLD to 20 ng/ℓ) with a mean concentration of 20 ng/ℓ and ranitidine (BLD to 30 ng/ℓ) with a mean concentration of 30 ng/ℓ, were also detected (Hapeshi et al., 2015).

Antiepileptics

A study on human pharmaceuticals in Jordanian wastewater samples reported the concentration of carbamazepine among the antiepileptic drugs in both influent and effluent samples as 0.7 to 3.6 ng/ℓ and 0.4

to 1.3 ng/ℓ, respectively (Al-Tarawneh et al., 2014). Subedi et al. (2017) conducted a study aimed at mass loading and removal of PPCPs, including psychoactives, antihypertensives, and antibiotics in two sewage treatment plants in Southern India, and detected antiepileptic carbamazepine at a concentration ranging from 240 to 750 and 45 to 770 ng/ℓ in influent and effluent samples, respectively. Hapeshi et al. (2015) also detected carbamazepine in both influent and effluent at a concentration ranging from 460 to 4 023 and BLD to 5 520 ng/ℓ, respectively, in their study conducted to determine licit and illicit drugs in urban wastewater in Cyprus.

Antipsychotic

Subedi et al. (2017) conducted a study aimed on mass loading and removal of PPCPs, including psychoactives, antihypertensives, and antibiotics in two sewage treatment plants in Southern India, and reported the concentration of quetiapine ranging from 17 to 76 ng/ℓ in influent samples. Furthermore, in effluent samples, quetiapine (16 to 24 ng/ℓ) and aripiprazole (38 to 150 ng/ℓ) were also detected among the antipsychotic drugs (Subedi et al., 2017).

Lipid regulators

Hapeshi et al. (2015) detected lipid regulators such as bezafibrate (519 to 1 610 ng/ℓ) with a mean concentration 1 104 ng/ℓ, gemfibrozil (71 to 1 080 ng/ℓ) with a mean concentration of 476 ng/ℓ, pravastatin (23 to 130 ng/ℓ) with a mean concentration of 70 ng/ℓ in influent samples in their study conducted to determine licit and illicit drugs in urban wastewater in Cyprus. The same study also detected bezafibrate (25 to 170 ng/ℓ) with a mean concentration of 108 ng/ℓ, gemfibrozil (BLD to 480 ng/ℓ) with a mean concentration of 139 ng/ℓ, and pravastatin (BLD to 8 ng/ℓ) with a mean concentration of 8 ng/ℓ in effluents samples (Hapeshi et al., 2015).

Antivirals

A study conducted in Zambia Lusaka to determine the occurrence of antibiotics and antiretroviral drugs in source-separated urine, groundwater, surface water and wastewater in the peri-urban area of Chunga, reported the mean concentrations of antiretroviral drugs such as nevirapine (680 ng/ℓ), zidovidine (66 590 ng/ℓ), and lamivudine (118 970 ng/ℓ) in influent samples. Furthermore, in the same study, nevirapine, zidovidine, and lamivudine were reported at mean concentrations of 1 720, 37 140 and 55 760 ng/ℓ in effluent samples, respectively (Ngumba et al., 2020). In Kenya, Kairigo et al. (2020) conducted a study to assess the contamination of surface water and river sediments by antibiotic and antiretroviral drug cocktails in low and middle-income countries aimed at the occurrence, risk and mitigation strategies, and reported the mean concentration of antiretroviral drugs such as lamivudine, zidovidine, and nevirapine in effluent as 847, 1.4, and 9.5 µg/ℓ, respectively (Kairigo et al., 2020).

Antiseptics

Subedi et al. (2017) conducted a study on mass loading and removal of PPCPs, including psychoactives, antihypertensives, and antibiotics in two sewage treatment plants in Southern India, and detected the concentration of triclocarban in both influents and effluents, ranging from 1 300 to 4 300, and 300 to 860 ng/ℓ, respectively. In a study conducted to determine the occurrence and risk assessment of emerging contaminants in a water reclamation and ecological reuse project in China, antiseptic triclosan was detected in influents at a concentration ranging from 219 to 718 ng/ℓ, with a mean concentration of 418 ng/ℓ, and in effluents ranging from 37 to 620 ng/ℓ, with a mean concentration of 204 ng/ℓ (Lin et al., 2020).

Table 2.2 Occurrence and concentration levels of pharmaceuticals and personal care products in international wastewater influents and effluents

Pharmaceutical and personal care products	Country	WWTP influent		WWTP effluent		References
		Range	Mean	Range	Mean	
Non-steroidal anti-inflammatory drugs (NSAIDs)						
Acetaminophen	England				47.5 ng/ℓ	[Wilkinson et al., 2017]
	India	5 400 to 11 000 ng/ℓ		330 to 1 200 ng/ℓ		[Subedi et al., 2017]
	Cyprus	7 871 to 232 300 ng/ℓ	11 5004 ng/ℓ	BLD to 650 ng/ℓ	553 ng/ℓ	[Hapeshi et al., 2015]
Diclofenac	Germany				2.1 µg/ℓ	[Ferrari et al., 2004]
	Taiwan	152 to 185 ng/ℓ		100 to 131 ng/ℓ		[Fang et al., 2012]
	England				86.5 ng/ℓ	[Wilkinson et al., 2017]
	Cyprus	1 202 to 3457 ng/ℓ	2 339 ng/ℓ	BLD to 2 950 ng/ℓ	804 ng/ℓ	[Hapeshi et al., 2015]
	Jordan	0.8 to 3.3ng/ℓ		ND to 1.1 ng/ℓ		[Al-Tarawneh et al., 2015]
Ibuprofen	Cyprus	1 680 to 5 315 ng/ℓ	2801 ng/ℓ	BLD to 82 ng/ℓ	43 ng/ℓ	[Hapeshi et al., 2015]
	Taiwan	724 to 2 200 ng/ℓ		552 to 1 600 ng/ℓ		[Fang et al., 2012]
	Jordan	ND to 5.7 ng/ℓ		ND to 2.2 ng/ℓ		[Al-Tarawneh et al., 2015]
	India			270 to 1 940 ng/ℓ		[Subedi et al., 2017]
Ketoprofen	Taiwan	128 to 184 ng/ℓ		68 to 128 ng/ℓ		[Fang et al., 2012]
	Cyprus	BLD to 956 ng/ℓ	900 ng/ℓ	BLD to 120 ng/ℓ	89 ng/ℓ	[Hapeshi et al., 2015]
Naproxen	Jordan	0.7 to 5.2 ng/ℓ		ND to 1.3 ng/ℓ		[Al-Tarawneh et al., 2015]
	Cyprus	BLD to 210 ng/ℓ	90 ng/ℓ			[Hapeshi et al., 2015]
Mefenamic acid	United Kingdom			28-176 ng/ℓ		[Zhou and Broodbank, 2014]
	India			320 to 750 ng/ℓ		[Subedi et al., 2017]
	Cyprus	1 040 to 2 040 ng/ℓ	1411 ng/ℓ	BLD to 310 ng/ℓ	68 ng/ℓ	[Hapeshi et al., 2015]
Indomethacin	United Kingdom			6 28 ng/ℓ		[Zhou and Broodbank, 2014]
	Cyprus	19 to 120 ng/ℓ	73 ng/ℓ	BLD to 110 ng/ℓ	23 ng/ℓ	[Hapeshi et al., 2015]
Tramadol	United States	23.04 ng/ℓ				[Glassmeyer et al., 2017]
Propyphenazone	Cyprus	BLD to 10 ng/ℓ	10 ng/ℓ			[Hapeshi et al., 2015]

Antibiotics						
Amoxicillin	Zambia		3 270 ng/ℓ		5 580 ng/ℓ	[Ngumba et al., 2020]
Erythromycin	Jordan	0.5 to 1.1 ng/ℓ		ND to 0.5 ng/ℓ		[Al-Tarawneh et al., 2015]
	Cyprus	BLD to 428 ng/ℓ	97 ng/ℓ	BLD to 140 ng/ℓ	32 ng/ℓ	[Hapeshi et al., 2015]
Fluoroquinolones	China	50.1 to 135.2 ng/ℓ	92.2 ng/ℓ	ND to 100.6 ng/ℓ	52.6 ng/ℓ	[Lin et al., 2020]
Sulfamethoxazole	Germany				2 µg/ℓ	[Ferrari et al., 2004]
	United States	161.1 ng/ℓ				[Glassmeyer et al., 2017]
	China	2.7 to 40.8 ng/ℓ	12.9 ng/ℓ	ND to 14.0 ng/ℓ	2.2 ng/ℓ	[Lin et al., 2020]
	Zambia		33 300 ng/ℓ		30 040 ng/ℓ	[Ngumba et al., 2020]
	Kenya			956.4 µg/ℓ		[Kairigo et al., 2020]
	Jordan	ND to 0.9 ng/ℓ		ND to 0.3 ng/ℓ		[Al-Tarawneh et al., 2015]
	India	55 to 690 ng/ℓ		120 to 420 ng/ℓ		[Subedi et al., 2017]
	Cyprus	178 to 350 ng/ℓ	305 ng/ℓ	BLD to 290 ng/ℓ	76 ng/ℓ	[Hapeshi et al., 2015]
Tetracycline	Zambia		220 ng/ℓ		4 590 ng/ℓ	[Ngumba et al., 2020]
Trimethoprim	Kenya				15.8 µg/ℓ	[Kairigo et al., 2020]
	Zambia		32 670 ng/ℓ		1 770 ng/ℓ	[Ngumba et al., 2020]
	India	68 to 400 ng/ℓ				[Subedi et al., 2017]
	Cyprus	30 to 130 ng/ℓ	71 ng/ℓ	BLD to 4 ng/ℓ	4 ng/ℓ	[Hapeshi et al., 2015]
Doxycycline	Zambia		4 490 ng/ℓ		5 280 ng/ℓ	[Ngumba et al., 2020]
Ciprofloxacin	Kenya				5.3 µg/ℓ	[Kairigo et al., 2020]
	Zambia		740 ng/ℓ		230 ng/ℓ	[Ngumba et al., 2020]
Ofloxacin	Cyprus	220 to 2 360 ng/ℓ	615 ng/ℓ	BLD to 353 ng/ℓ	218 ng/ℓ	[Hapeshi et al., 2015]
Lincomycin	India			280 to 510 ng/ℓ		[Subedi et al., 2017]
Norfloxacin	Kenya				4.2 µg/ℓ	[Kairigo et al., 2020]
	Zambia		100 ng/ℓ		80 ng/ℓ	[Ngumba et al., 2020]
Azithromycin	Cyprus			BLD to 70 ng/ℓ	38 ng/ℓ	[Hapeshi et al., 2015]
Oxytetiacycline	China	203.6 to 348.5 ng/ℓ	287.5 ng/ℓ	32.5 to 381.0 ng/ℓ	194.9 ng/ℓ	[Lin et al., 2020]
Florfenicol	China	ND to 297.3 ng/ℓ	216.6 ng/ℓ	ND to 219.6 ng/ℓ	112.8 ng/ℓ	[Lin et al., 2020]

Antiseptics						
Triclosan	China	219 to 718 ng/ℓ	418 ng/ℓ	37 to 620 ng/ℓ	204 ng/ℓ	[Lin et al., 2020]
Triclocarban	India	1 300 to 4 300 ng/ℓ		300 to 860 ng/ℓ		[Subedi et al., 2017]
Beta-blockers / Antihypertensives						
Atenolol	India	2 100 to 3 800 ng/ℓ				[Subedi et al., 2017]
	Cyprus	2 750 to 4 740 ng/ℓ	3 733 ng/ℓ	10 to 900 ng/ℓ	466 ng/ℓ	[Hapeshi et al., 2015]
Metoprolol	United States	37.8 ng/ℓ				[Glassmeyer et al., 2017]
	Cyprus	196 to 610 ng/ℓ	340 ng/ℓ	20 to 210 ng/ℓ	92 ng/ℓ	[Hapeshi et al., 2015]
Propranolol	Germany				0.29 µg/ℓ	[Ferrari et al., 2004]
	United Kingdom			8 to 35 ng/ℓ		[Zhou and Broodbank, 2014]
	India	42 to 62 ng/ℓ		36 to 52 ng/ℓ		[Subedi et al., 2017]
	Cyprus	BLD to 270 ng/ℓ	45 ng/ℓ	BLD to 90 ng/ℓ	40 ng/ℓ	[Hapeshi et al., 2015]
Sotalol	Cyprus	336 to 950 ng/ℓ	597 ng/ℓ	BLD to 330 ng/ℓ	121 ng/ℓ	[Hapeshi et al., 2015]
Nordiazepam	India	5 to 17 ng/ℓ		13 to 20 ng/ℓ		[Subedi et al., 2017]
Diltiazem	India	23 to 120 ng/ℓ		3 to 7 ng/ℓ		[Subedi et al., 2017]
Desacetyl diltiazem	India	20 to 64 ng/ℓ		28 to 65 ng/ℓ		[Subedi et al., 2017]
Verapami	India	16 to 103 ng/ℓ				[Subedi et al., 2017]
Norverapamil	India	65 to 550 ng/ℓ				[Subedi et al., 2017]
Venlafaxine	India	11 to 77 ng/ℓ		12 to 18 ng/ℓ		[Subedi et al., 2017]
Bupropion	India	13 to 32 ng/ℓ		13 to 16 ng/ℓ		[Subedi et al., 2017]
Diazepam	India			6 to 100 ng/ℓ		[Subedi et al., 2017]
Sertraline	India			8 to 21 ng/ℓ		[Subedi et al., 2017]
Famotidine	Cyprus	490 to 2 320 ng/ℓ	1 181 ng/ℓ	BLD to 20 ng/ℓ	20 ng/ℓ	[Hapeshi et al., 2015]
Ranitidine	Cyprus	28 to 640 ng/ℓ	207 ng/ℓ	BLD to 30 ng/ℓ	30 ng/ℓ	[Hapeshi et al., 2015]
Antiepileptics						
Carbamazepine	United States	269 ng/ℓ				[Glassmeyer et al., 2017]
	United States	35.7 ng/ℓ				[Glassmeyer et al., 2017]
	Germany				6.3 µg/ℓ	[Ferrari et al., 2004]
	United Kingdom			53 to 265 ng/ℓ		[Zhou and Broodbank, 2014]

	Jordan	0.7 to 3.6 ng/ℓ		0.4 to 1.3 ng/ℓ		[Al-Tarawneh et al., 2015]
	India	240 to 750 ng/ℓ		450 to 770 ng/ℓ		[Subedi et al., 2017]
	Cyprus	460 to 4023 ng/ℓ	1 720 ng/ℓ	BLD to 5 520 ng/ℓ	1 820 ng/ℓ	[Hapeshi et al., 2015]
Antipsychotics						
Thioridazine	United Kingdom			6 to 22 ng/ℓ		[Zhou and Broodbank, 2014]
Quetiapine	India	17 to 76 ng/ℓ		16 to 24 ng/ℓ		[Subedi et al., 2017]
Aripiprazole	India			38 to 150 ng/ℓ		[Subedi et al., 2017]
Lipid regulators						
Bezafibrate	Cyprus	519 to 1 610 ng/ℓ	1 104 ng/ℓ	25 to 170 ng/ℓ	108 ng/ℓ	[Hapeshi et al., 2015]
Clofibrac acid	Germany				1.6 µg/ℓ	[Ferrari et al., 2004]
	Taiwan	104 to 109 ng/ℓ		95 to 102 ng/ℓ		[Fang et al., 2012]
Gemfibrozil	Cyprus	71 to 1 080 ng/ℓ	476 ng/ℓ	BLD to 480 ng/ℓ	139 ng/ℓ	[Hapeshi et al., 2015]
Pravastatin	Cyprus	23 to 130 ng/ℓ	70 ng/ℓ	BLD to 8 ng/ℓ	8 ng/ℓ	[Hapeshi et al., 2015]
Antivirals						
Lamivudine	Zambia		118 970 ng/ℓ		55 760 ng/ℓ	[Ngumba et al., 2020]
	Kenya				847.1 µg/ℓ	[Kairigo et al., 2020]
Zidovudine	Zambia		66 590 ng/ℓ		37 140 ng/ℓ	[Ngumba et al., 2020]
	Kenya				1.4 µg/ℓ	[Kairigo et al., 2020]
Nevirapine	Zambia		680 ng/ℓ		1 720 ng/ℓ	[Ngumba et al., 2020]
	Kenya				9.5 µg/ℓ	[Kairigo et al., 2020]
Human indicators						
Caffeine	United States	124 ng/ℓ				[Glassmeyer et al., 2017]
	United States	37.8 ng/ℓ				[Glassmeyer et al., 2017]

2.5.1.3 Herbicides in surface water, groundwater and drinking water

According to Casida (2009), pesticides are chemicals applied with the aim of killing or injuring life. They are classified based on the target species they act on. For example, herbicides are chemicals with the capability of either killing or severely injuring plants (Casida, 2009). Several studies have indicated that the widespread use of agrochemicals such as herbicides have led to their introduction into various water matrices, as summarised in Table 2.3 and discussed in this section. A study conducted with the aim of determining emerging contaminants in urban groundwater sources in Africa, detected atrazine in Kabwe, Zambia, at a maximum concentration of 0.13 and 0.07 ng/ℓ in the dry and wet season, respectively. The same study also reported the maximum concentration of bromacil as 0.09 ng/ℓ in the wet season, while the concentrations of terbutryne in the dry and wet season were recorded as 0.03 and 0.02 ng/ℓ, respectively (Sorensen et al., 2015).

In the South Fork Zumbro River watershed in south-eastern Minnesota, US, a study was conducted on the sediment-water distribution of contaminants of emerging concern in a mixed use watershed, and detected herbicides such as atrazine in surface water at concentrations ranging from 1.8 to 390 ng/ℓ, with a mean concentration of 40 ng/ℓ, and acetochlor at concentrations of 1.2 to 180 ng/ℓ, with a mean concentration of 28 ng/ℓ (Fairbairn et al., 2015). A survey was conducted in Hungary to monitor pesticide residues in surface and groundwater and reported concentrations of trifluralin, atrazine, metribuzin, alachlor, prometryn, ethofumesate, metolachlor, 2-methyl-4chlorophenoxyacetic acid (MCPA), 2,4-Dichlorophenoxyacetic acid (2,4-D), and glyphosate in surface water ranging from 800 to 10 000, 500 to 15 000, 100 to 1 000, 1 to 10, 100 to 10 000, 10 to 30, 1 to 56 000, 5 to 300, 10 to 1 000, and 500 to 1 000 ng/ℓ, respectively (Székács et al., 2015).

Mawussi et al. (2009) conducted a study assessing average exposure to organochlorine pesticides in Southern Togo from water, maize (Zea mays) and cowpea (Vigna unguiculata), which detected 2,4-D in river water at a concentration ranging from 0.03 to 0.15 µg/ℓ. In the semiarid region of Argentina, Mas et al. (2020) conducted a study to determine pesticides in water sources used for human consumption and reported concentrations of herbicides such as 2,4-D, alachlor, glyphosate, and imazethapyr in surface water ranging from 0.015 to 0.925 µg/ℓ (0.084 µg/ℓ), 0.063 to 0.326 µg/ℓ (0.197 µg/ℓ), 0.1 to 35 µg/ℓ (1.251 µg/ℓ) and 0.001 to 0.161 µg/ℓ (0.015 µg/ℓ), respectively. Pandey et al. (2019) assessed glyphosate and fluridone concentrations in water columns and sediment leachate from Liberty Island of the Sacramento-San Joaquin Delta, California, and reported their respective mean concentrations as 0.2 ppb and 0.02 ppb after wash 1 retention.

In the Federal District and Eastern Goiás of Brazil, a study was conducted during the rainy and dry season targeting herbicides in water bodies of the Samambaia River sub-basin. During the rainy season, the study detected atrazine, bentazon, carfentrazone-ethyl, clomazone, flumioxazin, fomesafen, glyphosate, linuron, metribuzin, S-metolachlor, and sulfentrazone at a concentration ranging from 0.0080 to 1.7484, 0.0058 to 0.8310, 0.0021 to 0.0325, 0.0011 to 4.0621, 0.0008 to 0.0828, 0.0000 to 0.0040, 0.6078 to 1.0628, 0.0406 to 0.0599, 0.0017 to 0.8217, 0.1420 to 1.7800, and 0.0852 to 0.8471 µg/ℓ, respectively. Furthermore, the concentrations of atrazine, bentazon, carfentrazone-ethyl, clomazone, flumioxazin, fomesafen, glyphosate, linuron, metribuzin, S-metolachlor, and sulfentrazone ranged from 0.0130 to 0.5914, 0.0561 to 0.2500, 0.0020 to 0.0364, 0.0011 to 2.8621, 0.0000 to 0.0078, 0.0000 to 0.0126, 0.8048 to 11.3328, 0.0015 to 0.0109, 0.0007 to 0.2897, 0.0129 to 0.8430, and 0.0000 to 0.1421 µg/ℓ in the dry season, respectively (Correia et al., 2020).

Table 2.3 Occurrence and concentration levels of herbicides in international surface water, groundwater, and drinking water

Herbicides	Country	Concentration in various water matrices						References
		Surface water		Groundwater		Drinking water		
		Range	Mean	Range	Mean	Range	Mean	
2,4-Dichlorodiphenyl-dichloroethylene	Hungary	10 to 1 000 ng/ℓ						[Székács et al., 2015]
	Togo	0.03 to 0.15 µg/ℓ						[Mawussi et al., 2009]
	Argentina	0.015 to 0.925 µg/ℓ	0.084 µg/ℓ					[Mas et al., 2020]
Acetochlor	United States	1.2 to 180 ng/ℓ	28 ng/ℓ					[Fairbairn et al., 2015]
Alachlor	Hungary	1 to 10 ng/ℓ						[Székács et al., 2015]
	Argentina	0.063 to 0.326 µg/ℓ	0.197 µg/ℓ					[Mas et al., 2020]
Atrazine	Zambia			0.13 ng/ℓ				[Sorensen et al., 2015]
	USA	1.8 to 390 ng/ℓ	40 ng/ℓ					[Fairbairn et al., 2015]
	Hungary	500 to 15 000 ng/ℓ						[Székács et al., 2015]
	Brazil	0.0080 to 1.7484 µg/ℓ						[Correia et al., 2020]
Bentazon	Brazil	0.0058 to 0.8310 µg/ℓ						[Correia et al., 2020]
Bromacil	Zambia			0.09 ng/ℓ				[Sorensen et al., 2015]
Carfentrazone-ethyl	Brazil	0.0021 to 0.0325 µg/ℓ						[Correia et al., 2020]
Clomazone	Brazil	0.0011 to 4.0621 µg/ℓ						[Correia et al., 2020]
Ethofumesate	Hungary	10 to 30 ng/ℓ						[Székács et al., 2015]
Flumioxazin	Brazil	0.0008 to 0.0828 µg/ℓ						[Correia et al., 2020]
Fluridone	USA	0.02 ppb						[Pandey et al., 2019]
Fomesafen	Brazil	0.0000 to 0.0040 µg/ℓ						[Correia et al., 2020]
Glyphosate	Hungary	500 to 1 000 ng/ℓ						[Székács et al., 2015]
	USA	0.2 ppb						[Pandey et al., 2019]
	Argentina	0.1 to 35 µg/ℓ	1.251 µg/ℓ					[Mas et al., 2020]
	Brazil	0.6078 to 1.0628 µg/ℓ						[Correia et al., 2020]
Imazethapyr	Argentina	0.001 to 0.161 µg/ℓ	(0.015 µg/ℓ)					[Mas et al., 2020]
Linuron	Brazil	0.0406 to 0.0599 µg/ℓ						[Correia et al., 2020]
MCPA	Hungary	5 to 300 ng/ℓ						[Székács et al., 2015]
Metolachlor	Hungary	1 to 56 000 ng/ℓ						[Székács et al., 2015]
	Brazil	0.1420 to 1.7800 µg/ℓ						[Correia et al., 2020]

Herbicides	Country	Concentration in various water matrices						References
		Surface water		Groundwater		Drinking water		
		Range	Mean	Range	Mean	Range	Mean	
Metribuzin	Hungary	100 to 1 000 ng/ℓ						[Székács et al., 2015]
	Brazil	0.0017 to 0.8217 µg/ℓ						[Correia et al., 2020]
Prometryn	Hungary	100 to 10 000 ng/ℓ						[Székács et al., 2015]
Sulfentrazone	Brazil	0.0852 to 0.8471 µg/ℓ						[Correia et al., 2020]
Terbutryne	Zambia			0.03 ng/ℓ				[Sorensen et al., 2015]
Trifluralin	Hungary	800 to 10 000 ng/ℓ						[Székács et al., 2015]

2.5.1.4 Herbicides in wastewater influents and effluents

Only a few studies were conducted to determine the concentration of herbicides in international influent and effluent samples. A study on the occurrence and removal of triazine herbicides during wastewater treatment processes and their environmental impact on aquatic life in Baoding city, Hebei province in China, reported an average concentration of atrazine, simetryn, and prometryn in influent as 104.59, 87.23 and 28.79 ng/ℓ, respectively. In effluent samples their respective average concentrations were 89.04, 77.83 and 27.50 ng/ℓ, respectively (Wang et al., 2022).

2.5.1.5 Endocrine-disrupting compounds in surface water, groundwater and drinking water

Surface water, such as a river, is an easy way to discharge industrial waste, while groundwater is frequently polluted though leakage from landfill leachate, thus threatening aquatic ecosystems and possibly human health. Emerging contaminants are an environmental pollutant of increasing concern, which compromise the suitability of drinking water. Various classes of endocrine-disrupting compounds in various water matrices have progressively been detected in different locations and at different concentrations throughout the world (Wee and Aris, 2019) as shown in Table 2.4. A nationwide reconnaissance of contaminants of emerging concern in source and treated drinking water in the US, conducted in two phases, detected estrone during Phase 2 at a maximum concentration of 0.29 ng/ℓ (Glassmeyer et al., 2017).

In the Cancela-Tamandaí and João Goulart catchments in southern Brazil, a study was conducted to investigate the presence of emerging contaminants in urban water bodies, and the respective mean concentrations of 17-beta-estradiol, estriol, estrone, ethisterone, and megestrol acetate were recorded as 0.074, 0.074, 0.082, 0.017, and 0.012 µg/ℓ in the Cancela-Tamandaí catchment. Furthermore, their respective mean concentrations in the João Goulart catchment were 0.074, 0.089, 0.067, 0.013, and 0.012 µg/ℓ (Pivetta and Gastaldini, 2019).

A study was conducted in the Mississippi River in New Orleans, Louisiana, US, to simultaneously quantify polycyclic aromatic hydrocarbons, polychlorinated biphenyls, and PPCPs, and revealed estrone and 17-beta-estradiol at a maximum concentration of <1,5 and 5,0 ng/ℓ, respectively (Zhang et al., 2006). Lin et al. (2015) conducted a study in groundwater in Taiwan to determine the occurrence of pharmaceuticals, hormones, and perfluorinated compounds and reported estrone at a concentration ranging from 1.0 to 14.7 ng/ℓ, and 17-alpha-ethinylestradiol at a concentration of 1 822.2 ng/ℓ (Lin et al., 2015).

In the mangrove ecosystems of Singapore, a study was conducted on pharmaceutically active compounds and endocrine-disrupting chemicals in water, sediments and molluscs, and detected concentrations of steroid hormones such as estrone (E1), ranging from 0.02 to 2.9 ng/ℓ in surface water (Bayen et al., 2016). In Lagos, Nigeria, a study on the quantification of pharmaceutical residues in surface water impacted by wastewater and sewage sludge, detected a maximum concentration of 16-alpha-hydroxyestrone (< 0.01 µg/ℓ), 17-alpha-ethinylestradiol (< 0.01 µg/ℓ), betasitosterol (0.67 µg/ℓ), estriol (< 0.01 µg/ℓ), and estrone (< 0.01 µg/ℓ), in the surface water (Olarinmoye et al., 2016).

Lin et al. (2020), in their study of the occurrence and risk assessment of emerging contaminants in a water reclamation and ecological reuse project conducted in China, reported the concentration of estrone (E1), 17-beta-estradiol (E2), estriol (E3), ethinyl-estradiol (EE2) and bisphenol A (BPA) in river samples from ND to 128, ND to 53, ND to 58, ND to 124, and ND to 253 ng/ℓ, respectively. Esteban et al. (2014) conducted a study to analyse the occurrence of endocrine-disrupting compounds and estrogenic activity in the surface water of central Spain and reported a concentration of BPA at 27.6 ng/ℓ. Another study conducted in Nigeria on high concentrations of pharmaceuticals in a Nigerian river catchment, detected BPA at a concentration ranging from 2.3 to 59.2 ng/ℓ (Ogunbanwo et al., 2020).

Table 2.4 Occurrence and concentration levels of endocrine-disrupting compounds in international surface water, groundwater and drinking water

Endocrine-disrupting compounds	Country	Concentration in various water matrices						References
		Surface water		Groundwater		Drinking water		
		Range	Mean	Range	Mean	Range	Mean	
Oestrone	United States	<1 to 5 ng/ℓ						[Zhang et al., 2006]
	Taiwan			1.0 to 14.7 ng/ℓ				[Lin et al., 2015]
	Singapore	0.02 to 2.9 ng/ℓ						[Bayen et al., 2016]
	Nigeria	<.01 µg/ℓ						[Olarinmoye et al., 2016]
	China	ND to 128 ng/ℓ	34 ng/ℓ					[Lin et al., 2020]
	Brazil		0.082 µg/ℓ					[Pivetta and Gastaldini, 2019]
	Brazil		0.067 µg/ℓ					[Pivetta and Gastaldini, 2019]
17-beta-estradiol	United States	5						[Zhang et al., 2006]
	Nigeria	0.67 µg/ℓ						[Olarinmoye et al., 2016]
	China	ND to 53 ng/ℓ	24 ng/ℓ					[Lin et al., 2020]
	Brazil		0.074 µg/ℓ					[Pivetta and Gastaldini, 2019]
	Brazil		0.074 µg/ℓ					[Pivetta and Gastaldini, 2019]
17-alpha-ethinylestradiol	Taiwan			1 822.2 ng/ℓ				[Lin et al., 2015]
	Nigeria	<0.01 µg/ℓ						[Olarinmoye et al., 2016]
16-alpha-hydroxyestrone	Nigeria	<0.01 µg/ℓ						[Olarinmoye et al., 2016]
17-alpha-ethinylestradiol	China	ND to 124 ng/ℓ	26 ng/ℓ					[Lin et al., 2020]
Estriol	Nigeria	<0.01 µg/ℓ						[Olarinmoye et al., 2016]
	China	ND to 58 ng/ℓ	22 ng/ℓ					[Lin et al., 2020]
	Brazil		0.074 µg/ℓ					[Pivetta and Gastaldini, 2019]
	Brazil		0.089 µg/ℓ					[Pivetta and Gastaldini, 2019]
Bisphenol A	China	ND to 253 ng/ℓ						[Lin et al., 2020]
	Spain		27.6 ng/ℓ					[Esteban et al., 2014]
	Nigeria	2.3 to 59.2 ng/ℓ						[Ogunbanwo et al., 2020]
Ethisterone	Brazil		0.017 µg/ℓ					[Pivetta and Gastaldini, 2019]
	Brazil		0.013 µg/ℓ					[Pivetta and Gastaldini, 2019]
Megestrol acetate	Brazil		0.012 µg/ℓ					[Pivetta and Gastaldini, 2019]
	Brazil		0.012 µg/ℓ					[Pivetta and Gastaldini, 2019]

2.5.1.6 Endocrine-disrupting compounds in wastewater influents and effluents

Only a few studies have reported the concentration of endocrine-disrupting compounds in wastewater influents and effluents as summarised in Table 2.5. In southern England, a mean concentration of ethinylestradiol (0.932 ng/ℓ) was recorded in sewage treatment effluent samples collected in a study conducted on spatial distribution of organic contaminants in three rivers bound to suspended particulate matter and dissolved in water (Wilkinson et al., 2017). A study was conducted in China to determine the occurrence and risk assessment of emerging contaminants in a water reclamation and ecological reuse project, which reported the concentration of estrone (E1), 17-beta-estradiol (estradiol E2), estriol (E3), 17-alpha-ethinylestradiol (EE2) and BPA in influent samples ranging from 22 to 142, 31 to 88, ND to 102, ND to 110, and 41 to 1 020 ng/ℓ, respectively. Furthermore, effluent samples were also found to have concentrations of estrone (E1), 17-beta-estradiol (estradiol E2), estriol (E3), 17-alpha-ethinylestradiol (EE2) and BPA ranging from ND to 153, ND to 123, ND to 48, ND to 33, and ND to 180 ng/ℓ, respectively (Lin et al., 2020).

Table 2.5 Occurrence and concentration levels of endocrine-disrupting compounds in international wastewater influent and effluent

Endocrine-disrupting compounds	Country	Concentration				References
		WWTP influent		WWTP effluent		
		Range	Mean	Range	Mean	
Estrone	United States		0.29 ng/ℓ			[Glassmeyer et al., 2017]
	China	22 to 142 ng/ℓ	61 ng/ℓ	ND to 153 ng/ℓ	27 ng/ℓ	[Lin et al., 2020]
Estrone	China	31 to 88 ng/ℓ	54 ng/ℓ	ND to 123 ng/ℓ	26 ng/ℓ	[Lin et al., 2020]
Tamoxifen	UK			2 to 8 ng/ℓ		[Zhou and Broodbank, 2014]
17-alpha-ethinyl-estradiol	England				0.932 ng/ℓ	[Wilkinson et al., 2017]
	China	ND to 110 ng/ℓ	37 ng/ℓ	ND to 33 ng/ℓ	7 ng/ℓ	[Lin et al., 2020]
Estriol	China	ND to 102 ng/ℓ	59 ng/ℓ	ND to 48 ng/ℓ	22 ng/ℓ	[Lin et al., 2020]
Bisphenol A	China	41 to 1020 ng/ℓ	402 ng/ℓ	ND to 180 ng/ℓ	56 ng/ℓ	[Lin et al., 2020]

2.5.2 Occurrence of emerging contaminants in South Africa

2.5.2.1 Pharmaceuticals and personal care products in surface water, groundwater and drinking water

Studies in South Africa have shown that various emerging contaminants are usually detected in aquatic environments. Various studies has reported that PPCPs may occur in water matrices at low concentrations of nanogram or microgram per litre reliant to their possible sources. The incessant introduction of PPCPs have over-burdened and contaminated various receiving water bodies (Ojemaye, 2020). Several studies have scrutinised the occurrence of PPCPs in South African surface water, groundwater, and drinking water as discussed below and summarised in Table 2.6.

Non-steroidal anti-inflammatory drugs

Non-steroidal anti-inflammatory drugs that are most commonly detected in various South African water matrices include but are not limited to acetaminophen, aspirin, diclofenac, ibuprofen, ketoprofen, naproxen, fenoprofen, mefenamic acid, paracetamol, and codeine (Ademoyegun, 2017; Agunbiade and Moodley, 2014, 2016; Archer et al., 2017; Kanama et al., 2018; Mhuka et al., 2020). In a study conducted to determine PPCPs as endocrine-disrupting contaminants in South African surface water, the concentration of acetaminophen, diclofenac, ibuprofen, and ketoprofen in surface water ranged from 0.02 to 0.2, 0.3 to 2.2 , 0.1 to 0.6, and 0.01 to 0.8 µg/ℓ, respectively, in the Gauteng province (Archer et al., 2017). A study conducted in the Umgeni River

water system in KwaZulu-Natal, targeting pharmaceuticals as emerging organic contaminants, detected and reported concentrations of acetaminophen (5.8 to 58.7 µg/ℓ), aspirin (2.2 to 10.0 µg/ℓ), diclofenac (1.1 to 5.6 µg/ℓ), ibuprofen (0.8 to 18.9 µg/ℓ), and ketoprofen (0.4 to 8.2 µg/ℓ) (Agunbiade and Moodley, 2014).

Agunbiade and Moodley (2016) studied the occurrence and distribution patterns of acidic pharmaceuticals in surface water, wastewater, and sediment of the Msunduzi River in KwaZulu-Natal, and detected concentrations of aspirin (13.7 to 25.4 µg/ℓ), diclofenac (0.6 to 8.2 µg/ℓ), ibuprofen (0.4 to 0.7 µg/ℓ), and ketoprofen (0.4 to 0.7 µg/ℓ). Mhuka et al. (2020) screened PPCPs in wastewater and receiving waters in South Africa using LC Orbitrap Mass Spectrometer, and detected various NSAIDs such as diclofenac, fenoprofen, ibuprofen, ketoprofen, mefenamic acid, and naproxen in the upper stream of the Apies River in Pretoria at high concentrations of 81.98, 67.98, 8 651, 8.853, 91.15 and 137.9 ng/ℓ, respectively.

Antibiotics

Various researchers have detected several antibiotics such as ampicillin, chloramphenicol, erythromycin, fluoroquinolones, nalidixic acid, streptomycin, sulfamethoxazole, tetracycline, trimethoprim, tylosin, clarithromycin, ciprofloxacin, ofloxacin, norfloxacin, sulfadiazine, and doxycycline in water environments at various concentrations (Ademoyegun, 2017; Agunbiade and Moodley, 2014, 2016; Hendricks and Pool, 2012; Kanama et al., 2018; Matongo et al., 2015; Mhuka et al., 2020). Concentrations of antibiotics such as ampicillin, chloramphenicol, erythromycin, fluoroquinolones, nalidixic acid, streptomycin, tetracycline and tylosin were reported, ranging from 2.5 to 4.5, 0.5 to 0.7, 0.6 to 22.6, 0.7 to 6.9, 1.7 to 30.8, 0.8 to 8.4, 0.6 to 5.7, and 0.2 to 22.0 µg/ℓ, respectively, while sulfamethoxazole was reported at an average concentration of 3.68 µg/ℓ in a study conducted in the Umgeni River water system, KwaZulu-Natal, targeting pharmaceuticals as emerging organic contaminants (Agunbiade and Moodley, 2014).

Matongo et al. (2015) conducted a study to determine pharmaceutical residues in water and sediment of the Msunduzi River, KwaZulu-Natal, and reported concentrations of erythromycin ranging from 0.1 to 0.2 µg/ℓ, sulfamethoxazole ranging from 1.2 to 5.3 µg/ℓ and trimethoprim with a mean concentration of 0.3 µg/ℓ in surface water. A follow-up study was conducted in the Msunduzi River to determine the occurrence and distribution pattern of acidic pharmaceuticals in surface water, wastewater, and sediments, and detected ampicillin, fluoroquinolones, and nalidixic acid at concentrations ranging from 3.2 to 5.5, 2.4 to 14.3, and 12.4 to 23.5 µg/ℓ, respectively (Agunbiade and Moodley, 2016).

A study was conducted with the aim of determining the occurrence of PPCPs in wastewater and receiving waters in South Africa using an LC Orbitrap Mass Spectrometer and detected high concentrations of various antibiotics such as erythromycin (6.59 ng/ℓ), clarithromycin (5.480 ng/ℓ), ofloxacin (4.65 ng/ℓ), trimethoprim (114.8 ng/ℓ), sulfamethoxazole (237.4 ng/ℓ) and sulfadiazine (1.77 ng/ℓ) in the upper stream of the Apies River samples. Furthermore, ciprofloxacin and norfloxacin were below the limit of detection (< LOD) in the upper stream of the Apies River (Mhuka et al., 2020).

Beta-blockers

Among the beta-blockers, atenolol was reported by Agunbiade and Moodley (2014) in their study conducted to determine pharmaceuticals as emerging organic contaminants in the Umgeni River water system, KwaZulu-Natal, at a concentration ranging from 1.0 to 39.1 µg/ℓ. In a study conducted to determine PPCPs as endocrine-disrupting contaminants in South African surface waters, atenolol was detected in the Gauteng province at a concentration ranging from 0.1 to 0.5 µg/ℓ (Archer et al., 2017). Mhuka et al. (2020), in their study of the occurrence of PPCPs in wastewater and receiving waters in South Africa using LC Orbitrap Mass Spectrometer, detected metoprolol at a high concentration of 0.22 ng/ℓ in the upper stream samples of the Apies River.

Antiepileptics

Antiepileptics such as carbamazepine was detected in a study conducted to determine pharmaceutical residues in water and sediment of the Msunduzi River in KwaZulu-Natal, at a concentration ranging from 0.1 to 3.2 µg/ℓ in surface water (Matongo et al., 2015). In a scoping study and research strategy development on currently known and emerging contaminants influencing drinking water quality, the concentration of carbamazepine was reported in the Free State, KwaZulu-Natal, and Gauteng in drinking water ranging from 0.02 to 0.3, 0.01 to 0.02, and 0.03 to 0.1 µg/ℓ, respectively (Patterton, 2013). Furthermore, a study was conducted to determine PPCPs as endocrine-disrupting contaminants in South African surface waters and reported concentrations of carbamazepine in surface water ranging from 0.2 to 0.3 µg/ℓ in the Gauteng province (Archer et al., 2017).

It was Mhuka et al. (2020) who reported the highest concentrations of carbamazepine in their study conducted to determine the occurrence of PPCPs in wastewater and receiving waters in South Africa using an LC Orbitrap Mass Spectrometer. The study detected and reported its concentration ranging from 8.7 to 176 ng/ℓ in upper stream of Apies River samples. In another study targeting the emerging micro-pollutants in water systems in Gauteng, Mpumalanga, and North West Provinces, South Africa, the mean concentration of carbamazepine in Mpumalanga surface water was reported as 29 ng/ℓ while in Roodeplaat dam in Gauteng was 1.75 ng/ℓ. Furthermore, carbamazepine mean concentration of 52.35 ng/ℓ was reported in Hartbeespoort 8-Megalies River in Northwest Province (Wanda et al., 2017).

Antipsychotics and lipid regulators

Matongo et al. (2015) conducted a study focusing on pharmaceutical residues in water and sediment of Msunduzi River, KwaZulu-Natal and detected clozapine among the antipsychotics in surface water at a concentration ranging from 2.2 to 8.9 µg/ℓ. In another study conducted with the aim of determining PPCPs as endocrine-disrupting contaminants in South African surface waters, bezafibrate was one of the lipid regulators detected at a concentration ranging from 0.05 to 0.4 µg/ℓ in surface water of Gauteng Province (Archer et al., 2017).

Human indicators or psychomotor stimulants

Psychomotor stimulants such as caffeine was reported in surface water at a concentration ranging from 0.1 to 3.3 µg/ℓ in a study conducted to determine pharmaceuticals residues in water and sediment of the Msunduzi River in KwaZulu-Natal (Matongo et al., 2015). Archer et al. (2017) in their studies conducted with the aim of determining PPCPs as endocrine-disrupting contaminants in South African surface waters, confirmed the prevalent of caffeine in surface water around Gauteng at a concentration ranging from 0.6 to 6.6 µg/ℓ.

In a study aimed at the occurrence of emerging micro-pollutants in water systems in Gauteng, Mpumalanga, and North West provinces, South Africa, caffeine was detected in surface water from Mpumalanga province and Gauteng Roodeplaat dam at a mean concentration of 82.41 and 2.23 ng/ℓ, respectively. The same study also reported its mean concentration in surface water of 1-Krokodil River in the Northwest province as 81.24 ng/ℓ (Wanda et al., 2017). Mhuka et al. (2020) conducted a study to determine the occurrence of PPCPs in wastewater and receiving waters in South Africa using an LC Orbitrap Mass Spectrometer and detected caffeine in upper stream of Apies River at a concentration ranging from 4.09 to 2 785 µg/ℓ.

Antivirals

A group of antivirals have been detected in various South African aquatic environs. Some antivirals detected in South African aquatic systems include ribavirin, tenofovir, lamivudine, zalcitabine, stavudine, zidovudine, nevirapine, didanosine, lopinavir, ritonavir, efavirenz, famciclovir and penciclovir (Gerber, 2019; Mhuka et al., 2020; Osunmakinde et al., 2013; Wood et al., 2015). In a study conducted on endocrine-disrupting effects of

HIV antiretrovirals in the South African aquatic environment, nevirapine, lopinavir, ritonavir, and efavirenz were detected in the upper stream of the Olifantsfontein River at mean concentrations of 0.41, 24.35, 1.69 and 15.04 µg/ℓ, respectively (Gerber, 2019). In a study of the occurrence of PPCPs in wastewater and receiving waters in South Africa, using an LC Orbitrap Mass Spectrometer, Mhuka et al. (2020) detected various antivirals such as famciclovir, lamivudine, nevirapine, penciclovir, and ritonavir at high concentrations of 8.69, 8.912, 7.332, and 58.84 ng/ℓ, correspondingly, in upper stream samples of the Apies River.

A comprehensive study aimed at the occurrence of antiretroviral compounds used for HIV treatment in South African surface water detected several antivirals (Wood et al., 2015). Tenofovir was detected in surface water at a mean concentration of 0.25 µg/ℓ in Gauteng, whereas in the Free State its concentration in surface water ranged from 0.16 to 0.19 µg/ℓ. The same study reported the average concentration of zalcitabine in the Free State as 0.07 µg/ℓ. In Gauteng, mean concentrations zalcitabine in surface water and tap water were 0.03 and 0.008 µg/ℓ, respectively. Lamivudine was detected and reported at a concentration ranging from 0.09 to 0.24 µg/ℓ in surface water around Gauteng. In the Free State surface water, didanosine was detected at a mean concentration of 0.05 µg/ℓ. Furthermore, in surface water around Gauteng, stavudine ranged from 0.41 to 0.78 µg/ℓ. In Gauteng, the study also detected zidovudine in surface water at a concentration ranging from 0.22 to 0.62 µg/ℓ, whereas in tap water it was reported at an average concentration of 0.07 µg/ℓ. Nevirapine was detected in surface water at a concentration ranging from 0.24 to 1.48 µg/ℓ, whereas lopinavir was detected at a concentration ranging from 0.28 to 0.31 µg/ℓ (Wood et al., 2015).

Antiseptics

In the study conducted to determine triclosan and ketoprofen in river water and wastewater by solid-phase extraction (SPE) and HPLC, a concentration of triclosan among the antiseptics in surface water was detected and reported, ranging from 0.4 to 0.9 µg/ℓ around Gauteng (Madikizela et al., 2014).

Table 2.6 Occurrence and concentration levels of pharmaceutical and personal care products in South African surface water, groundwater and drinking water

Pharmaceutical and personal care product	Area	Concentration in various water matrices						References
		Surface water		Groundwater		Drinking water		
		Range	Mean	Range	Mean	Range	Mean	
Non-steroidal anti-inflammatory drugs (NSAIDs)								
Acetaminophen	Gauteng	0.02 to 0.2 µg/ℓ						[Archer et al., 2017]
	KwaZulu-Natal	5.8 to 58.7 µg/ℓ						[Agunbiade and Moodley, 2014]
Aspirin	KwaZulu-Natal	2.2 to 10.0 µg/ℓ						[Agunbiade and Moodley, 2014]
	KwaZulu-Natal	13.7 to 25.4 µg/ℓ						[Agunbiade and Moodley, 2016]
Diclofenac	Gauteng	0.3 to 2.2 µg/ℓ						[Archer et al., 2017]
	KwaZulu-Natal	1.1 to 15.6 µg/ℓ						[Agunbiade and Moodley, 2014]
	KwaZulu-Natal	0.6 to 8.2 µg/ℓ						[Agunbiade and Moodley, 2016]
	Gauteng	5.642 to 81.98 ng/ℓ	20.38 ng/ℓ					[Mhuka et al., 2020]
Ibuprofen	Gauteng	0.1 to 0.6 µg/ℓ						[Archer et al., 2017]
	KwaZulu-Natal	0.8 to 18.9 µg/ℓ						[Agunbiade and Moodley, 2014]
	KwaZulu-Natal	0.4 to 0.7 µg/ℓ						[Agunbiade and Moodley, 2016]
	Gauteng	< LOD to 8651 ng/ℓ	3 192 ng/ℓ					[Mhuka et al., 2020]
Ketoprofen	Gauteng	0.01 to 0.8 µg/ℓ						[Archer et al., 2017]
	KwaZulu-Natal	0.4 to 8.2 µg/ℓ						[Agunbiade and Moodley, 2014]
	KwaZulu-Natal	0.4 to 0.7 µg/ℓ						[Agunbiade and Moodley, 2016]
	Gauteng	< LOD to 8.853 ng/ℓ	4.289 ng/ℓ					[Mhuka et al., 2020]
Naproxen	Gauteng	0.2 to 1.9 µg/ℓ						[Archer et al., 2017]
	Gauteng	30.33 to 137.9 ng/ℓ	99.59 ng/ℓ					[Mhuka et al., 2020]
Fenoprofen	Gauteng	< LOD to 67.98 ng/ℓ						[Mhuka et al., 2020]
Mefenamic acid	Gauteng	2.239 to 91.15 ng/ℓ	12.87 ng/ℓ					[Mhuka et al., 2020]

Pharmaceutical and personal care product	Area	Concentration in various water matrices						References
		Surface water		Groundwater		Drinking water		
		Range	Mean	Range	Mean	Range	Mean	
Antibiotics								
Ampicillin	KwaZulu-Natal	2.5 to 14.5 µg/ℓ						[Agunbiade and Moodley, 2014]
	KwaZulu-Natal	3.2 to 5.5 µg/ℓ						[Agunbiade and Moodley, 2016]
Chloramphenicol	KwaZulu-Natal	0.5 to 10.7 µg/ℓ						[Agunbiade and Moodley, 2014]
Erythromycin	KwaZulu-Natal	0.6 to 22.6 µg/ℓ						[Agunbiade and Moodley, 2014]
	KwaZulu-Natal	0.1 to 0.2 µg/ℓ						[Matongo et al., 2015]
	Gauteng	< LOD to 6.59 ng/ℓ	1.57 ng/ℓ					[Mhuka et al., 2020]
Fluoroquinolones	KwaZulu-Natal	0.7 to 16.9 µg/ℓ						[Agunbiade and Moodley, 2014]
	KwaZulu-Natal	2.4 to 14.3 µg/ℓ						[Agunbiade and Moodley, 2016]
Nalidixic acid	KwaZulu-Natal	1.7 to 30.8 µg/ℓ						[Agunbiade and Moodley, 2014]
	KwaZulu-Natal	12.4 to 23.5 µg/ℓ						[Agunbiade and Moodley, 2016]
Streptomycin	KwaZulu-Natal	0.8 to 8.4 µg/ℓ						[Agunbiade and Moodley, 2014]
Sulfamethoxazole	KwaZulu-Natal		3.68 µg/ℓ					[Agunbiade and Moodley, 2014]
	KwaZulu-Natal	1.2 to 5.3 µg/ℓ						[Matongo et al., 2015]
	Gauteng	< LOD to 237.4 ng/ℓ	103.5 ng/ℓ					[Mhuka et al., 2020]
Tetracycline	KwaZulu-Natal	0.6 to 5.7 µg/ℓ						[Agunbiade and Moodley, 2014]
Trimethoprim	KwaZulu-Natal		0.3 µg/ℓ					[Matongo et al., 2015]
	Gauteng	6.9011 to 114.8 ng/ℓ	49.76 ng/ℓ					[Mhuka et al., 2020]
Tylosin	KwaZulu-Natal	0.2 to 22.0 µg/ℓ						[Agunbiade and Moodley, 2014]
Clarithromycin	Gauteng	< LOD to 5.480 ng/ℓ	3.194 ng/ℓ					[Mhuka et al., 2020]
Ciprofloxacin	North West	< LOD						[Kanama et al., 2018]
Ofloxacin	Gauteng	< LOD to 4.65 ng/ℓ						[Mhuka et al., 2020]
Norfloxacin	North West	< LOD						[Kanama et al., 2018]
Sulfadiazine	Gauteng	ND to 1.77 ng/ℓ	0.253 ng/ℓ					[Mhuka et al., 2020]

Pharmaceutical and personal care product	Area	Concentration in various water matrices						References
		Surface water		Groundwater		Drinking water		
		Range	Mean	Range	Mean	Range	Mean	
Antiseptics								
Triclosan	Gauteng	0.4 to 0.9 µg/ℓ						[Madikizela et al., 2014]
Beta-blockers								
Atenolol	KwaZulu-Natal	1.0 to 39.1 µg/ℓ						[Agunbiade and Moodley, 2014]
	Gauteng	0.1 to 0.5 µg/ℓ						[Archer et al., 2017]
Metoprolol	Gauteng	ND to 0.22 ng/ℓ	0.048 ng/ℓ					[Mhuka et al., 2020]
Antiepileptics								
Carbamazepine	Free State					0.02 to 0.3 µg/ℓ		[Patterton, 2013]
	KwaZulu-Natal					0.01 to 0.02 µg/ℓ		[Patterton, 2013]
	Gauteng					0.03 to 0.1 µg/ℓ		[Patterton, 2013]
	North West	0.1 to 3.2 µg/ℓ						[Matongo et al., 2015]
	Gauteng	0.2 to 0.3 µg/ℓ						[Archer et al., 2017]
	Gauteng		1.75 ng/ℓ					[Wanda et al., 2017]
	North West		52.35 ng/ℓ					[Wanda et al., 2017]
	Mpumalanga		29 ng/ℓ					[Wanda et al., 2017]
	Gauteng	8.774 to 176.0 ng/ℓ	58.51 ng/ℓ					[Mhuka et al., 2020]
Antipsychotics								
Clozapine	North West	2.2 to 8.9 µg/ℓ						[Matongo et al., 2015]
Lipid regulators								
Bezafibrate	Gauteng	0.05 to 0.4 µg/ℓ						[Archer et al., 2017]
Antivirals								
Tenofovir	Gauteng		0.25 µg/ℓ					[Wood et al., 2015]
	Free State	0.16 to 0.19 µg/ℓ						[Wood et al., 2015]
Lamivudine	Gauteng	0.09 to 0.24 µg/ℓ						[Wood et al., 2015]
	Gauteng	< LOD to 8.912 ng/ℓ	2.443 ng/ℓ					[Mhuka et al., 2020]
Zalcitabine	Free State		0.07 µg/ℓ					[Wood et al., 2015]

Pharmaceutical and personal care product	Area	Concentration in various water matrices						References
		Surface water		Groundwater		Drinking water		
		Range	Mean	Range	Mean	Range	Mean	
	Gauteng		0.03 µg/ℓ			0.008 µg/ℓ		[Wood et al., 2015]
Stavudine	Gauteng	0.41 to 0.78 µg/ℓ						[Wood et al., 2015]
Zidovudine	Gauteng	0.22 to 0.62 µg/ℓ				0.07 µg/ℓ		[Wood et al., 2015]
Nevirapine	Gauteng	0.24 to 1.48 µg/ℓ						[Wood et al., 2015]
	Gauteng		0.41 µg/ℓ					[Gerber, 2019]
	Gauteng	< LOQ to 7.332 ng/ℓ						[Mhuka et al., 2020]
Didanosine	Free State		0.05 µg/ℓ					[Wood et al., 2015]
Lopinavir	Gauteng	0.28 to 0.31 µg/ℓ						[Wood et al., 2015]
	Gauteng		24.35 µg/ℓ					[Gerber, 2019]
Ritonavir	Gauteng		1.69 µg/ℓ					[Gerber, 2019]
	Gauteng	< LOD to 58.84 ng/ℓ	25.54 ng/ℓ					[Gerber, 2019]
Efavirenz	Gauteng		15.04 µg/ℓ					[Gerber, 2019]
Famciclovir	Gauteng	< LOD to 8.69 ng/ℓ	2.51 ng/ℓ					[Mhuka et al., 2020]
Penciclovir	Gauteng	< LOD to 18.66 ng/ℓ	3.338 ng/ℓ					[Mhuka et al., 2020]
		Human indicators/Psychomotor stimulant						
Caffeine	KwaZulu-Natal	0.1 to 3.3 µg/ℓ						[Matongo et al., 2015]
	Gauteng	0.6 to 6.6 µg/ℓ						[Archer et al., 2017]
	North West	82.41 ng/ℓ				6.4 ng/ℓ		[Wanda et al., 2017]
	Gauteng		2.23 ng/ℓ					[Wanda et al., 2017]
	Mpumalanga		81.24 ng/ℓ					[Wanda et al., 2017]
	Gauteng	4.098 to 2 785 µg/ℓ	1 424 ng/ℓ					[Mhuka et al., 2020]

2.5.2.2 Pharmaceuticals and personal care products in wastewater influents and effluents

Non-steroidal anti-inflammatory drugs

The occurrence of PPCPs has also been detected in South African wastewater influents and effluents as summarised in Table 2.7. In a study aimed at assessing PPCPs and hormones in WWTPs receiving inflows from health facilities in the North West province, South Africa, the concentrations of non-steroidal anti-inflammatory drugs such as acetaminophen (21.27 to 119.50 µg/ℓ), diclofenac (0.12 to 10.34 µg/ℓ), ibuprofen (0.33 to 53.40 µg/ℓ), and ketoprofen (< LOQ to 0.65 µg/ℓ) were detected in influent samples. Furthermore, in effluent samples, their respective concentrations ranged from < LOQ to 11.39, 0.07 to 0.75, < LOQ to 13.66, and < LOQ to 0.24 µg/ℓ (Kanama et al., 2018).

In another study conducted to determine PPCPs as endocrine-disrupting contaminants in South African surface waters, NSAIDs were prevalent in wastewater influent and effluent in various concentrations (Archer et al., 2017). Acetaminophen was detected at a concentration ranging from 136.9 to 343.6 µg/ℓ in influent and 0.04 to 0.2 µg/ℓ in effluent. The study also reported diclofenac in influent and effluent at a concentration ranging from 2.7 to 5.6 and 2.2 to 2.5 µg/ℓ, respectively. Ibuprofen was detected in influent ranging from 9.1 to 15.8 µg/ℓ and in effluent ranging from 0.3 to 1.2 µg/ℓ. Furthermore, the same study detected ketoprofen in influent and effluent at a concentration ranging from 0.4 to 5.6 and 0.2 to 0.7 µg/ℓ, respectively (Archer et al., 2017).

A study conducted to determine the occurrence and distribution pattern of acidic pharmaceuticals in surface water, wastewater, and sediment of the Msunduzi River in KwaZulu-Natal reported the mean concentrations of diclofenac, ibuprofen, and ketoprofen in influent and effluent as 222.7 µg/ℓ and 123.7 µg/ℓ, 1.2 µg/ℓ and 1.1 µg/ℓ, and 3.2 µg/ℓ and 0.4 µg/ℓ, respectively (Agunbiade and Moodley 2016). Mhuka et al. (2020), in their study of the occurrence of PPCPs in wastewater and receiving waters in South Africa using an LC Orbitrap Mass Spectrometer, detected various NSAIDs such as diclofenac, fenoprofen, ibuprofen, ketoprofen, mefenamic acid, and naproxen in influent at high concentrations of 246.3, < LOD 76 377, 23.10, 91.15 and 546.1 ng/ℓ, respectively, whereas in effluent they were detected at a maximum concentration of 243.6, 207.6, 7 652, 49.48, 55.05 and 349.6 ng/ℓ, respectively.

Furthermore, a study by Ademoyegun (2017) conducted to evaluate some PPCPs and pesticide residues in selected WWTPs and receiving watersheds in the Eastern Cape, reported aspirin, ibuprofen, diclofenac, paracetamol, and codeine in influent at concentrations ranging from 1.45 to 4.00, 0.39 to 17.50, 0.04 to 5.46, and 0.77 to 35.01 µg/ℓ, and a high concentration of codeine as 0.35 µg/ℓ, whereas in effluent they ranged from 0.16 to 0.99, 0.10 to 5.27, 0.03 to 2.19, and 0.21 to 10.54 µg/ℓ, respectively, and a high concentration of codeine was 0.17 µg/ℓ.

Späth et al. (2021) conducted a study on biochar for the removal of detected micropollutants in South African domestic wastewater in a case study from a demonstration-scale decentralised wastewater treatment system in eThekwini and reported the average concentration of diclofenac, paracetamol, and tramadol in influent as 2 300, 140 000, and 330 ng/ℓ, respectively, while their respective mean concentration in effluent were reported as 2 100, 4 600, and 400 ng/ℓ.

Antibiotics

Ademoyegun (2017) conducted a study evaluating some PPCPs and pesticide residues in selected WWTPs and receiving watersheds in the Eastern Cape, and detected trimethoprim, chloramphenicol, and doxycycline in influent samples at high concentrations of 0.63, 1.74 and 0.19 µg/ℓ, while in effluent samples their respective concentrations were 0.41, 1.22 and 0.07 µg/ℓ. Another study was conducted in the North West province to assess PPCPs and hormones in WWTPs receiving inflows from health facilities, and reported respective concentrations of tetracycline, ciprofloxacin, and norfloxacin in influent ranging from 1.09 to 45.38, 0.08 to

1.40, and 0.03 to 0.35 µg/ℓ, while in effluent their respective mean concentrations ranged from 0.52 to 1.43, 0.12 to 2.00, and 0.10 to 1.53 µg/ℓ (Kanama et al., 2018).

Matongo et al. (2015), in their study to determine pharmaceutical residues in water and sediment of the Msunduzi River in KwaZulu-Natal, reported the mean concentration of erythromycin as 0.6 and 0.2 µg/ℓ in both influent and effluent, respectively. The same study also detected sulfamethoxazole in influent at a mean concentration of 34.5 µg/ℓ (Matongo et al., 2015). Another study on the effectiveness of sewage treatment processes to remove faecal pathogens and antibiotic residues in the Western Cape detected fluoroquinolones and sulfamethoxazole in influent and effluent at concentrations ranging from 0.09 to 0.1 and 0.07 to 0.09 µg/ℓ, respectively (Hendricks and Pool, 2012). Average concentrations of 6.6 and 8.9 µg/ℓ for ampicillin, 27.1 and 20.5 µg/ℓ for fluoroquinolones, and 29.9 and 25.2 µg/ℓ for nalidixic acid in influent and effluent, respectively, were recorded in a study conducted in the Msunduzi River in KwaZulu-Natal to determine the occurrence and distribution patterns of acidic pharmaceuticals in surface water, wastewater, and sediment (Agunbiade and Moodley, 2016).

Mhuka et al. (2020) detected and quantified erythromycin, clarithromycin, ciprofloxacin, norfloxacin, ofloxacin, trimethoprim, sulfamethoxazole, and sulfadiazine in influent at high concentrations of < LOD, 10.06, 77.04, 31.70, 67.50, 577.6, 2 405 and 0.42 ng/ℓ, respectively, in their study targeting PPCPs in wastewater and receiving waters in South Africa, using an LC Orbitrap Mass Spectrometer. The same study also reported the respective maximum concentrations of erythromycin, clarithromycin, ciprofloxacin, norfloxacin, ofloxacin, trimethoprim, and sulfamethoxazole as 11.89, 75.44, 5.59, 9.83, 86.51, 136.6, and 504.4 ng/ℓ in effluent, while sulfadiazine was not detected (Mhuka et al., 2020).

Späth et al. (2021) conducted a study on biochar for the removal of detected micro-pollutants in South African domestic wastewater in a case study from a demonstration-scale decentralised wastewater treatment system in eThekwini and reported the average concentration of ciprofloxacin, clindamycin, levofloxacin, sulfamethoxazole, and trimethoprim in influent as 1 300, 270, 25, 12 000, and 1 400 ng/ℓ, respectively, while in effluent their respective mean concentrations were 1 600, 270, 22, 2 500, and 290 ng/ℓ.

Beta-blockers

Among the beta-blockers, atenolol was detected in both influent and effluent samples at a concentration ranging from 1.08 to 8.34 and 0.33 to 3.22 µg/ℓ, in a study conducted to assess PPCPs and hormones in WWTPs receiving inflows from health facilities in the North West province (Kanama et al., 2018). In the Umgeni River water system, KwaZulu-Natal, a study was conducted to detect pharmaceuticals as emerging organic contaminants, and reported atenolol as one of the beta-blockers at a concentration ranging from 1.0 to 39.1 µg/ℓ (Agunbiade and Moodley, 2014). In another study targeting PPCPs as endocrine-disrupting contaminants in South African surface waters, atenolol was reported in influent at a concentration ranging from 1.6 to 2.5, and ranging from 0.4 to 0.7 µg/ℓ in effluent around Gauteng (Archer et al., 2017).

Osunmakinde et al. (2013) conducted a study to verify and validate analytical methods for testing the levels of pharmaceutical and personal health care products in treated drinking water and sewage in Gauteng, and reported a mean concentration of pindolol in influent and effluent as 0.03 and 0.00003 µg/ℓ, respectively. Mhuka et al. (2020), in their study of the occurrence of PPCPs in wastewater and receiving water in South Africa, using an LC Orbitrap Mass Spectrometer, detected metoprolol at a high concentration of 0.09 ng/ℓ in influent and at a high concentration of 2.22 ng/ℓ in effluent.

Antiepileptics

Among the antiepileptics, carbamazepine was reported at mean concentrations of 2.2 and 0.9 µg/ℓ in both influent and effluent in a study conducted to determine pharmaceutical residues in water and sediment of the Msunduzi River in KwaZulu-Natal (Matongo et al., 2015). Furthermore, Archer et al. (2017) studied the PPCPs

as endocrine-disrupting contaminants in South African surface waters and observed carbamazepine in influent at a concentration ranging from 0.3 to 0.6 µg/ℓ and in effluent at a mean concentration of 0.4 µg/ℓ around Gauteng. In another study targeting emerging micropollutants in water systems in the Gauteng, Mpumalanga and North West provinces in South Africa, a mean concentration of carbamazepine in the Mpumalanga effluent was reported as 58 µg/ℓ (Wanda et al., 2017).

Mhuka et al. (2020) conducted a study targeting PPCPs in wastewater and receiving waters in South Africa using an LC Orbitrap Mass Spectrometer and detected high concentrations of carbamazepine as 115.7 ng/ℓ in an influent and 416.3 ng/ℓ in an effluent sample. Ademoyegun's (2017) study aimed at evaluating PPCPs and pesticide residues in selected WWTPs and receiving watersheds in the Eastern Cape, and detected a high concentration of diazepam (0.90 µg/ℓ) and carbamazepine (2.61 µg/ℓ) in influent, while in effluent, their respective high concentrations were 0.69 and 1.33 µg/ℓ. A study on biochar for the removal of detected micropollutants in South African domestic wastewater which was a case study from a demonstration-scale decentralised wastewater treatment system in eThekwini, which reported the average concentrations of carbamazepine and lamotrigine in influent as 480 and 240 ng/ℓ, respectively. In effluent their respective mean concentrations were reported as 480 and 0 ng/ℓ, respectively (Späth et al., 2021).

Antipsychotic and lipid regulators

Among the antipsychotics, Matongo et al. (2015) reported a mean concentration of clozapine in influent and effluent as 8.6 and 9.6 µg/ℓ, respectively, in their study conducted to determine pharmaceutical residues in water and sediment of the Msunduzi River in KwaZulu-Natal, South Africa. Moreover, a study targeting PPCPs as endocrine-disrupting contaminants in South African surface waters detected bezafibrate as one of the lipid regulators in influent around Gauteng at concentrations ranging from 0.05 to 0.4 and 0.3 to 0.7 µg/ℓ in effluent (Archer et al., 2017).

Human indicators or psychomotor stimulants

In a study conducted to determine pharmaceutical residues in water and sediment of the Msunduzi River in KwaZulu-Natal, caffeine was one of the human indicators detected in influent and effluent at a mean concentration of 4.5 and 0.6 µg/ℓ, respectively (Matongo et al., 2015). It was also detected in influent and effluent around Gauteng at a concentration ranging from 5.1 to 1 214.4 and 0.5 to 3.8 µg/ℓ, respectively, in a study conducted by Archer et al. (2017) with the aim of determining PPCPs as endocrine-disrupting contaminants in South African surface waters.

Another study on the occurrence of emerging micro-pollutants in water systems in Gauteng, Mpumalanga, and the North West provinces, detected caffeine in influent and effluent in Mpumalanga at a mean concentration of 9.1 and 11 ng/ℓ, respectively (Wanda et al., 2017). Mhuka et al. (2020) conducted a study on the occurrence of PPCPs in wastewater and receiving waters in South Africa using an LC Orbitrap Mass Spectrometer, and indicated that influent samples were having a concentration of caffeine ranging from 1 170 to 60 136 ng/ℓ, while in influent samples caffeine ranged from 85.76 to 4 878 ng/ℓ (Mhuka et al., 2020).

Späth et al. (2021) conducted a study on *Biochar for the removal of detected micropollutants in South African domestic wastewater* in eThekwini, and reported the average concentration of caffeine in influent and effluent as 22 000 and 7 500 ng/ℓ, respectively. Caffeine was also reported at a concentration ranging from 4.69 to 69.49 µg/ℓ in influent and 0.98 to 12.77 µg/ℓ in effluent samples, in a study conducted to evaluate some PPCPs and pesticide residues in selected WWTPs and receiving watersheds in the Eastern Cape (Ademoyegun, 2017).

Antivirals

A study conducted by Späth et al. (2021) on *Biochar for the removal of detected micropollutants in South African domestic wastewater*, and reported an average concentration of abacavir, atazanavir, darunavir, lamivudine, nevirapine, raltegravir, and acyclovir as 100, 3 100, 14 000, 74 000, 350, 4 100 and 3 000 ng/ℓ, respectively. The study also detected the mean concentration of the same compounds in effluent as 540, 3 000, 10 000, 130 000, 350, 3 500, and 1 900 ng/ℓ, respectively.

Osunmakinde et al. (2013), in their study conducted in Gauteng to verify and validate analytical methods for testing the levels of pharmaceutical and personal health care products in treated drinking water and sewage, detected antivirals such as ribavirin in influent and effluent at a mean concentration of 0.02 and 0.00004 µg/ℓ, respectively. They also detected famciclovir at an average concentration of 0.02 µg/ℓ in influent and 0.00006 µg/ℓ in effluent (Osunmakinde et al., 2013). Wood et al. (2015) conducted a study targeting antiretroviral compounds used for HIV treatment in South African surface water and detected lopinavir in effluent at an average concentration of 0.13 µg/ℓ.

A study conducted to determine the occurrence of PPCPs in wastewater and receiving waters in South Africa using an LC Orbitrap Mass Spectrometer, detected concentrations of famciclovir, lamivudine, nevirapine, penciclovir, and ritonavir in influent as 17.67, 1 001, 26.34, 22.94, and 393.90 ng/ℓ, while in effluent samples they were detected as 7.17, 323.40, 80.53, 104.8, and 675.90 ng/ℓ, respectively (Mhuka et al., 2020). Späth et al. (2021) conducted a case study from a demonstration-scale decentralised wastewater treatment system in eThekwini and reported the average concentration of acyclovir as 3 000 and 1 900 ng/ℓ in both influent and effluent, respectively.

Antiseptics

Kanama et al. (2018) conducted a study in the North West province to assess PPCPs and hormones in WWTPs receiving inflows from health facilities, and detected triclocarban in influent and effluent at concentrations ranging from 0.23 to 1.75 and 0.01 to 0.46 µg/ℓ, respectively. Triclosan was reported at a concentration ranging from 2.45 to 18.73 µg/ℓ in influent samples and 0.10 to 11.05 µg/ℓ in effluent in a study conducted on the evaluation of some PPCPs and pesticide residues in selected WWTPs and receiving watersheds in the Eastern Cape (Ademoyegun, 2017). Another study conducted to determine triclosan and ketoprofen in river water and wastewater by SPE and HPLC, detected the concentration of triclosan among the antiseptics in both influent and effluent around Gauteng at a concentration ranging from 2.1 to 9.0 and 1.3 to 6.4 µg/ℓ, respectively (Madikizela et al., 2014).

Fragrance

Mhuka et al. (2020) conducted a study to quantify PPCPs in wastewater and receiving waters in South Africa using an LC Orbitrap mass spectrometer, and detected tonalide among the PCPs in influent at concentrations ranging from 0.21 to 80.16 ng/ℓ, with a mean concentration of 71.3 ng/ℓ. The study also detected tonalide at a concentration ranging from < LOD to 28.57 ng/ℓ, with a mean concentration of 7.247 ng/ℓ in effluent (Mhuka et al., 2020).

Insect repellent

In a study aimed at evaluating some PPCPs and pesticide residues in selected WWTPs and receiving watersheds in the Eastern Cape province in South Africa, mean concentrations of DEET in both influent and effluent were detected as 9.63 and 3.43 µg/ℓ, respectively (Ademoyegun, 2017).

Table 2.7 Occurrence of pharmaceuticals and personal care products in South African wastewater influent and effluents

Pharmaceuticals and personal care products	Area	WWTP influent		WWTP effluent		References
		Range	Mean	Range	Mean	
Non-steroidal anti-inflammatory drugs (NSAIDs)						
Acetaminophen	North West	21.27 to 119.50 µg/ℓ	49.79 µg/ℓ	< LOQ to 11.39 µg/ℓ	6.1 µg/ℓ	[Kanama et al., 2018]
	Gauteng	136.9 to 343.6 µg/ℓ		0.04 to 0.2 µg/ℓ		[Archer et al., 2017]
Aspirin	Eastern Cape	1.45 to 4.00 µg/ℓ	2.46 µg/ℓ	0.16 to 0.99 µg/ℓ	0.51 µg/ℓ	[Ademoyegun, 2017]
Diclofenac	North West	0.12 to 10.34 µg/ℓ	2.38 µg/ℓ	0.07 to 0.75 µg/ℓ	0.3 µg/ℓ	[Kanama et al., 2018]
	Gauteng	2.7 to 5.6 µg/ℓ		2.2 to 2.5 µg/ℓ		[Archer et al., 2017]
	KwaZulu-Natal		222.7 µg/ℓ		123.7 µg/ℓ	[Agunbiade and Moodley, 2016]
	Gauteng	12.16 to 246.3 ng/ℓ	147.5 ng/ℓ	5.56-243.6 ng/ℓ	74.44	[Mhuka et al., 2020]
	Eastern Cape	0.04 to 5.46 µg/ℓ	2.41 µg/ℓ	0.03 to 2.19 µg/ℓ	0.84 µg/ℓ	[Ademoyegun, 2017]
	KwaZulu-Natal		2 300		2 100	[Späth et al., 2021]
Ibuprofen	North West	0.33 to 53.40 µg/ℓ	16.44 µg/ℓ	< LOQ to 13.66 µg/ℓ	5.25 µg/ℓ	[Kanama et al., 2018]
	Gauteng	9.1 to 15.8 µg/ℓ		0.3 to 1.2 µg/ℓ		[Archer et al., 2017]
	KwaZulu-Natal		1.2 µg/ℓ		1.1 µg/ℓ	[Agunbiade and Moodley, 2016]
	Gauteng	568.7 to 76 377 ng/ℓ	15 831 ng/ℓ	< LOD to 7652 ng/ℓ	2504	[Mhuka et al., 2020]
	Eastern Cape	0.39 to 17.50 µg/ℓ	6.82 µg/ℓ	0.10 to 5.27 µg/ℓ	1.56 µg/ℓ	[Ademoyegun, 2017]
Ketoprofen	North West	< LOQ to 0.65 µg/ℓ	0.39 µg/ℓ	< LOQ to 0.24 µg/ℓ		[Kanama et al., 2018]
	Gauteng	0.4 to 5.6 µg/ℓ		0.2 to 0.7 µg/ℓ		[Archer et al., 2017]
	KwaZulu-Natal		3.2 µg/ℓ		0.4 µg/ℓ	[Agunbiade and Moodley, 2016]
	Gauteng	< LOD to 23.10 ng/ℓ		< LOD to 49.48 ng/ℓ	13.38 ng/ℓ	[Mhuka et al., 2020]
Naproxen	Gauteng	2.9 to 5.5 µg/ℓ		1.8 to 2.9 µg/ℓ		[Archer et al., 2017]
	Gauteng	16.85 to 546.1 ng/ℓ	64.07 ng/ℓ	13.09 to 349.6 ng/ℓ	122.3 ng/ℓ	[Mhuka et al., 2020]
Fenoprofen	Gauteng	< LOD ng/ℓ	< LOD ng/ℓ	< LOD to 207.6 ng/ℓ	46.8 ng/ℓ	[Mhuka et al., 2020]
Mefenamic acid	Gauteng	11.30 to 91.15 ng/ℓ	31.95 ng/ℓ	4.789 to 55.05 ng/ℓ	19.99 ng/ℓ	[Mhuka et al., 2020]
	KwaZulu-Natal		330 ng/ℓ		400 ng/ℓ	[Späth et al., 2021]
Paracetamol	Eastern Cape	0.77 to 35.01 µg/ℓ	13.64 µg/ℓ	0.21 to 10.54 µg/ℓ	3.11 µg/ℓ	[Ademoyegun, 2017]

Pharmaceuticals and personal care products	Area	WWTP influent		WWTP effluent		References
		Range	Mean	Range	Mean	
	KwaZulu-Natal		140 000 ng/ℓ		4 600 ng/ℓ	[Späth et al., 2021]
Codeine	Eastern Cape	LOQ to 0.35 µg/ℓ	0.18 µg/ℓ	LOQ to 0.17 µg/ℓ	0.09 µg/ℓ	[Ademoyegun, 2017]
Antibiotics						
Ampicillin	KwaZulu-Natal		6.6 µg/ℓ		8.9 µg/ℓ	[Agunbiade and Moodley, 2016]
Chloramphenicol	Eastern Cape	0.07 to 1.74 µg/ℓ	0.34 µg/ℓ	0.02 to 1.22 µg/ℓ	0.27 µg/ℓ	[Ademoyegun, 2017]
Erythromycin	KwaZulu-Natal		0.6 µg/ℓ		0.2 µg/ℓ	[Matongo et al., 2015]
	Gauteng	< LOD	< LOD	< LOD to 11.89 ng/ℓ	4.01 ng/ℓ	[Mhuka et al., 2020]
Fluoroquinolones	KwaZulu-Natal		27.1 µg/ℓ		20.5 µg/ℓ	[Agunbiade and Moodley, 2016]
	Western Cape		0.09 to 0.1 µg/ℓ		0.07 to 0.09 µg/ℓ	[Hendricks and Pool, 2012]
Nalidixic acid	KwaZulu-Natal		29.9 µg/ℓ		25.2 µg/ℓ	[Agunbiade and Moodley, 2016]
Levofloxacin	KwaZulu-Natal		25 ng/ℓ		22 ng/ℓ	[Späth et al., 2021]
Nalidixic acid	KwaZulu-Natal		34.5 µg/ℓ			[Matongo et al., 2015]
	Western Cape	0.1 to 0.2 µg/ℓ		0.08 to 0.1 µg/ℓ		[Hendricks and Pool, 2012]
	Gauteng	52.92 to 2 405 ng/ℓ		34.93 to 504.4 ng/ℓ		[Mhuka et al., 2020]
Tetracycline	North West	1.09 to 45.38 µg/ℓ	11.04 µg/ℓ	0.52 to 1.43 µg/ℓ	0.95 µg/ℓ	[Kanama et al., 2018]
Trimethoprim	Gauteng	16.61 to 577.6 ng/ℓ	108.7 ng/ℓ	< LOD to 136.6 ng	50.4 ng/ℓ	[Mhuka et al., 2020]
	Eastern Cape	0.05 to 0.63 µg/ℓ	0.17 µg/ℓ	0.03 to 0.41 µg/ℓ	0.16 µg/ℓ	[Ademoyegun, 2017]
	KwaZulu-Natal		1 400 ng/ℓ		290 ng/ℓ	[Späth et al., 2021]
Clarithromycin	Gauteng	< LOD to 10.06 ng/ℓ	0.45 ng/ℓ	< LOD to 75.44 ng/ℓ	9.84 ng/ℓ	[Mhuka et al., 2020]
Clindamycin	KwaZulu-Natal		270 ng/ℓ		270	[Späth et al., 2021]
Ciprofloxacin	North West	0.12 to 2.00 µg/ℓ	0.99 µg/ℓ	0.08 to 1.40 µg/ℓ	0.51 µg/ℓ	[Kanama et al., 2018]
	Gauteng	< LOQ to 77.04 ng/ℓ	35.32 ng/ℓ	< LOD to 5.59	1.03 ng/ℓ	[Mhuka et al., 2020]
	KwaZulu-Natal		1 300 ng/ℓ		1 600 ng/ℓ	[Späth et al., 2021]
Ofloxacin	Gauteng	24.66-67.50 ng/ℓ	36.39 ng/ℓ	11.54 to 86.51 ng/ℓ	42.05 ng/ℓ	[Mhuka et al., 2020]
Norfloxacin	North West	0.10 to 1.53 µg/ℓ	0.42 µg/ℓ	0.03 to 0.35 µg/ℓ	0.12 µg/ℓ	[Kanama et al., 2018]
	Gauteng	< LOD to 31.70 ng/ℓ	3.12 ng/ℓ	< LOD to 9.83	0.61 ng/ℓ	[Mhuka et al., 2020]
Sulfadiazine	Gauteng	< LOD to 0.42 ng/ℓ	0.05 ng/ℓ			[Mhuka et al., 2020]

Pharmaceuticals and personal care products	Area	WWTP influent		WWTP effluent		References
		Range	Mean	Range	Mean	
Doxycycline	Eastern Cape	ND to 0.19 µg/ℓ		ND to 0.07 µg/ℓ		[Ademoyegun, 2017]
Sulfamethoxazole	KwaZulu-Natal		12 000		2 500	[Späth et al., 2021]
Antiseptics						
Triclosan	Gauteng	2.1 to 9.0 µg/ℓ		1.3 to 6.4 µg/ℓ		[Madikizela et al., 2014]
	Eastern Cape	2.45 to 18.73 µg/ℓ	10.23 µg/ℓ	0.10 to 11.05 µg/ℓ	10.23 µg/ℓ	[Ademoyegun, 2017]
Triclocarban	North West	0.23 to 1.75 µg/ℓ	0.76 µg/ℓ	0.01 to 0.46 µg/ℓ	0.11 µg/ℓ	[Kanama et al., 2018]
N,N-Diethyltoluamide (DEET)	Eastern Cape		9.63 µg/ℓ		3.43 µg/ℓ	[Ademoyegun, 2017]
Tonalide	Gauteng	0.21-80.16 ng/ℓ	71.3 ng/ℓ	< LOD to 28.57 ng/ℓ	7.247 ng/ℓ	[Mhuka et al., 2020]
Beta-blockers						
Atenolol	North West	1.08 to 8.34 µg/ℓ	4.41 µg/ℓ	0.33 to 3.22 µg/ℓ	1.19 µg/ℓ	[Kanama et al., 2018]
	Gauteng	1.6 to 2.5 µg/ℓ		0.4 to 0.7 µg/ℓ		[Archer et al., 2017]
Metoprolol	Gauteng	< LOD to 0 .09 ng/ℓ		< LOD to 2.22 ng/ℓ	0.6 ng/ℓ	[Mhuka et al., 2020]
Pindolol	Gauteng		0.03 µg/ℓ		0.00003 µg/ℓ	[Osunmakinde et al., 2013]
Antiepileptics						
Carbamazepine	KwaZulu-Natal		2.2 µg/ℓ		0.9 µg/ℓ	[Matongo et al., 2015]
	Gauteng	0.3 to 0.6 µg/ℓ			0.4 µg/ℓ	[Archer et al., 2017]
	Mpumalanga				58 ng/ℓ	[Wanda et al., 2017]
	Gauteng	< LOQ to 115.7 ng/ℓ	30.89 ng/ℓ	< LOQ to 416.3 ng/ℓ	193.6 ng/ℓ	[Mhuka et al., 2020]
	Eastern Cape	0.05 to 2.61 µg/ℓ	0.5 µg/ℓ	0.03 to 1.33 µg/ℓ	0.5 µg/ℓ	[Ademoyegun, 2017]
	KwaZulu-Natal		480 ng/ℓ		480 ng/ℓ	[Späth et al., 2021]
Lamotrigine	KwaZulu-Natal		240 ng/ℓ		0 ng/ℓ	[Späth et al., 2021]
Diazepam	Eastern Cape	0.20 to 0.90 µg/ℓ	0.29 µg/ℓ	0.06 to 0.69 µg/ℓ	0.29 µg/ℓ	[Ademoyegun, 2017]
Antipsychotics						
Clozapine	KwaZulu-Natal		8.6 µg/ℓ		9.6 µg/ℓ	[Matongo et al., 2015]
Lipid regulators						
Bezafibrate	Gauteng	1.4 to 3.0 µg/ℓ		0.3 to 0.7 µg/ℓ		[Archer et al., 2017]

Pharmaceuticals and personal care products	Area	WWTP influent		WWTP effluent		References
		Range	Mean	Range	Mean	
Antivirals						
Abacavir	KwaZulu-Natal		100 ng/ℓ		540 ng/ℓ	[Späth et al., 2021]
Atazanavir	KwaZulu-Natal		3 100 ng/ℓ		3 000 ng/ℓ	[Späth et al., 2021]
Acyclovir	KwaZulu-Natal		3 000 ng/ℓ		1 900 ng/ℓ	[Späth et al., 2021]
Ribavirin	Gauteng		0.02 µg/ℓ		0.00004 µg/ℓ	[Osunmakinde et al., 2013]
Lamivudine	Gauteng	< LOD to 1 001 ng/ℓ	267.5 ng/ℓ	< LOD to 323.40 ng/ℓ	28.07 ng/ℓ	[Mhuka et al., 2020]
	KwaZulu-Natal		350 ng/ℓ		350 ng/ℓ	[Späth et al., 2021]
Zidovudine	Gauteng			0.45 to 0.97 µg/ℓ		[Wood et al., 2015]
Nevirapine	Gauteng	< LOQ to 26.34 ng/ℓ	9.383 ng/ℓ	< LOQ to 80.53 ng/ℓ	9.931 ng/ℓ	[Mhuka et al., 2020]
	KwaZulu-Natal		74 000 ng/ℓ		130 000 ng/ℓ	[Späth et al., 2021]
Lopinavir	Gauteng				0.13 µg/ℓ	[Wood et al., 2015]
Ritonavir	Gauteng	4.08 to 393.90 ng/ℓ	72.77 ng/ℓ	14.43 to 675.90 ng/ℓ		[Gerber, 2019]
Famciclovir	Gauteng		0.02 µg/ℓ		0.00006 µg/ℓ	[Osunmakinde et al., 2013]
	Gauteng	< LOD to 17.67 ng/ℓ	0.86 ng/ℓ	< LOD to 7.17 ng/ℓ	1.21 ng/ℓ	[Mhuka et al., 2020]
Penciclovir	Gauteng	< LOD to 22.94 ng/ℓ	4.24 ng/ℓ	16.31 to 104.8 ng/ℓ	56.05 ng/ℓ	[Mhuka et al., 2020]
Raltegravir	KwaZulu-Natal		4 100 ng/ℓ		3 500 ng/ℓ	[Späth et al., 2021]
Human indicators/Psychomotor stimulant						
Caffeine	KwaZulu-Natal		4.5 µg/ℓ		0.6 µg/ℓ	[Matongo et al., 2015]
	Gauteng	5.1 to 1214.4 µg/ℓ		0.5 to 3.8 µg/ℓ		[Archer et al., 2017]
	Mpumalanga		9.1 ng/ℓ		11 ng/ℓ	[Wanda et al., 2017]
	KwaZulu-Natal		22 000 ng/ℓ		7 500 ng/ℓ	[Späth et al., 2021]
	Gauteng	1170 to 60 136 ng/ℓ	28 171 ng/ℓ	85.76 to 4 878 ng/ℓ	1 533 ng/ℓ	[Mhuka et al., 2020]
	Eastern Cape	4.69 to 69.49 µg/ℓ	10.79 µg/ℓ	0.98 to 12.77 µg/ℓ	10.79 µg/ℓ	[Ademoyegun, 2017]

2.5.2.3 Herbicides in surface water, groundwater and drinking water

Agriculture is well developed in South Africa and contributes approximately 12.5% to the gross domestic product. South Africa is one of the countries with utmost use of pesticides in sub-Saharan Africa, with approximately 8 000 listed pesticide formulations (Dalvie et al., 2009). The use of pesticides in agricultural activities have caused serious environmental pollution and several studies have highlighted the prevalence of pesticides in South African surface water and groundwater (Dabrowski et al., 2002; London et al., 2000; Sereda and Meinhardt, 2005) as shown in Table 2.8.

A study conducted by Curchod et al. (2020) on temporal variations of pesticide mixtures in rivers of three agricultural watersheds during a major drought in the Western Cape, South Africa, reported the concentrations of S-metolachlor, simazine, terbuthylazine, atraton, prometryn, terbutryn, atrazine, diuron, propyzamide, haloxyfop, MCPA, and oxyfluorfen ranging from 1.6 to 15.6, 6.8 to 67.4, 71.8 to 717.0, 5.7 to 56.9, 0.8 to 8.0, 4.3 to 43.2, 2.3 to 23.2, 5.9 to 59.0, 6.3 to 63.2, 0.1 to 1.2, 13.4 to 133.4, and 0.2-2.1 ng/ℓ, respectively.

Horn et al. (2019) conducted a study aimed at assessing glyphosate, 2,4-D and Cry proteins in surface water of South Africa and detected 2,4-D in River (A1) and Dam (A2) from Farm A around the Free State at mean concentrations of 0.93 and 0.72 µg/ℓ, respectively, after spraying. In Farm B, located at the border between the North West and the Free State, 2,4-D was also detected at mean concentrations of 1.02 µg/ℓ and 0.96 µg/ℓ after spraying and at the end of the season, respectively. The same study also detected 2,4-D in Dam (B3) located at the border separating the North West and Free State, before spraying, after spraying and at the end of the season at a mean concentration of 0.74, 0.90 and 0.92, respectively (Horn et al., 2019).

A study conducted in Cape Town to identify and quantify chemicals of emerging concern (persistent organic and inorganic pollutants) in some selected marine environments, reported the mean concentration of various herbicides such as alachlor, metolachlor, butachlor, simazine, and atrazine in seawater 1 as < LOQ, 0.3, 0.5, 1.4, and 1.9 ng/ℓ, respectively. In seawater 2, their respective mean concentrations were 3.4, 2.3, 1.6, 4.2 and 1.6 ng/ℓ, respectively (Ojemaye, 2020).

Table 2.8 Occurrence of herbicides in South African surface water, groundwater and drinking water

Herbicides	Area	Concentration in various water matrices						References
		Surface water		Groundwater		Drinking water		
		Range	Mean	Range	Mean	Range	Mean	
2,4-D	Free State		0.93 µg/ℓ					[Horn et al., 2019]
	Free State		0.72 µg/ℓ					[Horn et al., 2019]
	North West/Free State		1.02 µg/ℓ					[Horn et al., 2019]
	North West/Free State		0.96 µg/ℓ					[Horn et al., 2019]
	North West/Free State		0.74 µg/ℓ					[Horn et al., 2019]
	North West/Free State		0.90 µg/ℓ					[Horn et al., 2019]
	North West/Free State		0.92 µg/ℓ					[Horn et al., 2019]
Alachlor	Cape Town		< LOQ					[Ojemaye, 2020]
	Cape Town		3.4 ng/ℓ					[Ojemaye, 2020]
Atraton	Western Cape	5.7 to 56.9 ng/ℓ						[Curchod et al., 2020]
Atrazine	Western Cape	2.3 to 23.2 ng/ℓ						[Curchod et al., 2020]
	Cape Town		1.9 ng/ℓ					[Ojemaye, 2020]
	Cape Town		1.6 ng/ℓ					[Ojemaye, 2020]
Butachlor	Cape Town		0.5 ng/ℓ					[Ojemaye, 2020]
	Cape Town		1.6 ng/ℓ					[Ojemaye, 2020]
Diuron	Western Cape	5.9 to 59.0 ng/ℓ						[Curchod et al., 2020]
Haloxyfop	Western Cape	0.1 to 1.2 ng/ℓ						[Curchod et al., 2020]
MCPA	Western Cape	13.4 to 133.4 ng/ℓ						[Curchod et al., 2020]
Oxyfluorfen	Western Cape	0.2 to 2.1 ng/ℓ						[Curchod et al., 2020]
Prometryn	Western Cape	0.8 to 8.0 ng/ℓ						[Curchod et al., 2020]
Propyzamide	Western Cape	6.3-63.2 ng/ℓ						(Curchod et al., 2020]
S-metolachlor	Western Cape	1.6 to 15.6 ng/ℓ						[Curchod et al., 2020]
	Cape Town		0.3 ng/ℓ					[Ojemaye, 2020]
	Cape Town		2.3 ng/ℓ					[Ojemaye, 2020]
Simazine	Western Cape	6.8 to 67.4 ng/ℓ						[Curchod et al., 2020]
	Cape Town		1.4 ng/ℓ					[Ojemaye, 2020]
	Cape Town		4.2 ng/ℓ					[Ojemaye, 2020]
Terbuthylazine	Western Cape	71.8 to 717.0 ng/ℓ						[Curchod et al., 2020]
Terbutryn	Western Cape	4.3 to 43.2 ng/ℓ						[Curchod et al., 2020]

2.5.2.4 Herbicides in wastewater influents and effluents

The study conducted by Späth et al. (2021) in eThekwini, reported the average concentrations of tebuthiuron and terbuthylazine in influent as 96 and 41 ng/ℓ, respectively. In effluent their respective mean concentrations were reported as 110 and 53 ng/ℓ (Späth et al., 2021).

A study conducted with the aim of developing and applying SPE, ultrasonic extraction and soxhlet extraction for the analysis of pesticides in water, soil, sediment and sludge in KwaZulu-Natal, reported simazine, and atrazine, during the cold season at an average concentration of 9.7 and 7.8 µg/ℓ, respectively, in influent around the Darvill site. In effluents, these compounds were reported as 28 and 9.0 µg/ℓ, respectively. The study also detected simazine, atrazine, ametryn and terbuthylazine in influent around Amanzimtoti at average concentrations of 8.2, 2.5, 6.2, and 8.0 µg/ℓ, respectively. In effluent, their respective average concentrations were reported as 17, 49, 17, and 2.9 µg/ℓ, respectively (Kunene, 2019).

2.5.2.5 Endocrine-disrupting compounds in surface water, groundwater and drinking water

From the literature review, endocrine-disrupting chemicals that are mostly detected in surface water, groundwater and drinking water around South Africa, included compounds such as 4-octylphenol, cholesterol, estrone, 17-beta-estradiol, 17-alpha-ethinylestradiol, coprostanol, progesterone, stigmasterol, 4-nonylphenol, Di(2-ethylhexyl) phthalate, and BPA as shown in Table 2.9. A study was conducted targeting estrogenic activity, chemical levels and health risk assessment of municipal distribution point water from Pretoria and Cape Town, and detected eoestrone (E1) in drinking water at a concentration ranging from 0.002 to 0.004 µg/ℓ in Pretoria and 0.0004 to 0.001 µg/ℓ in Cape Town (Van Zijl et al., 2017).

Mhuka et al. (2020), in their study aimed at the occurrence of PPCPs in wastewater and receiving water in South Africa using an LC Orbitrap Mass Spectrometer, detected compounds such as estradiol, estriol, estrone and testosterone at high concentrations of 644.0, 244.5, 63.04 and < LOD ng/ℓ, respectively, in the upper stream of the Apies River.

Van Wyk et al. (2014) conducted a laboratory and field studies targeting pesticides as endocrine disruptors in South Africa and reported eoestradiol (E2) in surface water in Mpumalanga at a concentration ranging from 0.001 to 0.03 µg/ℓ. In Gauteng and the Western Cape, a study was conducted to determine estrogen activity and endocrine-disrupting chemical status in water obtained from selected distribution points and in drinking water, and eoestradiol (E2) was detected in Gauteng at a concentration ranging from 0.04 to 0.37 µg/ℓ, while in the Western Cape, it was ranging from 0.05 to 0.37 µg/ℓ (De Jager et al., 2013).

Furthermore, a laboratory and field studies targeting pesticides as endocrine disruptors in South Africa reported 17-alpha-ethinylestradiol (EE2) in surface water around Mpumalanga at a concentration ranging from 0.001 to 0.01 µg/ℓ (Van Wyk et al., 2014). Another study targeting estrogenic activity, chemical levels and health risk assessment of municipal distribution point water from Gauteng and Western the Cape also detected an average concentration of 17-alpha-ethinylestradiol (0.00002 µg/ℓ) in drinking water around Pretoria (Van Zijl et al., 2017).

Table 2.9 Occurrence of endocrine-disrupting compounds in South African surface water, groundwater and drinking water

Endocrine-disrupting compounds	Area	Concentration in various water matrices						References
		Surface water		Groundwater		Drinking water		
		Range	Mean	Range	Mean	Range	Mean	
Estrone	Pretoria					0.002 to 0.004 µg/ℓ		[Van Zijl et al., 2017]
	Cape Town					0.0004 to 0.001 µg/ℓ		[Van Zijl et al., 2017]
	Gauteng	7.124 to 63.04 ng/ℓ	30.39 ng/ℓ					[Mhuka et al., 2020]
Estradiol	Mpumalanga	0.001 to 0.03 µg/ℓ						[Van Wyk et al., 2014]
	Gauteng					0.04 to 0.37 µg/ℓ		[De Jager et al., 2013]
	Western Cape					0.05 to 0.37 µg/ℓ		[De Jager et al., 2013]
	Gauteng	134.7 to 644.0 ng/ℓ	362.2 ng/ℓ					[Mhuka et al., 2020]
17-alpha-ethinyl-estradiol	Mpumalanga	0.001 to 0.01 µg/ℓ						[Van Wyk et al., 2014]
	Pretoria					0.00002 µg/ℓ		[Van Zijl et al., 2017]
Estriol	Gauteng	81.30 to 244.5 ng/ℓ	134.7 ng/ℓ					[Mhuka et al., 2020]

Endocrine-disrupting compounds in wastewater influents and effluents

Detection of endocrine-disrupting compounds has been reported in different regions of the country as shown in Table 2.10. A study was conducted to assess PPCPs and hormones in WWTPs receiving inflows from health facilities in the North West and reported the concentration of estrone ranging from 0.013 to 0.053 µg/ℓ, estradiol ranging from 0.008 to 0.035 µg/ℓ, 17-alpha-ethinylestradiol) ranging from 2.654 to 9.833 µg/ℓ, and estriol ranging from 0.134 to 1.480 µg/ℓ in influent samples. The same study also reported the concentration of estrone ranging from 0.007 to 0.041 µg/ℓ, estradiol ranging from 0.008 to 0.0191 µg/ℓ, 17-alpha-ethinylestradiol ranging from 0.448 to 4.608 µg/ℓ, and estriol ranging from 0.111 to 0.539 µg/ℓ (Kanama et al., 2018).

Manickum and John (2014) in their study of occurrence, fate and environmental risk assessment of endocrine-disrupting compounds at the WWTPs in Pietermaritzburg, reported estrone (E1) at high concentrations of 0.35 µg/ℓ in influent and 0.08 µg/ℓ in effluent. The same study also detected estradiol (E2) ranging from 0.02 to 0.20 µg/ℓ in influent and 0.004 to 0.11 µg/ℓ in effluent. Furthermore, they detected 17-alpha-ethinylestradiol in both influent and effluent at a concentration ranging from 0.01 to 0.095 µg/ℓ and 0.001 to 0.008 µg/ℓ, respectively. Progesterone and testosterone were reported in influent at a concentration ranging from 0.16 to 0.90 µg/ℓ and 0.12 to 0.64 µg/ℓ, respectively. Furthermore, their respective mean concentration in effluent was recorded as 0.03 µg/ℓ and 0.03 µg/ℓ (Manickum and John, 2014).

Another study conducted to determine the occurrence of PPCPs in wastewater and receiving waters in South Africa using an LC Orbitrap Mass Spectrometer, detected estradiol, estriol, estrone and testosterone in influent at high concentrations of 2 206, 1 313, 35.96, and 44.09 ng/ℓ, while in effluent they were detected as 7 133, 779.1, 60.83 and 5.83 ng/ℓ, respectively (Mhuka et al., 2020).

Table 2.10 Occurrence of endocrine-disrupting compounds in South African wastewater influent and effluent

Endocrine-disrupting compounds	Area	WWTP influent		WWTP effluent		References
		Range	Mean	Range	Mean	
Estrone	North West	0.013 to 0.053 µg/ℓ	0.031 µg/ℓ	0.007 to 0.041 µg/ℓ	0.023 µg/ℓ	[Kanama et al., 2018]
	KwaZulu-Natal	0.01 to 0.35 µg/ℓ		0.003 to 0.08 µg/ℓ		[Manickum and John, 2014]
	Gauteng	< LOD to 35.96 ng/ℓ	7.951 ng/ℓ	< LOD to 60.83 ng/ℓ		[Mhuka et al., 2020]
Oestradiol	North West	0.008 to 0.035 µg/ℓ	0.022 µg/ℓ	0.008 to 0.0191 µg/ℓ	0.014 µg/ℓ	[Kanama et al., 2018]
	KwaZulu-Natal	0.02 to 0.20 µg/ℓ		0.004 to 0.11 µg/ℓ		[Manickum and John, 2014]
	Gauteng	66.45-2206 ng/ℓ	1204 ng/ℓ	154.1 to 7133 ng/ℓ	2415 ng/ℓ	[Mhuka et al., 2020]
17-alpha-ethinyl-estradiol	North West	2.654 to 9.833 µg/ℓ	5.601 µg/ℓ	0.448 to 4.608 µg/ℓ	1.344 µg/ℓ	[Kanama et al., 2018]
	KwaZulu-Natal	0.01 to 0.095 µg/ℓ		0.001 to 0.008 µg/ℓ		[Manickum and John, 2014]
Estriol	North West	0.134 to 1.480 µg/ℓ	0.463 µg/ℓ	0.111 to 0.539 µg/ℓ	0.233 µg/ℓ	[Kanama et al., 2018]
	Gauteng	53.23 to 1313 ng/ℓ	250.3 ng/ℓ	56.53 to 779.1 ng/ℓ	275.1 ng/ℓ	[Mhuka et al., 2020]
Progesterone	KwaZulu-Natal	0.16 to 0.90 µg/ℓ			0.03 µg/ℓ	[Manickum and John, 2014]
Testosterone	KwaZulu-Natal	0.12 to 0.64 µg/ℓ			0.03 µg/ℓ	[Manickum and John, 2014]
	Gauteng	< LOD to 44.09 ng/ℓ	18.19 ng/ℓ	< LOD to 5.83 ng/ℓ	0.576 ng/ℓ	[Mhuka et al., 2020]

2.6 REMOVAL MECHANISMS AND ADVANCED TREATMENT OF EMERGING CONTAMINANTS IN WATER ENVIRONMENT

2.6.1 Removal mechanism

Emerging contaminants are removed through commonly used mechanisms such as biodegradation, sorption, photolysis and volatilisation. Biodegradation and sorption processes are the most important methods with the ability to eliminate contaminants from the sewage wastewater (Chang et al., 2011; Janna, 2011). A process of how these removal mechanisms work is summarised in this section.

2.6.1.1 Biodegradation

Biodegradation is one of the most important mechanisms used to eliminate emerging pollutants. Its aim is to decrease the organic matter concentrations in WWTPs by converting the decomposable materials into an acceptable end product. Furthermore, it aims at eliminating nutrients such as phosphorus and nitrogen. In biological processes, nitrification and denitrifications are the leading processes that occur. Nitrification is the process whereby ammonia is converted into nitrate. When nitrosomonas bacteria oxidise ammonia to nitrite (NO_2-N) and nitrobacter bacteria oxidise nitrite to nitrate (NO_3-N), this biological process happens. Factors such as dissolved oxygen, pH, temperature, metals, acids, and free ammonia effect the pace of nitrification. Although nitrification may be influenced by such factors, it needs a long retention period, a low food-to-microorganism ratio, and a long mean cell residence time or age of the sludge (Langford and Lester, 2003).

In order to acquire an appropriate end-product, denitrification plays a crucial role. It is thought to be the biological conversion of nitrate to nitrogen gas (N_2), which is accomplished by a heterotrophic bacteria that obtains oxygen from either dissolved oxygen or nitrate molecules. The process of denitrification takes place only when the level of oxygen is low and bacteria use nitrate-oxygen (anoxic condition) (Janna, 2011). The biodegradation process takes place in aerobic and anaerobic periods (Langford and Lester, 2003). The degradation rates of contaminants of emerging concern are different. Other emerging contaminants are readily biodegradable, some may persist for a few days, whereas other possess resilient and non-degradable characteristics (Benotti and Brownawell, 2009; Joss et al., 2004). Even though the process of biodegradation

is regarded as very important, there is still a paucity of information on the biodegradation of many contaminants of emerging concerns and the aspects that influence their rate of degradation (Janna, 2011).

2.6.1.2 Sorption

It also plays a crucial role in pollution fate in aquatic ecosystems. Sorption is regarded as a process whereby more lipophilic (hydrophobic) pollutants are separated into settled sewage solids in the primary sedimentation tank or into biomass in the biological stage. The compound sorption potential are classified based on their octanol-water coefficient value such as log K_{ow} < 2.5, which is a low sorption potential, log K_{ow} 2.5 to 4.0, which is a medium sorption potential, and log K_{ow} > 4.0, which is regarded as high sorption potential (Janna, 2011). The sorption potential of a contaminant is determined or predicted by the ratio between the concentrations in the solid and liquid phases at equilibrium conditions known as solid-water distribution coefficient (Kd) (Suárez et al., 2008). Absorption and adsorption are the two processes of a sorption mechanism. Absorption is defined as the hydrophobic interaction of the aliphatic and aromatic chemical compound groups with the lipophilic cell membrane of the microorganisms and the lipid fractions of the sludge. In the absorption process, the contaminant sorption possibility is determined by the octanol-water partition coefficient (K_{ow}). Adsorption is defined as the electrostatic relationship between positively charged groups of chemicals with the negatively charged surfaces of the microbes, which are highly influenced by the dissociation coefficient (Ka) of the compounds (Ternes et al., 2004).

2.6.1.3 Photolysis

The photolysis process is accountable for the total or incomplete elimination of some emerging contaminants (Janna, 2011). Certain contaminants of emerging concern may be certainly degraded, or slowly degraded, whereas other chemical compounds are unaffected by the process of photolysis (Gomez et al., 2008; Yamamoto et al., 2009). The removal rate of emerging contaminants under the photolysis process is influenced by factors such as pH, level of oxygen, compound structural properties, and amount of organic matter (Neamtu and Frimmel, 2006). Furthermore, the structure of the sewage treatment works may influence removal of some emerging contaminants during photolysis, for example big aeration tanks or polishing lagoons permit occurrence of some photolysis (Janna, 2011).

2.6.1.4 Volatilisation

Volatilisation is the process of removing some volatile organic chemical compounds from wastewater to the atmosphere. The potential of organic compounds to be removed from wastewater is predicted based on Henry's law constant (Hc) and the octanol-water partition coefficient (Kow). This prediction method states that a chemical compound has a low volatilisation potential when Hc < 1×10^{-4} and Hc/Kow <1×10^{-9}, and a high volatilisation potential when Hc > 1×10^{-4} and Hc/Kow > 1×10^{-9} (Janna, 2011; Rogers, 1996). However, in emerging contaminants that have chemical compounds with hydrophilic behaviour, this process is regarded as insignificant. For example, musk fragrances have Hc and Hc/Kow higher than the limit mentioned above (Rogers, 1996); therefore, a high potential volatilisation may occur particularly in an aerated biological treatment due to the abundance of air (Janna, 2011; Ternes et al., 2004).

2.6.2 Advanced treatment

Current wastewater treatment processes are unable to entirely remove some of the emerging contaminants that lead to their introduction into natural water systems (Deeb et al., 2017). However, advanced treatment methods such as pressure-driven membrane filtration, direct oxidation, sand filtration and activated carbon are some of the alternative solutions (Cochran, 2018; Janna, 2011).

2.6.2.1 Pressure-driven membrane filtration

Pressure-driven membrane filtration is a tertiary treatment process for eliminating contaminants of emerging concern (Schaar et al., 2010) by forcing water through semi-permeable membranes against a concentration gradient (Cochran, 2018). Pollutants are physically eliminated from the membranes by pore size limits or electrostatic repulsion (Cochran, 2018), and its elimination proficiency is uppermost in reverse osmosis, trailed by nanofiltration, ultrafiltration, and microfiltration (Liu et al., 2009). Microfiltration and ultrafiltration offer pre-treatment for nanofiltration and reverse osmosis (Oulton and Cwiertny, 2010). The usage of reverse osmosis and nanofiltration is well known in the elimination of micropollutants for high-quality drinking water or industrially processed water. These tertiary treatment methods have the ability to eliminate high quantities of emerging pollutants and, consequently, they are progressively applied in newer advanced wastewater treatment systems (Cochran, 2018).

2.6.2.2 Direct oxidation

The direct oxidation method has the ability to effectively remove emerging pollutants from the aqueous environment by chemically decomposing the substances into their fundamental molecular components, such as carbon dioxide through a process known as mineralisation (Schonherr et al., 2017). At higher concentrations, chemical oxidants such as chlorine, chlorine dioxide, and ozone can accomplish elimination of emerging pollutants (Lee and Von Gunten, 2010). However, at greater doses, chlorination and ozonation processes may possibly generate detrimental by-products such as bromate and N-nitrosodimethlyamine, which are potentially more harmful than the original chemical. To ensure that emerging contaminants and by-products are completely removed, water toxicity must be assessed prior to and after chemical treatment, or an extra treatment step must be adopted after direct oxidation (Almomani et al., 2016; Knopp et al., 2016). Furthermore, the effectiveness of chlorination and ozonation can be limited by organic matter and other constituents in the water, which are regarded as the predecessors of by-product generation (Oulton and Cwiertny, 2010). Although ozonation cannot entirely eliminate emerging pollutants such as pharmaceuticals, the direct oxidation method can greatly decrease their pharmacological consequences (Almomani et al., 2016).

2.6.2.3 Sand filtration

Sand filters are frequently used to eliminate suspended particles from drinking water and tertiary wastewater treatment. The biological activity of the filter aids in the breakdown and removal of emerging contaminants. Sand filters can be added after a chemical treatment phase, such as direct oxidation, to aid in the total removal of emerging contaminants, parent chemicals and breakdown products (Cochran, 2018; Knopp et al., 2016).

2.6.2.4 Activated carbon

Activated carbon is combined with the treatment procedure either through granular or powdered activated carbon. For the elimination of emerging contaminants in tertiary treatments, granular activated carbon is contained in a column, whereas powdered activated carbon is added and recirculated internally. These forms of activated carbons are regarded as alternative methods to chemical tertiary treatment methods due to their abilities to eliminate high quantities of emerging contaminants (Karelid et al., 2017). Biologically activated carbon can be applied for tertiary treatment in addition to granular activated carbon and powdered activated carbon as it has a biofilm on the material surface that both biodegrades and sorbs pollutants (Oulton and Cwiertny, 2010). To promote the elimination of emerging pollutants in tertiary treatments, adsorption onto activated carbon is frequently applied (Karelid et al., 2017). Generally, the combination of activated carbon adsorption and chemical processes have an effective elimination rate of emerging pollutants although the elimination effectiveness is reliant on the adsorption capacity of the activated carbon (Esplugas et al., 2007). This factor restricts the effectiveness of activated carbon as the capacity of adsorption is understood to decline over time (Cochran, 2018; Liu et al., 2009).

2.7 ANALYTICAL PROCEDURE FOR DETECTION OF EMERGING CONTAMINANTS

The availability of precise analytical techniques that can be effective in detecting emerging contaminants at a low concentration level (ng/ℓ or lower) is needed to accurately assess risk assessment of contaminants and for the monitoring of the quality of water. The key steps in obtaining accurate analytical data take into account the sampling process, sample conveyance, extraction of samples, and suitable analytical methods. The most widely used analytical methods for detection of contaminants of emerging concern are GC, or HPLC (Swartz et al., 2018).

2.7.1 Sample preparation and extraction process

After collection of a water sample, the sample is then filtered and concentrated by a variety of pre-concentration procedures before extraction. This is done to enrich polar or nonpolar compounds. After filtration, the filters are washed with methanol due to the fact that some fraction of the target compound may be removed with the suspended solids. Extraction and clean-up are critical steps in transferring analytes of interest from a complicated environment to a simple solution. It also helps to reduce or remove interference co-eluted with analytes before analysis by purifying the extract. The extraction process may involve using liquid-liquid extraction; liquid micro-extraction or SPE (Moodley et al., 2016).

Liquid-liquid extraction is known to have an advantage of freedom from the influence of several particulates, as well as exclusion of the need to filter the sample. In extraction of various emerging contaminants liquid-liquid extraction has shown a recovery rate of more than 70% for most analytes (Robles-Molina et al., 2013). However, its major setback is that it encompasses a process that is strenuous and requires the use of a large amount of organic solvents. Another challenge in extraction of diverse chemical compounds is the lack of a universal solvent for the elution of analytes and this problem is exacerbated in high matrix samples such as sewage effluent. Liquid-liquid extraction is frequently applied in cleaner samples from river and stream water (Moodley et al., 2016).

Liquid micro-extraction is a technique that utilises microlitre volumes of approximately <100 µℓ for the extraction and/or preconcentration of analytes of interest (Alexovič et al., 2016, Dimpe et al., 2016). The advantages of a liquid micro-extraction method are that it has low cost of operation, uses a low volume of solvents, generates less waste, and is easy to operate. It is also characterised by a short time of extraction, and very high enrichment factors. However, the use of a small volume of solvent may cause analyte losses and the solvents used may not be effective for a wide range of analytes. Furthermore, some solvents used in this method are considered highly toxic, and it may result in loss of precision (Alexovič et al., 2016, Dimpe and Nomngongo, 2016; Moodley et al., 2016).

The most commonly used method for extraction of samples from the water environment is the solid-phase extraction (SPE). In SPE, the micro and lyophilisation method of extraction may also be utilised. Sample extraction and clean-up can be conducted simultaneously with the SPE technique. Cartridges packed with sorbents such as C-18, ion-exchange phases, polymeric phases and nonpolar phases are mostly used in SPE. For the off-line SPE, polymeric, octadecylsilica, or hydrophilic-lipophilic, balanced with either disks or cartridges at low pH, is used (Petrovic et al., 2003). In preconcentration of polar and nonpolar compounds hydrophilic-lipophilic balanced cartridges are the most preferred. For direct extraction and analysis an online automated SPE is done by coupling an automated SPE directly to LC-MS or LC-MS2 (Swartz et al., 2018).

2.7.2 Chromatography analysis

Highly sensitive and selective analytical methods such as GC and LC combined with MS are crucial in the analysis of various emerging contaminants (Galindo-Miranda et al., 2019). Liquid chromatography, combined with tandem mass spectrometry (LC-tandem-MS), is one of the most widely used techniques for the analysis of various groups of emerging contaminants occurring in an aqueous environment (Galindo-Miranda et al.,

2019; Hermes et al., 2018; Rivera-Jaimes et al., 2018). LC-tandem-MS can minimise the time of preparing samples and permits for the detection of polar and non-volatile compounds (Galindo-Miranda et al., 2019). It can achieve a little higher LOD than GC-MS and allows identification of high polar organic pollutants in the environment at ng/ℓ levels. For sample preparation and preconcentration methods, it can be coupled with on-line devices such as SPE methods (Swartz et al., 2018). The use of chromatographic systems at very high pressure, such as ultra-HPLC, is used to speed up analysis and reduce solvent intake (Galindo-Miranda et al., 2019). The combination of high pressure and 1.7 µm particle-size columns saves time and solvent, without compromising sensitivity or peak resolution (Chauveau-Duriot et al., 2010; Galindo-Miranda et al., 2019).

GC-MS is considered a highly effective method of separation although it needs an extended sample derivatisation processes to ensure analyte volatility (Galindo-Miranda et al., 2019; Kanani et al., 2008). It offers higher separation effectiveness and lower operational cost with no matrix effect problems found in LC-MS (Galindo-Miranda et al., 2019; Reemtsma and Quintana, 2006). In order to increase separation of chemical compounds in a complex matrix, a newly developed two-dimensional GC (GC×GC) is frequently used (Gómez et al., 2011; Jover et al., 2009; Leonhardt et al., 2015; Organtini et al., 2014; Prebihalo et al., 2015; Wanda et al., 2017). Two-dimensional GC entails the connection of two chromatographic columns having complementary polarities that, when coupled, boost the separation capacity of the arrangement. Furthermore, a modulator device connects the columns, essentially decoupling elution on each column (Edwards et al., 2011; Galindo-Miranda et al., 2019).

2.7.3 Detection systems

GC or HPLC are the most widely used analytical instruments for the detection of emerging contaminants. Single quadruple MS, tandem MS (MS2), triple quadrupole MS, ion-trap MS, and time-of-flight MS are some of the detection systems used in different ionisation modes, for example atmospheric chemical pressure ionisation and electrospray ionisation (Swartz et al., 2018). Hybrid instruments, QqToF, QqLIT and Orbitrap have become more commonly used mass analysers of emerging contaminants in an aqueous environment because of their effectiveness to achieve precise mass measurements and acquire crucial qualitative full scan spectra data (Gago-Ferrero et al., 2017; Galindo-Miranda et al., 2019; Gros et al., 2013; Petrovic and Barceló, 2013; Pitarch et al., 2016).

2.7.4 Ionisation sources

Ion sources are used in mass spectrometers to create ions with positive or negative charges (Galindo-Miranda et al., 2019; Ho et al., 2003). To enable the passage of ions from a solution into the gaseous phase without fragmentation, the ionisation source relies on electrical energy (Banerjee and Mazumdar, 2012). Ions pass through the mass analyser and, depending on their mass/charge ratio, arrive at various components of the detector, allowing them to be identified (Galindo-Miranda et al., 2019; Ho et al., 2003). The most frequently used ion sources are electrospray ionisation and electron impact. For the GC spectrometry mechanisms, electron impact is the most frequently used ionisation technique. However, for analysis of liquid chemical and biochemical compound samples, the electrospray ionisation method is commonly applied as it ionises molecules directly from the liquid phase (Wilm, 2011). The ionisation source connected to LC is regarded as the most extensively used technique (Hermes et al., 2018; Osorio et al., 2016; Rivera-Jaimes et al., 2018).

2.7.5 Other analytical techniques

2.7.5.1 Capillary electrophoresis technique

The capillary electrophoresis technique is a method mostly used for the analysis of PPCPs in an aqueous solution. Separation takes place in fused silica capillaries and in order to achieve separation, a high voltage is often applied through buffer field capillaries. It has high, effective and analysing speed, less use of reagent, less sample intake, and it is quick to develop. Furthermore, it is less selective as compared to HPLC. In most

cases, it is used as a complementary or alternative technique because its separation selectivity can be similar to that of HPLC. When combined with the mass spectrometry, the capillary electrophoresis technique has the highest potential (Swartz et al., 2018).

2.7.5.2 Bioanalytical techniques

Bioanalytical methods are very crucial in monitoring of some endocrine-disrupting compounds, PPCPs. This method employs a biological end-point associated with a certain sort of toxicity or chemical class. The simplest bioanalytical procedures are receptor-binding assays and cellular bioassays with fast reaction times, great sensitivity, and minimal cost. *In vivo* bioassays are also utilised to identify distinct kinds of endocrine-disrupting chemicals. Despite the fact that each instrumental and bioanalytical method has benefits and drawbacks, a combination of these methods is the most likely to discover and quantify endocrine-disruptive chemicals. This strategy, which may use bioassay-directed fractionation to drive instrumental analysis towards revelation of dangerous chemicals, is commonly viewed as toxicity identification or evaluation (Swartz et al., 2018).

2.8 THEORY OF ECOLOGICAL RISK ASSESSMENT FOR EMERGING CONTAMINANTS

2.8.1 Ecological risk assessment theory

Ecological risk assessment methods are centred on acute and chronic toxicity studies that measure the toxic effects on the most sensitive organisms within the environments. To assess acute toxicity, data is generated centred on temporary toxicity consequences or effects of less than twenty-four hours (< 24 h). It is regarded as an effect concentration in 50% of the experimental population (EC_{50}) or a lethal dosage in 50% of the experimental population (LD_{50}). To assess chronic toxicity, the data is generated centred on prolonged toxicity effects of more than twenty-four hours (> 24 h). It is measured in terms of concentration with no observed effect concentration (NOEC) in the experimental population, or lowest observed concentration with an effect in the experimental population. Therefore, to determine the predicted no-effect concentration (PNEC) of particular emerging contaminants these toxicity results are corrected by an assessment factor. After correction of the toxicity data by an assessment factor, the risk quotient (RQ) is obtained by comparing the PNEC with either predicted environmental concentrations or measured environmental concentrations (MEC) of the emerging contaminant of interest. An RQ value that is above 1 (RQ > 1) or equivalent to 1 (RQ = 1) signifies emerging contaminants of environmental concern (Archer et al., 2017).

2.9 IMPLICATIONS OF EMERGING CONTAMINANTS ON THE ENVIRONMENT AND HUMAN HEALTH

Although there are advanced treatment techniques in water and wastewater treatment processes, to achieve total removal of emerging contaminants in water or wastewater treatment facilities is impossible, and as a result, emerging contaminants end up reaching the natural water resources (Houtman, 2010; Kümmerer, 2009). The occurrence of these contaminants in the environment at a very low concentrations, ranging from nanograms per litre to micrograms per litre, and may have serious environmental and human health implications (Harrison et al., 2006; Tijani et al., 2013).

2.9.1 Effects of pharmaceuticals and personal care products

Exposure to non-steroid and anti-inflammatory drugs may lead to serious health and environmental implications. Diclofenac is associated with elevated levels of the enzyme cytochrome P450 and vetellogenin protein, estrogenic effects, reduced thyroid hormone levels in male and female patients, and reduced thyroid hormone levels in fish (Archer et al., 2017; Bishnoi et al., 1994; Hong et al., 2007; Saravanan et al., 2014). Furthermore, diclofenac may affect the liver and kidneys in aquatic organisms (Ngqwala and Muchesa, 2020). Exposure to ibuprofen may increase vetellogenin production in male fish, decrease reproduction rates in fish, rise estradiol hormone levels and aromatase enzyme activity, and decreased testosterone hormone levels.

Furthermore, it may disrupt thyroid hormone-mediated reprogramming in tadpoles (Archer et al., 2017; Han et al., 2010; Nesbitt, 2011; Veldhoen et al., 2014). Naproxen may cause health implications such as reduced thyroid hormone levels in male and female patients; and reduced egg fertilisation in fish (Archer et al., 2017; Bishnoi et al., 1994; Nesbitt, 2011). Acetaminophen exposure is associated with a high-level regulation of CYP11β2 gene expression and progesterone hormone levels (Archer et al., 2017; Gracia et al., 2007).

Exposure to antiepileptics such as carbamazepine may lead to reduced steroid hormone levels in male and female patients. It may also cause reduction of 11-ketotestosterone in male fish (Archer et al., 2017; Galus et al., 2013a or b; Herzog et al., 2005; Svalheim et al., 2009).

Excessive uterine weight in female rats; estrogenic response, multiplying of cells; modulation of testicular structure, and induced vitellogenin production in male fish may occur as a result of the exposure to antidepressants such as fluoxetine (Archer et al., 2017; Gracia et al., 2007; Müller et al., 2012; Schultz et al., 2011).

Antiseptics such as triclosan may cause reduced T4 hormone levels in female rats, reduced sperm counts in male fish, reduced hatchability and time of hatching of fertilised eggs in fish. Furthermore, in tadpoles it may cause reduced levels of T3 hormone and thyroid-related gene expressions (Ahn et al., 2008; Archer et al., 2017; Christen et al., 2010; Crofton et al., 2007; Ishibashi et al., 2004; Raut and Angus, 2010). Exposure to triclocarban is associated with activation of estrogen receptor target genes in female ovaries, enhanced testosterone action through interaction with the androgen receptor, and agonist of estrogen receptor and/or androgen receptor-responsive gene expression (Ahn et al., 2008; Archer et al., 2017; Christen et al., 2010; Yueh et al., 2012).

Exposure to ultraviolet screens such as benzophenones is associated with agonistic binding to the human estrogen receptor, induced breast cancer cell proliferation, increased uterine weight in female rats, increase in plasma vetellogenin concentrations and increase in estrogen receptors in the liver of male fish (Inui et al., 2003; Schlumpf et al., 2001). It may lead to endocrine-disrupting effects such as disruption of the hypothalamic-pituitarythyroid axis, reproductive and developmental function. Furthermore, dermatitis may occur as a result of exposure to sunscreens (Heurung et al., 2014).

Antibiotics such as amoxicillin may lead to high regulation of CYP19 and CYP17 gene expression and estradiol hormone levels (Archer et al., 2017; Gracia et al., 2007). Erythromycin may cause high regulation of CYP11β2 gene expression and progesterone/estradiol hormone levels; and low regulation of testosterone hormone levels (Archer et al., 2017; Gracia et al., 2007). Cephalexin is associated with high regulation of CYP19 gene expression and low regulation of testosterone hormone levels (Archer et al., 2017; Gracia et al., 2007). Oxytetracycline is a cause of high regulation of CYP19 and 3βHSD2 gene expression, increased estradiol hormone levels and aromatase enzyme activity (Archer et al., 2017; Gracia et al., 2007; Ji et al., 2010). Exposure to sulfathiazole can cause high regulation of CYP17 and CYP19 gene expression, increased estradiol hormone levels and aromatase enzyme activity, and increased estradiol hormone levels in male fish (Ji et al., 2010). Doxycycline is associated with high regulation of CYP19 gene expression, while tylosin is a cause of high regulation of CYP11β2 gene expression, low regulation of testosterone and estradiol hormone levels (Gracia et al., 2007).

Furthermore, exposure to beta-blockers such as propranolol may have toxic effects on zooplankton and benthic organisms (Ngqwala and Muchesa, 2020). A lipid regulator such as bezafibrate may cause reduction in levels of plasma 11-ketotestosterone in fish, while clofibrate is associated with high regulation of CYP11β2 gene expression, and low regulation of testosterone hormone levels (Archer et al., 2017; Gracia et al., 2007; Velasco-Santamaría et al., 2011).

2.9.2 Effects of herbicides

Although herbicides are very important in maintenance of good quality and protection of crops or raw materials, they are of serious concern in human health as they may gather in the human cell membrane and interferes with normal body functioning. Exposure to water contaminated with herbicides through dermal contact or ingestion may cause serious health implications (Kumar et al., 2013; Syafrudin et al., 2021). Atrazine is a well-recognised herbicide with endocrine-disrupting effects. Human exposure to atrazine may lead to increased risk of developing hypospadias, cryptorchidism, and small penis. Furthermore, its exposure is associated with increased risk of cancers, reproduction deficiency, and antibiotic resistance (Agopian et al., 2013; Manahil, 2017).

Exposure to triazines lead to irritation, carcinogenic and teratogenic effects (Sathiakumar et al., 2011). Exposure to 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) may cause nausea, dizziness, and vomiting (Bradberry et al., 2004). 2.4-D may cause pigmentation of tubular cells in kidneys (FAO, 1996; Mendes et al., 2019). The dipyridyl compounds paraquat and diquat are associated with vomiting, which leads to dehydration (Ronnen et al., 1995). Glyphosate exposure may lead to seizures, respiratory arrest, coma, disturbance of consciousness and irritation (Sathiakumar et al., 2011).

Diclofop-methyl may cause liver effects such as enlargements and enzymatic changes. Diuron is associated with weight loss, increased liver weight, and blood effects. MCPA is associated with effects on the kidney such as increase of absolute and relative weight, urinary bilirubin, crystals, and pH. It may also cause systemic, hepatic, testicular, reproductive, and developmental effects, and have an effect on the nervous system. Metribuzin has been reported to cause liver effects such as increased incidence and severity of mucopolysaccharide droplets (FAO, 1996; Mendes et al., 2019)

Picloram may lead to changes in body and liver weights and clinical chemistry parameters. Other effects associated with picloram include effects on kidney such as ratio of liver weight and body weight, and histopathology. Simazine may cause changes in body weight and effects on serum and thyroid gland. Trifluralin is believed to lead in changes of liver and spleen weights and serum chemistry (FAO, 1996; Mendes et al., 2019).

Other pesticides such as organophosphate insecticides lead to serious health implications such as smaller head size, lower birth weight, attention problems, neurodevelopmental deficits, and reduction in childhood IQ in preschool-aged children (Manahil, 2017; Rauh et al., 2012). Exposure to carbamates insecticides may produce clinical signs and symptoms such as miosis, salivation, sweating, tearing, rhinorrhea, behavioural change, abdominal pain, vomiting, diarrhea (Rosman et al., 2008). Cyclodienes, hexachlorocyclohexane isomers, and DDT may lead to dizziness, headache, anorexia, nausea, vomiting, malaise, dermatitis, diarrhea, muscle weakness, tremors, spasms, mental confusion, and anxiety (Barr and Needham, 2002).

Furthermore, fungicides such as dithiocarbamates comprise two groups of dimethyldithiocarbamate and ethylenebisdithiocarbamate, depending on which metal cation is present in the chemical structure. Their exposure may lead to carcinogenic, teratogenic action and thyroid problems (Belpoggi et al., 2002; Costa, 2008).

2.9.3 Effects of endocrine-disrupting compounds

The implications associated with exposure to endocrine-disrupting compounds may be either temporal or permanent, acute or chronic depending on the type of chemical, kind of tissue exposed, dosage, timing and exposure period. Furthermore, metabolism and removal from the body, as well as the level of toxicity may influence effects of endocrine-disrupting compounds. Exposure to natural and synthetic steroid hormones is associated with serious medical conditions on both aquatic and terrestrial animals (Olujimi et al., 2010).

Natural estrogens are regarded as carcinogenic to humans, thus synthetic estrogens may have related characteristics. Prenatal exposure to both natural and synthetic estrogens may lead to development of vaginal and breast cancers in humans and uterine cancers in animals (Birnbaum and Fenton, 2003). Exposure to low level of estrogen 17-alpha-ethinylestradiol may expand fish livers and affect the sexual characteristics of male fish in surface water (Ngqwala and Muchesa, 2020).

Diethylstilbestrol exposure may cause development of vaginal cancer, reproductive tract abnormalities in females and semen irregularities in males (Solomon and Schettler, 2000). In females it may trigger vaginal, cervical, and ovarian cancer; infertility, and abnormal uterine development. In males it may cause testicular cancer, hypospadias, cryptorchidism, and reduced quality and quantity of semen (Arman et al., 2021; Chen et al., 2021; Newbold, 1995*;* Richardson and Kimura, 2020; Sasaki and Terasaki, 2018).

Exposure to BPA is associated with foetal toxicity, changes in maternal behaviour, enlarged prostate, reduced sperm count, obesity and diabetes in mice. Furthermore, it may trigger the proliferation of human breast cancer cells (Nagel et al., 1999). In females, BPA exposure may reduce egg quality (Souter et al., 2013), while in men, it may cause low sperm counts (Cao et al., 2012; Nordkap et al., 2012).

Phthalates exposure may cause cryptorchidism, hypospadias, prostate disease and testicular cancer. It is linked to genital abnormalities in boys, reduced sperm counts, endometriosis, and elements of metabolic disruption including obesity. Furthermore, it may trigger early onset of puberty and premature breast development in young girls and abnormal sexual differentiation in male rats. Phthalates are regarded as chemical compounds with carcinogenicity and teratogenicity effects in both animals and humans (Gore et al., 2014). Furthermore, human health consequences associated with exposure to DDTS include reduced fertility, urogenital birth defects (males), impaired breast feeding, type 2 diabetes and cancer. It may also lead to bone disorders and decreased bone mineral density (Gore et al., 2014).

2.10 MITIGATION OF RISKS ASSOCIATED WITH EMERGING CONTAMINANTS

To control the influx of emerging contaminants into the environment and minimise the risk associated with their exposure, there is a need to implement mitigation strategies. Regulating the release of emerging contaminants into the environment is one of the best strategies to manage their influx and toxic effects. This is achievable by proper monitoring and regulating point sources such as industries, hospitals, and water treatment facilities, together with the maintenance and enforcement of standard procedures for every source effluent streams. Point source separation can be part of a sustainable solution for industries, hospitals, and water treatment facilities (Mutiyar and Mittal, 2014). Medicines that are environmentally benign, have low noxiousness, do not bioaccumulate, and have a short environmental persistence, may help to reduce the amount of pharmaceuticals that end up in the environment (Clark et al., 2008; Gunnarsson et al., 2009).

Classification and labelling methods may also play a crucial role in reducing emerging contaminant risks. This strategy entails identifying and labelling all active medicinal compounds with information on their environmental implications in order to educate the general public. The information is made available to people through websites and information booklets (Boxall, 2012; Clark et al., 2008). Although inappropriate medical drug disposal has a minimal impact on total environmental pollution, taking back unused or expired medication may help to mitigate their quantities in landfill sites and aqueous environments and their possible health risks (Daughton and Ruhoy, 2009). According to Boxall (2012), the effectiveness of this strategy rests on teaching people the possible environmental implications of unused or expired medical drugs.

Furthermore, improvements in agricultural practices may protect water bodies and also contribute to the reduction of risks associated with the presence of emerging contaminants in the environment. Changes in treatment timings and intensities, as well as manure application rates and timings, may help to reduce discharges of emerging contaminants into the environment. Furthermore, developing a standard operating process for applying manure to unstable slopes and defining buffer zones could help to reduce risks (Pope

et al., 2009). Injection application is better than broadcast application as it can minimise overland runoff of PPCPs (Topp et al., 2008). The application of sewage sludge in the dry season may reduce the possibility of some chemical compounds to be introduced into surface water (Boxall, 2012). Improving management of pesticides may limit introduction of pesticides into groundwater or surface water. This can be done by reducing the amount of product available for loss, reducing storage and handling losses, reduce the potential for transport and providing a mechanism for deposition (Aydinalp and Porca, 2004).

2.11 CONCLUSION

Wastewater treatment plants, agricultural runoff, PPCPs manufacturing sites, and aquaculture are the main contributors of emerging pollutants into the water environment. Current wastewater treatment technologies are unable to entirely remove emerging pollutants during treatment processes which lead to the introduction of emerging contaminants in an aqueous environment. Emerging pollutants introduced into the water bodies on a regular basis may have negative consequences on aquatic creatures throughout their life cycle. The general public need to be educated on the proper disposal of unused or expired medical drugs to reduce their concentration in the environment. It is clear from this review that more studies on monitoring, remediating and assessing the risk associated with the presence of emerging contaminants in an aqueous environment are required, particularly in African countries like South Africa.

CHAPTER 3: METHODOLOGY

3.1 INTRODUCTION

This section discusses the methods that were used to achieve the Aims 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 and risks 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 metres 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. Bloemfontein's population 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).

The surface water environment is thought to include a number of rivers, including the Modder (Lekatlong), Renosterspruit, Kaalspruit, Korannaspruit, Kleinmodder, 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, the Welbedacht Dam, Mockes Dam and Maselspoort Dam provide services to the city of Bloemfontein. Water for domestic, agricultural, and industrial usage in the Botshabelo and Thaba 'NChu districts is largely provided by the Rusfontein 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).

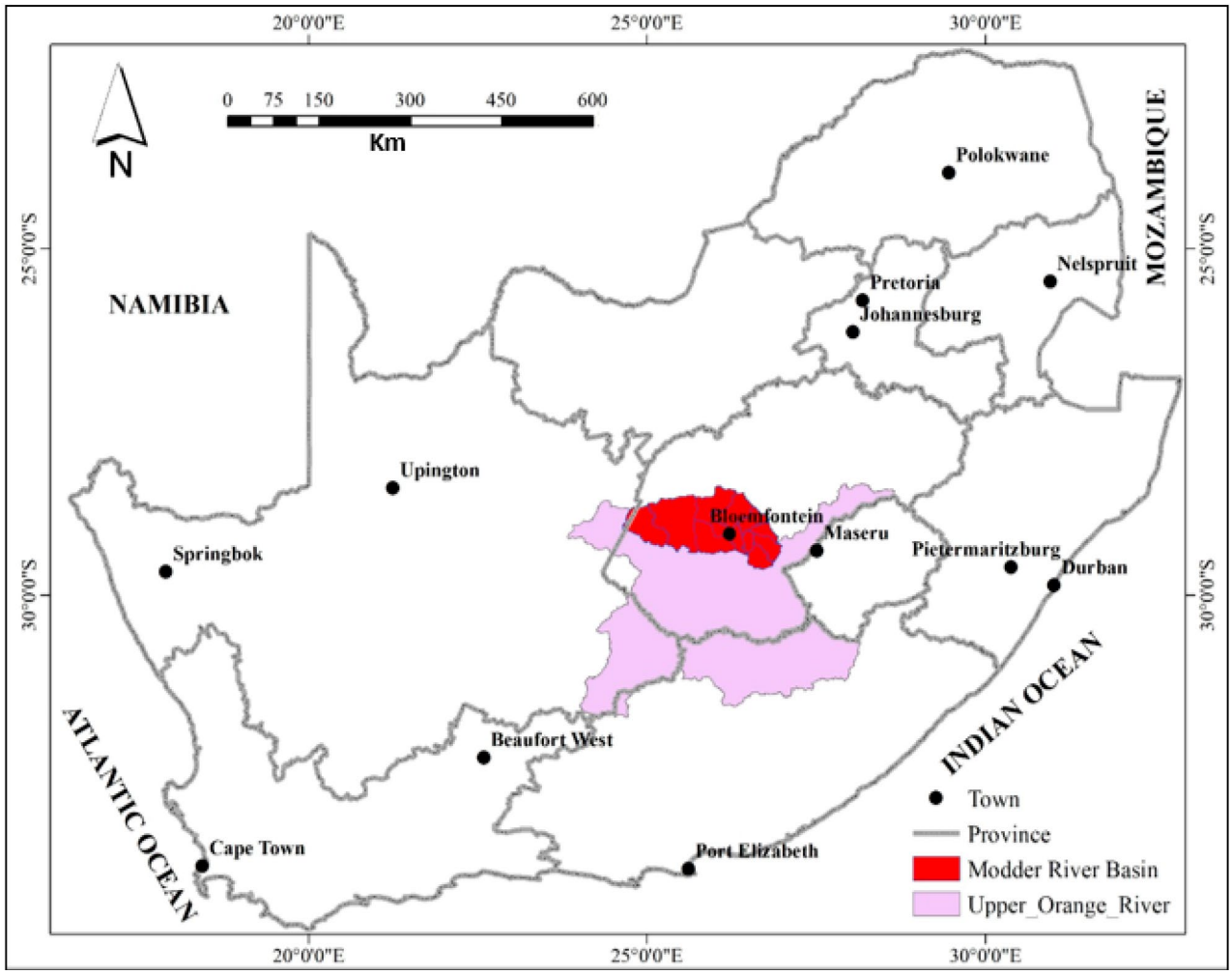


Figure 3.1 Location of the study area (Adopted from Oke and Alowo, 2021)

3.3 MATERIAL AND METHODS

3.3.1 Sample collection and handling

A total of 72 samples were collected during the spring (18), summer (18), winter (18) and autumn (18) seasons as shown in Figure 3.2. Sources of water targeted in this study include rivers (SWRS03, SWBS04, SWKOR05, SWMOR06 and SWKLM07); dams (SWMSO1, SWMD02, SWKD08, SWSD09, and SWRUSD10); wastewater influent (WWTP01I, WWTP02I, and WWTP03I); wastewater treatment effluent (WWTP01E, WWTP02E and WWTP03E) and treated drinking water (TWWRUS01 and TWWMSP02) as presented in Table 3.1. All water samples were collected in 750 mℓ mℓ cleaned bottles (Appendix A) using grab sampling throughout the project. At the site of sampling, the 750 mℓ mℓ cleaned bottles were labelled for identification convenience at the laboratory and 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 the collected samples were kept in a cooler box filled with ice cubes. After the sampling campaign, the samples were transported to the Biotechnology laboratory at the University of Free State. The samples were kept at 4ºC until analysis (Appendix A).

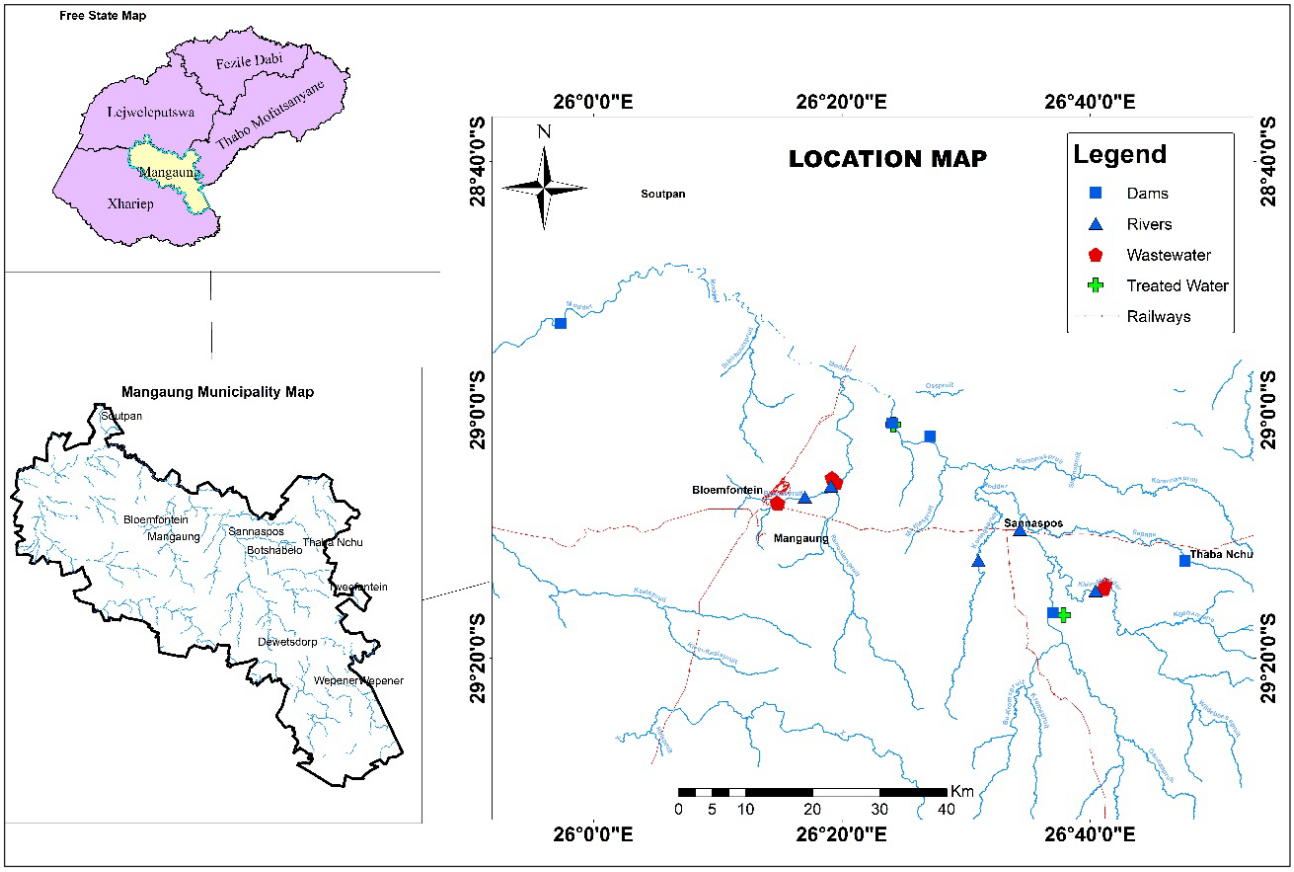


Figure 3.2 Sampling points within Modder River catchment

Table 3.1 Location of sampling points around the study area

Item	Sample ID	Coordinates		Elevation	Site description
		Latitude	Longitude		
			Dams		
1	SWMSO1	29° 01' 4.9" S	26° 24' 2.7" E	1 344 m	Collected at Maselspoort Dam
2	SWMD02	29° 02' 8.4" S	26° 27' 5.8" E	1 354 m	Collected at Mockes Dam
3	SWKD08	28° 53' 03" S	25° 57' 21 E	1 226 m	Collected at Krugersdrift Dam
4	SWSD09	29° 12' 10" S	26° 47' 38" E	1 460 m	Collected at Seralo Dam
5	SWRUSD10	29° 16' 20" S	26° 37' 00" E	1 370 m	Collected at Rustfontein Dam
			Rivers		
6	SWRS03	29° 06' 9.6" S	26° 19' 7.2" E	1 379 m	Collected at Renosterspruit River
7	SWBS04	29° 07' 2.4" S	26° 17' 1.5" E	1 390 m	Collected at Bloemspruit River
8	SWKOR05	29° 12' 8.3" S	26° 31' 0.4" E	1 334 m	Collected at Koringspruit River
9	SWMOR06	29° 09' 39.3" S	26° 34' 20.3" E	1 327 m	Collected at Modder River (Lekatlong)
10	SWKLM07	29° 14' 34.3" S	26° 40' 26.2" E	1 373 m	Collected at Kleinmodder River
			Wastewater treatment plants		
11	WWTP01I	29° 05' 29" S	26° 19' 12" E	1 386 m	Influent from Bloemfontein North East wastewater treatment plant (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
15	WWTP03I	29° 07' 27.4" S	26° 14' 46.7" E	1 558 m	Influent from Bloemspruit WWTP
16	WWTP03E	29° 07' 31.8" S	26° 14' 51.8" E	1 364 m	Effluent from Bloemspruit WWTP
			Treated drinking water		
17	TWWRUS01	29° 16' 31" S	26° 37' 51" E	1 366 m	Treated water from Rustfontein WWTP
18	TWWMSP02	29° 01' 10.3" S	26° 24' 9.2" E	1 339 m	Treated water from Maselspoort WWTP

3.3.2 Sample preparation and extraction

The chemical standards of high purity (> 98%) for acetaminophen, carbamazepine, ibuprofen, triclosan, atrazine, terbuthylazine, simazine, metolachlor, 17-alpha-ethinylestradiol, estradiol, progesterone and testosterone were procured from Sigma Aldrich (St Louis, Missouri, US), and Dr Ehrenstorfer (Augsburg, Germany). The HPLC grade methanol, ammonium hydroxide, acetonitrile, and formic acid were also purchased from Sigma Aldrich in St. Louis, MO, US. Moreover, ultra-pure water (99%) used during experiments were obtained from Millipore (Burlington, Massachusetts, US). The SPE cartridges (Strata C18, 6 mℓ) were obtained from Phenomenex (Torrance, Los Angeles, US). The stock solutions for individual standard were prepared in 1 µg/L methanol. After preparation, the stock solutions were stored in amber glass bottles at 4°C.

The methods of sample extraction for targeted compounds, namely acetaminophen, carbamazepine, ibuprofen, triclosan, atrazine, terbuthylazine, simazine, metolachlor, 17-alpha-ethinylestradiol, estradiol, progesterone and testosterone were modified from methods reported by Odendaal et al. (2015). Concisely, samples received were filtered through glass fibre filters to remove particulate matter. The ultra-pure water (99%), spiked with emerging contaminants' chemical standards, was used to improve SPE parameters. In order to identify the cartridge with the best recovery, various SPE cartridges with different sorbent characteristics were analysed. The SPE cartridges were equilibrated with 6 mℓ methanol and Milli-Q® water before extraction. Afterward, samples were loaded at a flow rate of approximately 6 mℓ per minute. The sample cartridges were cleaned with 6 mℓ purified water and dried for 20 minutes under vacuum. A 2 mℓ methanol was used to slowly elute the bound sample from the dried cartridges, followed by 2 mℓ Ethyl acetate. The eluant was vacuum dried until almost dry using a Thermo Scientific Savant Speedvac SC 210A concentrator (Waltham, Massachusetts, US). The extract was reconstituted in 1 mℓ purified water and 0.1% formic acid.

3.3.3 Sample analysis

A high-performance chromatography (Agilent 1200) connected to ABSCIEX 4000 QTRAP hybrid triple quadrupole ion trap mass spectrometer with a Shimadzu ultra-fast LC stack as a front end was used to analyse water samples. During the analysis, two types of analyses were carried out: screening for unknown analytes and targeted analyte quantitation. AB SCIEX Analyst 1.5 software was used for all data acquisition and processing.

3.3.3.1 Analysis of unknown analytes

On the instrument, a multiple reaction monitoring information-dependent acquisition-enhanced product ion MRM-IDA-EPI workflow was used to analyse the sample for unknown analytes. The instrument was used in triple quadrupole mode during a multiple reaction monitoring (MRM) scan type, where every ionised analyte (the precursor) eluting off the column was fragmented in the collision cell to produce fragment masses. A transition was made up of two masses: the precursor mass and one fragment mass. During an analysis cycle, the instrument jumps between different transitions in an MRM transition list, with each cycle typically lasting a few seconds. When a transition was detected, the instrument responded and a chromatogram was produced. When the instrument's response exceeded a certain threshold, it switched from triple quadrupole to ion trap mode. The precursor was fragmented in a subsequent analysis cycle, and all fragment masses were recorded; this is known as product ion formation. These fragments were gathered in the third quadrupole, which functioned as an ion trap. An enriched spectrum was created, with all fragments originating from a single precursor. These fragmentation profiles of an analyte were as unique to that analyte as fingerprints are to a human individual. Unknown analytes were identified with high certainty when used to query a spectral library. During these screening experiments, the instrument searched for the presence of a predefined list of analytes. These analytes were divided into two groups based on their ability to ionise. When each analyte was present, one MRM was used to trigger fragmentation and fragment collection. The obtained fragmentation profiles were

compared to a library of tandem mass spectrometry (MS/MS) fragmentation spectra from hundreds of compounds.

3.3.3.2 Quantitation of targeted analytes

Samples were analysed in both positive and negative ionisation mode. In positive ionisation mode, a 20 µℓ of each extracted sample was separated on a C18 (150 mm × 4.6 mm, Gemini NX, Phenomenex) column at a flow rate of 300 µℓ/min using a five-minutes gradient from 5% solvent A (H_2O / 0.1% formic acid) to 95% solvent B (methanol / 0.1% formic acid) with a total run time of nine minutes to allow for column re-equilibration. Eluting analytes were electrospray ionised in the TurboV ion source with a heater temperature of 500°C to evaporate excess solvent, 40 psi nebuliser gas, 40 psi heater gas, and a curtain gas of 15 psi. The ion spray voltage was set to 5 500 V. In negative ionisation mode, 20 µℓ of each extracted sample was separated on a C18 (150 mm×4.6 mm, Gemini NX, Phenomenex) column at a flow rate of 300 µℓ/min using 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. Eluting analytes were electrospray ionised in the TurboV ion source with a heater temperature of 500°C to evaporate excess solvent, 40 psi nebuliser gas, 40 psi heater gas, and a curtain gas of 15 psi. The ion spray voltage was set to -4 500V. The targeted analyses were carried out using multiple reaction monitoring transitions per analyte. The quantifier was the peak area on the chromatogram generated by the first and most sensitive transition, while the qualifier was the peak area generated by the second transition. The qualifier serves as an additional level of confirmation for the presence of the analyte' and the retention time for these two transitions must be the same. Detail information on the list of transitions is included in Appendix B of this report.

3.3.4 Method verification and quality control

To validate the performance of the instrument, selectivity, linearity, and quantification limits were determined. For selectivity, samples were submitted in batches with solvent blank runs between each sample analysed and quality control samples of known concentration interspersed. To evaluate linearity, a four-point calibration curve was generated for each analyte with concentrations ranging from 0.001 ppm to 1 ppm and a linear fit through the origin producing a correlation coefficient (r) value greater than 0.98. For each compound, the instrument limit of quantification was determined. The quantification limits for all analytes ranged from 0.0001 mg/ℓ to 0.1 mg/ℓ (Table 3.2). Laboratory blanks were used as quality control parameters to ensure that there was no external contamination, and all equipment were thoroughly cleaned.

Table 3.2 Measurement of linearity and limit of quantification

Analyte	Linearity (r^2) value	Limit of quantification (LOQ) (mg/ℓ)
Acetaminophen	0.99	0.0001
Simazine	0.99	0.01
Atrazine	0.99	0.0001
Terbuthylazine	0.99	0.0001
Carbamazepine	0.99	0.01
Metolachlor	0.99	0.0001
Testosterone	0.99	0.001
Progesterone	0.99	0.001
Ibuprofen	0.99	0.1
Estradiol	0.99	0.01
Triclosan	0.99	0.1
17-alpha-ethinyl-estradiol	0.99	0.1

3.3.5 Multivariate statistical analysis

The descriptive statistics of the data collected was performed on the Microsoft Excel software and presented in simple descriptive statistics (minimum, maximum, mean, and standard deviation). Furthermore, the interrelationships and the potential sources of emerging contaminants in water sources were determined by exploring different statistical methods such as Pearson's correlation coefficients, principal component analysis (PCA), and hierarchical cluster analysis.

3.3.6 Environmental risk assessment of emerging contaminants

3.3.6.1 Individual risk assessment of emerging contaminants

The ecological risk assessment for individual analytes in water sources within the Modder River catchment was assessed by the RQ method. This method was centred on acute and chronic toxicity studies which measures the toxic effects on the most sensitive organisms within the environments (Archer et al., 2017). The RQ value was determined by comparing the MEC and the PNEC using Equation 1:

$$RQ = \frac{MEC}{PNEC} \quad (1)$$

The PNEC was obtained by dividing the value of acute (short-term) or chronic (long-term) toxicity by an assessment factor. During the process of determining the predicted no-effect concentration of a particular emerging contaminant in water sources, the toxicity results were corrected by an assessment factor as shown in Equation 2. Acute toxicity was considered as the median lethal concentration (LC_{50}) or mean effective concentration (EC_{50}), in which case the assessment factor is 1 000. Chronic toxicity was given by NOEC, in which case the assessment factor can be 100, 50, 10 for algae, daphnids, and fish, respectively (Nannou et al., 2022; Vasilachi et al., 2021). After correction of the toxicity data by an assessment factor, the RQ was obtained by comparing the PNEC with MEC of the emerging contaminant of interest (Archer et al., 2017).

$$PNEC = \frac{EC_{50}}{AF} \; or \; PNEC = \frac{NOEC}{AF} \quad (2)$$

In this study, RQ represented the RQ calculated by EC_{50} or NOEC. The MEC represented the measured concentration. PNEC was the predicted no effect concentration which was the maximum concentration of a drug known to have no adverse effects on microorganisms or ecosystems in the environment. Risks were classified as either low ($RQ \leq 0.1$), medium ($0.1 < RQ < 1$), or high ($RQ \geq 1$) (Pei et al., 2022; Vasilachi et al., 2021). Published LC_{50}, EC_{50} and NOEC values for algae, daphnids and fish, which were used as toxicity endpoint in this study, are attached in Appendix C.

3.3.6.2 Mixture risk assessment of emerging contaminants

The study adopted a concentration addition method to assess mixture toxicity of emerging contaminants towards algae, daphnids, and fish. Concentration addition in this study was approximated by sums of RQ mixture (RQmix) values and sums of toxic units (TUsum) as proposed by Backhaus and Faust (2012), Backhaus and Karlsson (2014), Backhaus et al. (2013), Białk-Bielińska et al. (2022), Kienzler et al. (2019) and Maasz et al. (2019). The RQmix method uses the sum of RQs as an alternate for concentration addition-based predictions. The concentration addition assumes that the components of the mixture have the same molecular site of action and can be regarded as dilutions of one another. In this method, the RQs for individual substances obtained using Equation 3 were used to determine the environmental RQmix. The environmental risk mixture for emerging contaminants were summed up using Equation 3:

$$RQ_{mix} = \sum_{i=1}^{n} RQ_i \quad (3)$$

Summation of RQmix can be used as a screening-level approach (Backhaus and Faust, 2012). In this approach, when the RQmix was below 1 (RQmix < 1), it connoted a sufficient safety for the ecosystem. When the RQmix was above 1 (RQmix > 1), the environmental quality standard was exceeded (Backhaus and Faust, 2012; Backhaus and Karlsson, 2014; Bouzas-Monroy et al., 2022; Kienzler et al., 2019).

Additionally, when the risk mixture was above 1 (RQmix >1), the mixture risk assessment was refined in order to follow the conceptual foundation of concentration addition based on the TUsum applied for each trophic level. Afterward, the TUsum was treated using Equation 4 as if it was an estimate for an individual chemical.

$$TUsum = \max\left(TUsum_{algae}, TUsum_{invert}, TUsum_{fish}\right) \times AF$$

$$TUsum = \max\left(\sum_{i=1}^{n} \frac{MEC}{EC50_{algae}}, \sum_{i=1}^{n} \frac{MEC}{EC50_{invert}}, \sum_{i=1}^{n} \frac{MEC}{EC50_{fish}}\right) \times AF \quad (4)$$

The TUsum was the sum of toxic units. In this approach, the toxic unit was defined as the ratio between the MEC and a respective measured or predicted effect concentration (EC_{50}) for algae, daphnids and fish. The RQ of the mixture was defined as the highest TUsum between the three trophic levels such as algae, daphnids and fish (Backhaus and Faust, 2012; Backhaus and Karlsson, 2014; Finckh et al., 2022; Kienzler et al., 2019). The TUsum above 1 shows an ecosystem at risk, while a TUsum below 1 indicates sufficient safety for the ecosystem.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 INTRODUCTION

This chapter presents and discusses qualitative and quantitative data for emerging contaminants in rivers, dams, treated drinking water, wastewater influent and effluent. The quantitative data of targeted emerging contaminants covered all seasons of the year (spring, summer, autumn and winter). Their concentrations are given in milligram per litre. The results are presented and discussed in relation to their water sources.

4.2 SCREENING AND SELECTION OF EMERGING CONTAMINANTS

4.2.1 Screening of unknown analytes

Most studies on emerging contaminants in South Africa only monitor known or targeted compounds in the water environment, mostly in the Gauteng, and KwaZulu-Natal provinces (Archer et al., 2017; Madikizela et al., 2017; Mhuka et al., 2020). Information on the occurrence of emerging contaminants in the water environment is scarce in provinces such as the Free State. According to the NORMAN database, there are over 700 compounds classified as emerging pollutants (Ternes, 2006). As a result, Liquid chromatography-tandem mass spectrometry (LC-MS/MS) analysis was used to perform an initial screening of emerging contaminants found in rivers, dams, treated drinking water, and WWTPs. This study was critical in the Free State province because it provides information on a variety of unknown analytes that may also contribute to negative environmental health risks. Barack et al. (2019) echoed these sentiments, stating that qualitative screening aids in the identification of the majority of unexpected and unknown analytes that may also lead to adverse health risks in the environment. The initial screening results in this study revealed 32 analytes under pharmaceutical and pesticide groups as presented in Table 4.1. From these groups, 14 classes of emerging contaminants, including stimulants, NSAIDs, illicit drugs, lipid regulators, antiepileptics, antibiotics, antidepressants, antidiabetics, beta-blockers, antivirals, diuretics, herbicides, fungicides, and insecticides were detected (Figure 4.1). These analytes contaminated water sources as rivers > dams = effluent > influent > treated drinking water (Figure 4.2). Their detection rates are discussed in relation to their water sources.

Table 4.1 Qualitative non-target screening and occurrence (%) of emerging contaminants in the Modder River catchment

Analytes		Dams		Rivers		Influent		Effluent		Treated drinking water	
		N = 5	DF (%)	N = 5	DF (%)	N = 3	DF (%)	N = 3	DF (%)	N = 2	DF (%)
Pharmaceuticals											
NSAIDs	Diphenhydramine	–	–	4	80	–	–	–	–	–	–
	Orphenadrine	1	20	3	60	–	–	–	–	–	–
	Cyclicine	–	–	1	20	1	33	–	–	–	–
	Paracetamol	–	–	1	20	3	100	–	–	–	–
Antibiotics	Sulfamethoxazol	–	–	1	20	–	–	–	–	–	–
Antiepileptics	Carbamazepine	1	20	–	–	–	–	–	–	–	–
Antidiabetics	Metformin	4	80	2	40	2	66	1	33	–	–
Antidepressants	Sertaline	–	–	–	–	1	33	–	–	–	–
Lipid regulators	Bezafibrate	–	–	2	40	1	33	1	33	–	–
	Atorvastatin	–	–	–	–	–	–	1	33	–	–
Betablockers	Cimetidine	–	–	–	–	–	–	1	33	–	–
Antivirals	Lamivudine	–	–	1	20	–	–	–	–	–	–
Illicit drugs	THC-COOH	–	–	1	20	1	33	1	33	–	–
	Ecgoninemethylester	–	–	–	–	–	–	2	66	–	–
	Methamphetamine	–	–	3	60	2	66	2	66	–	–

Analytes		Dams		Rivers		Influent		Effluent		Treated drinking water	
		N = 5	DF (%)	N = 5	DF (%)	N = 3	DF (%)	N = 3	DF (%)	N = 2	DF (%)
Stimulants	Nicotine	5	100	2	40	–	–	1	33	1	50
	Amphetamine	–	–	–	–	2	66	2	66	–	–
	Ephedrine	3	60	3	60	2	66	3	100	–	–
	Theophylline	1	20	1	20	2	66	1	33	–	–
	Hordenine	–	–	1	20	1	33	–	–	–	–
Diuretics	Hydrochlorothiazide	–	–	–	–	2	66	1	33	–	–
					Pesticides						
Herbicides	Sebuthylazine	4	80	2	40	1	33	1	33	1	50
	Atrazine	4	80	1	20	1	33	–	–	2	100
	Terbuthylazine	5	100	3	60	1	33	3	100	2	100
	Metolachlor	2	40	2	40	–	–	1	33	1	50
	Simazine	–	–	2	40	–	–	1	33	–	–
	Tebuthiuron	–	–	–	–	–	–	–	–	1	50
Fungicides	Carbendazim	–	–	1	20	1	33	2	66	–	–
Insecticides	Diazinon	–	–	1	20	–	–	–	–	–	–
	Carbaril	–	–	–	–	–	–	1	33	–	–
	Imidacloprid	–	–	–	–	–	–	1	33	–	–
	Propoxur	–	–	–	–	–	–	1	33	–	–

Notation: n = number of samples; DF = detection frequency; THC-COOH = 11-nor-9-carboxy-Δ9-tetrahydrocannabinol

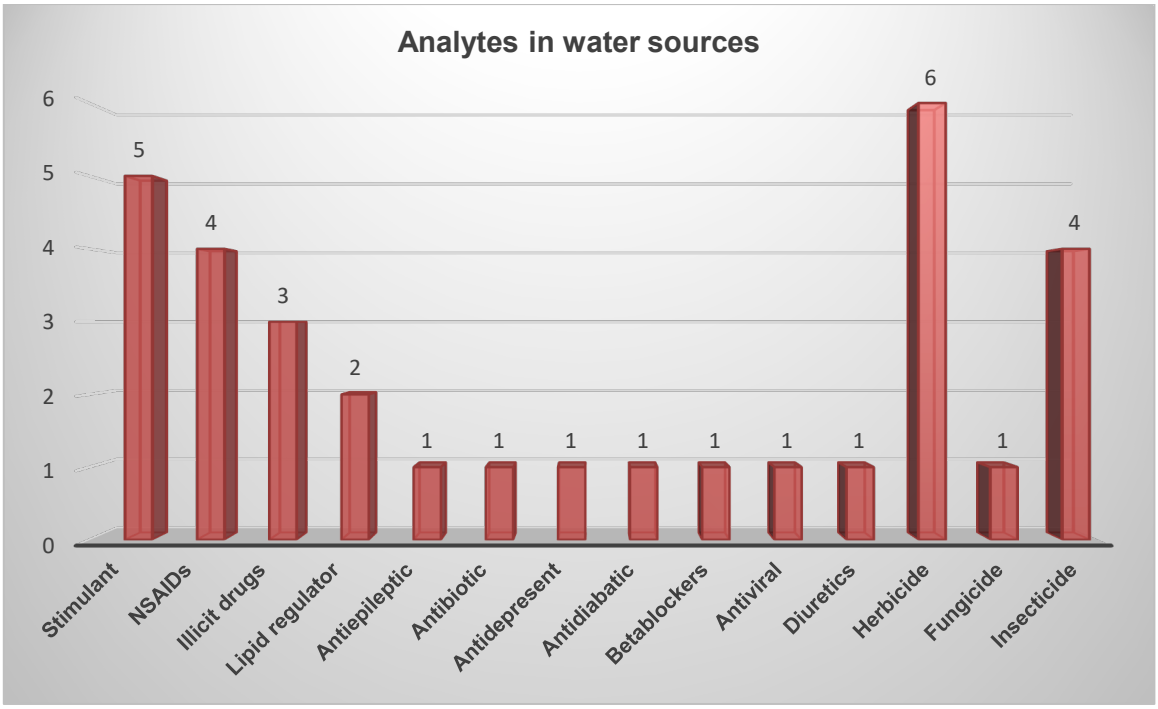


Figure 4.1 Screening of emerging contaminants in the Modder River catchment

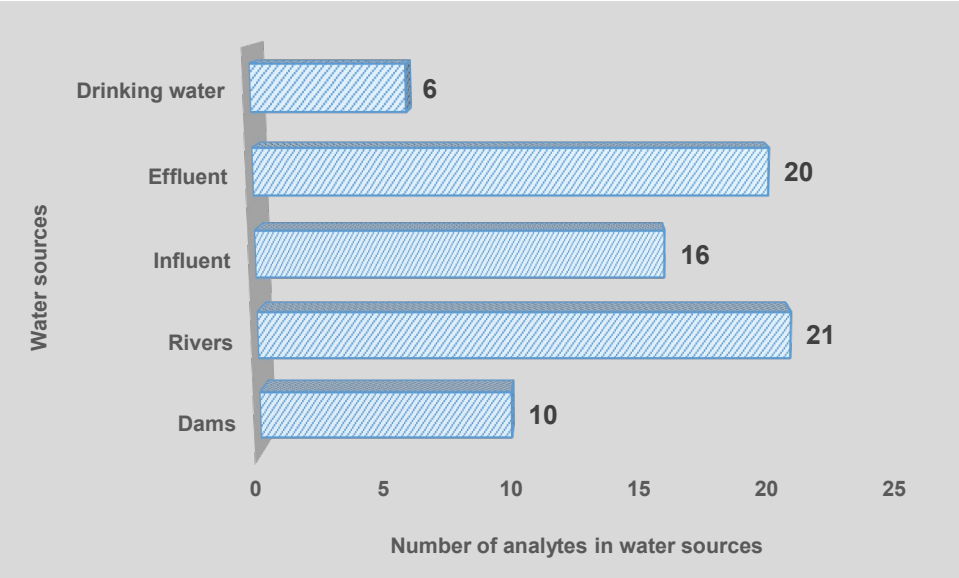


Figure 4.2 Detection of analytes per water source in the Modder River catchment

4.2.1.1 Screening of analytes in rivers

As shown in Table 4.1, two groups of emerging contaminants, namely pharmaceuticals and pesticides, were detected. This outcomes are comparable to the findings of Hollender et al. (2017), who reported pharmaceuticals and pesticides as the two groups regularly detected in the Rhine River. Under pharmaceuticals, NSAIDs, stimulants, illicit drugs, diabetics, lipid regulators, antibiotics, and antivirals were detected, while under pesticides herbicides, fungicides, and insecticides were detected. No other classes of emerging contaminants were found. From these two groups of emerging contaminants, NSAIDs, stimulants and herbicides were the utmost detected classes of analytes. A similar screening study for emerging pollutants in rivers in the Gauteng province of South Africa found NSAIDs to be one of the most detected classes of emerging contaminants (Rimayi et al., 2019). In this study, NSAIDs such as diphenhydramine was found in 80% of the river samples. Other analytes found in 60% of the river samples included an NSAID (orphenadrine); herbicide (terbuthylazine); stimulants (ephedrine); and an illicit drug (methamphetamine). Previous researches on emerging contaminants in aqueous environments found terbuthylazine in the Western Cape, South Africa (Curchod et al., 2020), ephedrine in South African surface waters (Archer et al., 2017), diphenhydramine, and methamphetamine in rivers in the Gauteng province (Rimayi et al., 2019). Although nicotine, paracetamol, and sulfamethoxazole were least detected in this study, their occurrence were also detected in many rivers of the world such as the Pienaars River in South Africa, the Madejera River in Tunisia, the Yamuna River in India, the Torrens River in Australia, the Piracicaba River in Brazil and the Trinity River, US (Wilkinson et al., 2022). The high detection of diphenhydramine could be attributed to the fact that it is an over-the-counter medication used to treat a variety of symptoms, including insomnia, fever, insect bites, and eczema. Herbicides are effective at controlling invasive plants in agricultural lands. Orphenadrine is a prescription medication that may help to alleviate the symptoms of Parkinson's disease, such as trembling. Methamphetamine is an illegal stimulant that can be smoked or injected into veins to keep people awake and is popular at parties. Ephedrine is primarily prescribed to treat asthma and nasal congestion. As a result, the presence of these compounds in more river samples suggests that community members use herbicides, medical drugs, and possibly abuse drugs. Agriculture is a major economic activity in the Free State province, so the detection of herbicides in rivers as a result of runoff from agricultural fields was expected. Additionally, because WWTPs are the carriers of the majority of emerging contaminants (Nannou et al., 2022; Wang et al., 2022), wastewater effluents discharged from these plants into streams may introduce emerging contaminants such as pharmaceuticals and pesticides. Some of the rivers run through townships and cities; hence, direct urination by community

members, runoff from clogged sewerage systems, or improper waste disposal may have introduced the detected drugs into the rivers.

4.2.1.2 Screening of analytes in dams

Emerging contaminants in dam samples showed different trends from those detected in river samples. As presented in Table 4.1, among the pharmaceuticals only stimulants, antidiabetics, NSAIDs, and antiepileptic drugs were detected, while herbicides were the only class of pesticides detected in dam samples. From these classes of emerging contaminants, the stimulant nicotine and the herbicide terbuthylazine were the most detected contaminants as they were detected in 100% of the collected dam samples. Herbicides (atrazine and sebuthylazine) and the antidiabetic (metformin) were also found in 80% of the collected samples. In the Hartbeespoort Dam, South Africa, triazine herbicides such as atrazine and terbuthylazine were also detected (Rimayi et al., 2018), which correspond to the outcomes of this study. Moreover, atrazine, terbuthylazine, and sebuthylazine were also found in surface water in Cape Town, South Africa (Ojemaye, 2020), Hungary surface water (Székács et al., 2015), and the South Fork Zumbro River watershed in the US (Fairbairn et al., 2015). Another study found the antidiabetic metformin in surface water around the Gauteng province in South Africa (Rimayi et al., 2019). Various researchers have discovered stimulants such as nicotine in South African surface water (Matongo et al., 2015; Rimayi et al., 2019; Wood et al., 2015). The use of herbicides to control aquatic weeds in dams may have contributed to their concentrations in this study. Herbicides, according to Pandey et al. (2019), can be used to control invasive plants in water. The detected herbicides could also be a result of runoff from nearby agricultural fields. The application of herbicides to manage or kill weeds in a well-maintained large open turf witnessed near some of the dams that serve as conference centres may be the source of herbicides found in the dam water. Rimayi et al. (2018) mentioned that most of the triazine herbicides, such as atrazine and terbuthylazine, are used or applied to kill unwanted grasses or weeds. Furthermore, nicotine is a stimulant and anxiolytic that can be used recreationally, whereas metformin is used to treat high blood sugar levels. During the sampling campaign, it was discovered that the majority of the dams serve as conference and resort centres with lodging houses that use septic tanks. As a result, septic tanks may introduce pollutants such as nicotine and metformin, particularly during the rainy season when the water table rises. Improper disposal of medical drugs by visitors may also contribute to traces of these contaminants. Moreover, effluents from WWTPs are mostly released in nearby streams. Therefore, rivers that discharge their water in these dams may introduce traces of these compounds in dams.

4.2.1.3 Screening of analytes in wastewater treatment plants

Pharmaceuticals such as stimulants, NSAIDs, illicit drugs, diuretics, antidiabetics, antidepressants, and lipid regulators were detected In influent samples. Pesticides such as herbicides and fungicides were detected in influent samples as presented in Table 4.1. It was only paracetamol that was detected in 100% of the collected influent samples. Paracetamol is a pain reliever and fever reducer that is widely available in supermarkets. The detection of paracetamol in all collected samples may be attributed to the fact that the selected WWTPs are located in the city where the use of drugs is expected to be high. According to Naji et al. (2017), detection of medical drugs is expected to be high in urban areas as the use of drugs is high, which support the current findings. The detection of paracetamol in wastewater influents was also reported by other researchers in Oslo, Norway (Thomas et al., 2007); Eastern Cape province, South Africa (Ademoyegun, 2017); North West province, South Africa (Kanama et al., 2018); eThekwini, South Africa (Späth et al., 2021) and in Vidyaranyapuram, India (Shipingana et al., 2022). Most of the WWTPs in this region receive wastewater from domestic, industrial areas and hospitals. Human excretion and flushing of expired or unused medical drugs may have contributed to the high detection of these compounds in the Free State region's wastewater influents. This also demonstrate high reliance of these drugs within the study area. Furthermore, wastewater from factories and hospitals may also be attributed as a source of this compound.

Moreover, stimulants, illicit drugs, NSAIDs, lipid regulators, antidiabetics, beta-blockers, and diuretics were the pharmaceutical classes detected in effluent samples while herbicides, fungicides and insecticides were the detected classes of pesticides. From these classes of contaminants, herbicide (terbuthylazine) and stimulant (ephedrine) were detected in 100% of the collected samples. In KwaZulu-Natal, South Africa (Kunene, 2019), and in eThekwini, South Africa (Späth et al., 2021), terbuthylazine was also detected in effluent samples. The presence of these compounds in effluent samples demonstrates that traditional WWTPs are incapable of completely removing them. Montagner et al. (2019), also reported that WWTPs in São Paulo State, Brazil were unable to eliminate most of the emerging contaminants. This was also confirmed by other researchers (Cardini et al., 2021; Grandclément et al., 2017). The WWTPs chosen in this study were not built with the intention of removing emerging contaminants received from domestic, industrial, and hospital wastewater. All of the WWTPs use primary treatment which involves removal of suspended solids by flotation, settling, and screening mechanism and secondary treatment for removal of remaining organic matter via trickling filters utilising bacteria-coated stones and bacteria-activated sludge. Therefore, it can be said that the processes employed in these WWTPs are unable to remove some of the emerging contaminants and need improvement. In order to limit emerging contaminant pollution, according to Morin-Crini et al. (2022), tertiary treatment systems should be added in WWTPs.

In South Africa, wastewater effluent is typically discharged into nearby streams, introducing pollutants into the aqueous environment. As a result, prioritising these chemicals in pollution monitoring studies is critical. Not only will this protect aquatic life, but it will also preserve or sustain South Africa's water resources. Moreover, wastewater effluent in this study were found to have more analytes than influent samples as presented in Table 4.2. The occurrence of high concentrations of some emerging contaminants in effluent than influent was also reported by other authors (Köck-Schulmeyer et al., 2013; Ofrydopoulou et al., 2021). According to Kortesmäki et al. (2020), non-removal and the present of higher concentration of some analytes in effluent than influent may be attributed to factors such as wastewater composition, structure of the analytes and conversion of the conjugated metabolites to the parent compound by enzymatic processes in the WWTPs. Their high detection in effluent than influent may also be influenced by factors such as working faults of the WWTPs and the current electricity load shedding problems in the country.

Table 4.2 Composition of influent and effluent samples.

Wastewater influent	Wastewater effluent
Cyclicine	Metformin
Paracetamol	Bezafibrate
Metformin	Atorvastin
Bezafibrate	Cimetidine
THC-COOH	THC-COOH
Methamphetamine	Ecgoninemethylester
Amphetamine	Methamphetamine
Ephedrine	Nicotine
Theophylline	Amphetamine
Hordenite	Ephedrine
Hydrochlorothiazine	Theophylline
Sebuthylazine	Hydrochlorothiazine
Atrazine	Sebuthylazine
Terbuthylazine	Terbuthylazine
Carbendazim	Metolachlor
	Simazine
	Carbendazim
	Carbaril
	Imidacloprid
	Propoxur

Notation: THC-COOH = 11-nor-9-carboxy-Δ9-tetrahydrocannabinol

4.2.1.4 Screening of analytes in treated drinking water

In treated drinking water, one class of pharmaceuticals (stimulants) and one class of pesticides (herbicides) were detected as presented in Table 4.1. Herbicides atrazine and terbuthylazine were detected in 100% of the collected treated drinking water samples. Analytes such as tebuthiuron, metolachlor, sebuthylazine, and nicotine were detected in less than 60% of the collected samples. The outcomes of this study are comparable to the findings of the screening study conducted by Odendaal et al. (2015) to investigate contaminants of emerging concern in drinking water in South Africa. They detected terbuthylazine in 100% of the samples collected, which is similar to the findings of this study. Caldas et al. (2019) reported that atrazine was the most detected in their monitoring study of pesticides in drinking water in Southern Brazil. Furthermore, in a nationwide survey of emerging pollutants in Brazilian waters, atrazine was detected in 75% of the collected treated drinking water samples, which is less than the current findings (Machado et al., 2016). The use of herbicides to control weeds in dams used as a source of water in WWTPs may be the source of these herbicides. Rivers that discharge their water into these dams may contain traces of herbicides as they mostly receive wastewater effluents. The high detection of atrazine in water sources may also be connected to their nature of being persistent. Almberg et al. (2018) reported that herbicides such as atrazine are persistent in soil and their transport to water, making it the most commonly detected pesticide in water sources. Moreover, the presence of pesticides in treated drinking water revealed that the methods used in selected WWTPs are incapable of removing these compounds which include abstraction, macro/micro sieving, coagulation, flocculation, sedimentation, filtration, and disinfection. Long-term exposure to these herbicides may have negative consequences for water users in the Free State province. These pesticides should be prioritised in treatment processes in order to find the best methods for their removal. In addition, pollution monitoring and toxicity studies should prioritise them and determine whether their concentrations have any negative effects on water consumers.

4.2.2 Selection of target analytes

Twelve organic contaminants were targeted for analysis and monitoring using LC-MS. These contaminants were pharmaceuticals (acetaminophen, ibuprofen, and carbamazepine), PCPs (triclosan), herbicides (atrazine, simazine, terbuthylazine, and metolachlor), and steroid hormones (17-alpha-ethinylestradiol, estradiol, progesterone, testosterone). They were chosen primarily for their frequency of detection in water sources, availability of reagents, and reported potential implications for the aquatic environment and human health. As the targeted steroid and hormonal compounds were not detected in the screening of results, the motivation for their selection was based on the fact that they are endocrine-disruptor compounds, their frequent existence in water sources (Yazdan et al., 2022) and partial removal in WWTPs (Volker et al., 2019).

4.3 CONCENTRATION OF EMERGING CONTAMINANTS IN THE MODDER RIVER CATCHMENT

4.3.1 Emerging contaminants in rivers

4.3.1.1 Pharmaceuticals and personal care products

Among the PPCPs, acetaminophen, carbamazepine, ibuprofen, and triclosan were the only contaminants detected in rivers within the Modder River catchment (Table 4.3). During spring seasons their concentrations ranged from < LOQ to 0.15 mg/ℓ, < LOQ to 0.88 mg/ℓ, < LOQ to 3.44 mg/ℓ and < LOQ to 0.09 mg/ℓ, respectively. Their respective average concentrations were 0.12 mg/ℓ, 0.57 mg/ℓ, 2.22 mg/ℓ and < LOQ. In the summer season, their concentrations were < LOQ, 0.40 to 1.43 mg/ℓ, 0.38 to 2.11 mg/ℓ, and < LOQ, respectively. Their average concentrations were < LOQ, 0.7 mg/ℓ, 1.16 mg/ℓ and < LOQ, respectively. During the autumn season they showed concentrations ranging from < LOQ, < LOQ to 0.32 mg/ℓ, < LOQ to 2.26 mg/ℓ and < LOQ, with average concentrations of < LOQ, 0.25 mg/ℓ, 0.92 mg/ℓ and < LOQ, respectively. Moreover, the winter season showed concentrations of these contaminants as < LOQ to 0.03 mg/ℓ, < LOQ to 0.36 mg/ℓ, < LOQ to 0.60 mg/ℓ, and < LOQ with average concentrations of < LOQ, 0.31 mg/ℓ, 2.20 mg/ℓ and < LOQ, respectively.

Among the PPCPs, ibuprofen had the highest average concentrations, followed by carbamazepine in all seasons. Their average concentrations were in the range of ibuprofen > carbamazepine > acetaminophen > triclosan. Seasonally, the autumn season recorded the highest mean concentration of PPCPs and they ranged as spring > winter > summer > autumn. The concentrations of ibuprofen were higher than those reported in the Mississippi River, US (Zhang et al., 2006), Hanoi in Vietnam (Tran et al., 2014), Chongqing in China (Yan et al., 2015), the Msunduzi River in South Africa (Agunbiade and Moodley, 2016), and the Apies River in South Africa (Mhuka et al., 2020). Moreover, similar cases of the occurrence of carbamazepine in rivers were also reported by other researchers (Archer et al., 2017; Glassmeyer et al., 2017; Hossain et al., 2018; Vumazonke et al., 2020; Wanda et al., 2017; Wilkinson et al., 2022). The majority of the rivers in this study run through townships, the city centre, and agricultural farms. Illegal waste dumping near rivers was visible in the majority of the townships. Ibuprofen is used to treat pain and fever, which are common illnesses in many communities (Ekinci et al., 2020). Given that ibuprofen is used to treat a variety of diseases and is available without a prescription, it was not surprising that it was the leading pollutant in river water. The presence of carbamazepine as a prescription drug may have been influenced by the presence of patients suffering from seizures and bipolar disorder in those areas (Nannou et al., 2022). Waste dumped near rivers that run through these settlements may contain unwanted or expired medical drugs such as ibuprofen and carbamazepine, introducing these contaminants into the rivers. Some of the emerging contaminants may be spread into water bodies by WWTPs in the city and other townships that discharge their effluents into nearby streams. Furthermore, farmhouses equipped with septic tanks and latrine toilets may have an impact on the concentration of these pharmaceutical compounds in nearby rivers. Wastewater effluents discharged in rivers may also introduce traces of PPCPs.

4.3.1.2 Pesticides

As presented in Table 4.3, the groups of pesticides detected in rivers were herbicides, namely atrazine, metolachlor, simazine and terbuthylazine. These herbicide concentrations in the spring season were recorded as 0.002 to 0.06, 0.003 to 0.03, < LOQ to 5.67, and 0.007 to 0.21 mg/ℓ, with average concentrations of 0.03, 0.01, 1.82 and 0.06 mg/ℓ, respectively. In the summer season, their concentrations were 0.03 to 0.11, 0.02 to 0.12, 0.10 to 3.22 and 0.03 to 0.14 mg/ℓ, with average concentrations of 0.05, 0.06, 1.04 and 0.08 mg/ℓ, respectively. In the autumn season, their concentrations were 0.0014 to 0.03, 0.001 to 0.03, < LOQ to 0.91 and 0.002 to 0.03 mg/ℓ, with average concentrations of 0.69, 0.02, 0.69, and 0.01 mg/ℓ, respectively. Moreover, the winter season had concentrations ranging from 0.002 to 0.32, < LOQ to 0.004, < LOQ to 0.61 and 0.001 to 0.16 mg/ℓ, with average concentrations of 0.08, 0.12, 0.37 and 0.05 mg/ℓ, respectively.

Overall in rivers, the herbicide simazine had the highest average concentrations, followed by atrazine. Their overall average concentrations ranged as simazine > atrazine > metolachlor > terbuthylazine. Seasonally, their highest sum of concentrations were recorded during the spring season and their trend was spring > autumn > summer > winter. The occurrences of herbicides in surface water such as rivers were also reported by other researchers in Kabwe, Zambia (Sorensen et al., 2015), metolachlor in the Samambaia River basin, Brazil (Correia et al., 2020), terbuthylazine in the Western Cape, South Africa (Curchod et al., 2020). The presence of herbicides in river water was not surprising in this study area, particularly trazines, such as atrazine, simazine, and terbuthylazine, which were the leading herbicides in river samples. Trazine herbicides are considered to be effective and low-cost compounds that are primarily used in crop production (Wang et al., 2022). The agricultural sector is the backbone of the economy of the Free State province. It is known for producing a lot of maize, soybeans, wheat, sorghum, sunflower, potatoes, groundnuts, and wool. All of these activities necessitate the use of weed control herbicides before, during, and after the production season. Moreover, Bloemfontein is the only significant development in the Modder River catchment (Pretorius et al., 2005). The city of Bloemfontein is characterised by well-developed roads, public parks, industrial areas, and golf clubs. With all these noticeable areas, significant amounts of herbicides are applied to control weeds in paved areas, parks, golf courts, roadsides, buildings, and industrial areas. Runoff from agricultural fields,

roads, public squares, golf courses, and industrial areas may increase herbicide concentrations in nearby streams.

4.3.1.3 Steroid hormones

As presented in Table 4.3, 17-alpha-ethinylestradiol, estradiol, progesterone, and testosterones were the only steroids detected. They were detected at concentrations ranging as 0.09 to 25 mg/ℓ, < LOQ to 0.08 mg/ℓ, < LOQ, and < LOQ, with average concentrations of 12.18 mg/ℓ, 0.07 mg/ℓ, < LOQ, and < LOQ in the spring season, respectively. During the summer season, their concentrations ranged from 1.08 to 14.5 mg/ℓ, < LOQ, < LOQ and < LOQ, respectively. During the autumn season, their average concentrations were < LOQ to 53.80 mg/ℓ, < LOQ, < LOQ, and < LOQ, respectively, while their respective average concentrations were 31.55 mg/ℓ, < LOQ, < LOQ and < LOQ. Moreover, in the winter season, the average concentrations ranged from 0.28 to 23.50 mg/ℓ, < LOQ, < LOQ and < LOQ, with an average concentration of 12.34 mg/ℓ, < LOQ, < LOQ and < LOQ, respectively.

The concentration of 17-alpha-ethinylestradiol was the highest in all seasons. Its most notable concentration was recorded in the autumn season. Their overall average concentrations were 17-alpha-ethinylestradiol > Estradiol = progesterone = testosterone. They recorded the highest average concentration in the autumn seasons and their trend was autumn > winter > spring > winter. When compared to other studies, the concentration of 17-alpha-ethinylestradiol was higher than the one reported in Lagos in Nigeria (Olarinmoye et al., 2016), and in China (Lin et al., 2020). The presence of steroid hormones in the rivers studied may have been influenced by WWTPs that discharge effluent into 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 likely to be contaminated by these compounds as a results of illegal dumping of household wastes (e.g. medical drugs) near the rivers. According to Forghani et al. (2018), estradiol is a natural estrogenic hormone released by humans and livestock. Animals that drink the water from these rivers, as well as people who visit them, may end-up introducing these hormones into the river water through open urination and defecation. In summation, the concentration of the emerging contaminants were highest in the autumn season, which shows that the autumn season was the largest contributor to river pollution in the Modder River catchment (Figure 4.3). It was mostly contributed by 17-alpha-ethinylestradiol, simazine and ibuprofen, which make them contaminants of concern in this catchment.

Table 4.3 Occurrence of emerging contaminants in rivers

Compound	Concentration (mg/ℓ)											
	Spring (n = 5)			Summer (n = 5)			Autumn (n = 5)			Winter (n = 5)		
	DF	Min-Max	Mean	DF	Min-Max	Mean	DF	Min-Max	Mean	DF	Min-Max	Mean
Pharmaceuticals and personal care products												
Acetaminophen	2	< LOQ to 0.15	0.12	0	< LOQ	-	0	< LOQ	-	1	< LOQ to 0.03	-
Carbamazepine	4	< LOQ to 0.68	0.57	4	0.40 to 1.43	0.7	4	< LOQ to 0.32	0.25	4	< LOQ to 0.36	0.31
Ibuprofen	4	< LOQ to 3.44	2.22	4	0.38 to 2.11	1.16	3	< LOQ to 2.26	0.92	4	< LOQ to 0.60	2.20
Triclosan	1	< LOQ to 0.09	-	0	< LOQ	-	0	< LOQ	-	0	-	-
Pesticides (herbicides)												
Atrazine	5	0.002 to 0.06	0.03	5	0.03 to 0.11	0.05	5	0.0014 to 0.03	0.69	5	0.002 to 0.32	0.08
Metolachlor	5	0.003 to 0.03	0.01	5	0.02 to 0.12	0.06	5	0.0007 to 0.03	0.02	4	< LOQ to 0.004	0.12
Simazine	4	< LOQ to 5.67	1.82	4	0.10 to 3.22	1.04	2	< LOQ to 0.91	0.69	2	< LOQ to 0.61	0.37
Terbuthylazine	5	0.007 to 0.21	0.06	5	0.03 to 0.14	0.08	5	0.0016 to 0.03	0.01	5	0.01 to 0.16	0.05
Endocrine-disrupting compound (steroid hormones)												
17-alpha-ethinylestradiol	5	0.09-25	12.18	5	1.08 to 14.5	7.79	4	< LOQ to 53.80	31.55	5	0.28-23.5	12.34
Estradiol	2	< LOQ to 0.08	0.07	0	< LOQ	-	0	< LOQ	-	0	-	-
Progesterone	0	< LOQ	-	0	< LOQ	-	0	< LOQ	-	0	-	-
Testosterone	0	< LOQ	-	0	< LOQ	-	0	< LOQ	-	0	-	-

Notation: LOQ = limit of quantification, DF = detection frequency, n = number of samples, min = minimum concentration, max = maximum concentration, mg/ℓ = milligram per litre

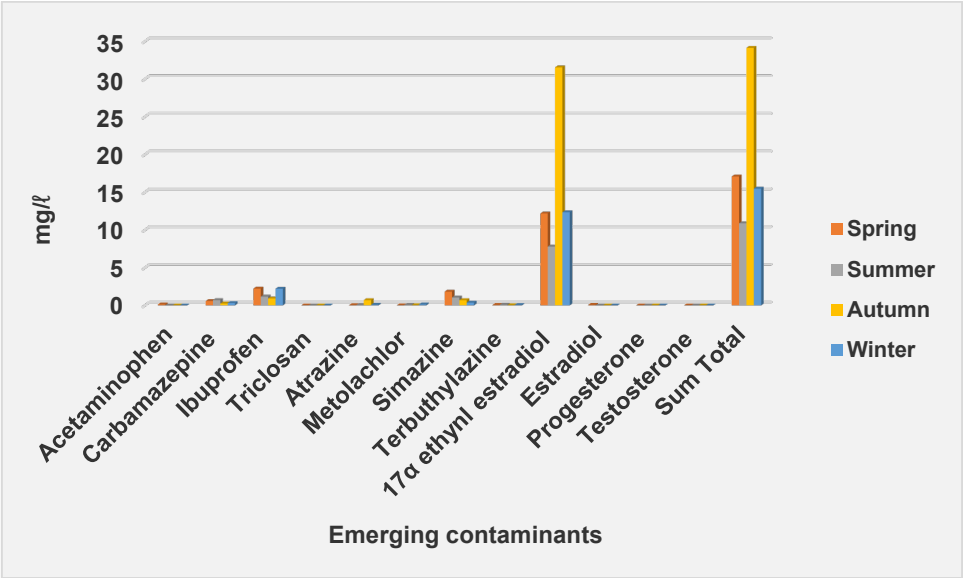


Figure 4.3 Occurrence of emerging contaminants in rivers within the Modder River catchment

4.3.2 Emerging contaminants in dams

4.3.2.1 Pharmaceuticals and personal care products

The concentrations of acetaminophen, carbamazepine, ibuprofen, and triclosan in dams are presented in Table 4.4. Their respective concentrations in the spring season ranged from < LOQ to 0.12 mg/ℓ (0.07 mg/ℓ), 0.01 to 0.63 mg/ℓ (0.29 mg/ℓ), < LOQ to 0.81 mg/ℓ (0.3 mg/ℓ) and < LOQ, respectively. In the summer season, they were detected as < LOQ, 0.01 to 0.21 mg/ℓ (0.12 mg/ℓ), < LOQ and < LOQ, respectively. During the autumn season, they were detected as < LOQ to 0.09 mg/ℓ (< LOQ), 0.03 to 0.19 mg/ℓ (0.08 mg/ℓ), < LOQ to

0.03 mg/ℓ (0.02 mg/ℓ) and < LOQ, respectively. Moreover, their respective concentrations in the winter season were detected as < LOQ, < LOQ to 0.08 mg/ℓ (0.06 mg/ℓ), < LOQ to 0.10 mg/ℓ (< LOQ) and < LOQ.

The PPCPs recorded the highest average concentration in the spring seasons and their trend was spring > summer > autumn > winter. The concentration of carbamazepine was found to be the highest in all seasons. Their overall average concentrations ranged as carbamazepine > ibuprofen > acetaminophen > triclosan. The presence of carbamazepine as a leading contaminant in dam samples indicates that carbamazepine is a commonly used drug in and around the Modder River catchment. Anticonvulsants such as carbamazepine is regarded as a prescription drug that works in the brain and nervous system to control seizures, pain and bipolar disorder (Kanama et al., 2018; Nannou et al., 2022). The concentrations of ibuprofen in dams can be explained by the fact that analgesics and non-steroid anti-inflammatory drugs are available without a prescription and are used to treat pain and inflammation, which are symptoms of a variety of diseases (Nannou et al., 2022). Ibuprofen is a medication that is used to manage and treat inflammatory diseases, rheumatoid arthritis, pain, fever, and dysmenorrhea (Ekinci et al., 2020). Some of the dams in this study are close to settlements, open to the public, and serve as resorts, conference centres, and fishing spots. People who visit these resorts or live near these dams may have urinated near the dams or improperly disposed of these drugs. Illegal dumping of household waste containing unused or unfinished medication, as well as sewage runoff from nearby communities observed during a site visit, may have contributed to the concentration of these compounds. Furthermore, lodging houses and some farmhouses with septic and latrine toilets near some of the dams may have leaked these contaminants.

4.3.2.2 Pesticides

As presented in Table 4.4, the concentrations of targeted herbicides such as atrazine, metolachlor, simazine, and terbuthylazine in dams were recorded as 0.008 to 0.03 mg/ℓ (0.01 mg/ℓ), 0.002 to 0.03 mg/ℓ (0.01 mg/ℓ), < LOQ to 0.20 mg/ℓ, and 0.01 to 0.06 mg/ℓ (0.03 mg/ℓ) in the spring season, respectively. During the summer season, their respective concentrations were recorded as 0.02 to 0.04 mg/ℓ (0.03 mg/ℓ), 0.01 to 0.04 mg/ℓ (0.03 mg/ℓ), < LOQ to 0.24 mg/ℓ (0.13 mg/ℓ) and 0.02 to 0.08 mg/ℓ (0.05 mg/ℓ). During the autumn season, their respective concentrations were recorded as 0.003 to 0.02 mg/ℓ (0.01 mg/ℓ), 0.01 to 0.02 mg/ℓ (0.01 mg/ℓ), < LOQ to 0.29 mg/ℓ (0.12 mg/ℓ) and 0.003 to 0.03 mg/ℓ (0.01 mg/ℓ). Moreover, their concentrations in the winter season were recorded as 0.01 to 0.08 mg/ℓ (0.04 mg/ℓ), 0.003 to 0.02 mg/ℓ (0.04 mg/ℓ), < LOQ to 0.23 mg/ℓ (0.14 mg/ℓ) and 0.01 to 0.03 mg/ℓ (0.02 mg/ℓ), respectively.

The targeted pesticides recorded the highest average concentration in the summer season. Their sum seasonal concentrations were trending as summer > winter > autumn > spring. Among the detected herbicides, simazine had the highest average concentrations in all seasons. Their overall average concentrations ranged from simazine > terbuthylazine > atrazine > metolachlor. The occurrence of herbicides such as atrazine and terbuthylazine in dams were also reported in the Hartbeespoort Dam in South Africa (Rimayi et al., 2018). High concentrations of pesticides in dams may be attributed to the fact that the dams are located nearby agricultural fields (of which maize crops is common), which necessitate the application of these herbicides to kill weeds. Substantial quantities are also utilised in forests, industrial areas, public areas, parks, golf courts, and sports grounds for weed control and maintenance. Runoff from these areas may introduce simazine, terbuthylazine, atrazine, and metolachlor in dams. Pandey et al. (2019) also stated that these herbicides can be used to control invasive plants in water. As a result, the presence of these herbicides in dams could be attributed to their use to control aquatic weeds such as algae and submerged weeds.

4.3.2.3 Steroid hormones

Table 4.4 presents the concentrations of 17-alpha-ethinylestradiol, estradiol, progesterone and testosterone detected in dams within the Modder River catchment. In all seasons, only 17-alpha-ethinylestradiol was detected, while the concentrations of other contaminants were below the limit of quantifications (< LOQ). Its concentrations ranged from 0.28 to 6.13 mg/ℓ (3.67 mg/ℓ), 1.83 to 3.40 mg/ℓ (1.83 mg/ℓ), 1.30 to 14.80 mg/ℓ

(6.90 mg/ℓ) and 0.39 to 4.62 mg/ℓ (2.78 mg/ℓ) during the spring, summer, autumn and winter seasons. The most notable concentration of steroid hormones was recorded in the autumn season. Their sum seasonal concentrations were trending as autumn > spring > winter > summer. Among the detected steroid hormones, 17-alpha-ethinylestradiol had the utmost concentrations in all seasons. The overall average concentrations of steroid hormones varied as 17-alpha-ethinylestradiol > estradiol = progesterone = testosterone.

In the Joao Goulart catchments in Brazil (Pivetta and Gastaldini, 2019), and in Nigerian river catchments (Ogunbanwo et al., 2020), the concentrations of 17-alpha-ethinylestradiol were lower than those detected in the Modder River catchment. The 17-alpha-ethinylestradiol, a synthetic estrogenic compound, is commonly used as the active ingredient in many oral contraceptives and postmenopausal hormone therapy (Kanama et al., 2018). 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. Some steroid hormones may be leaked into fresh water from septic tanks in some farmhouses and dams with resorts. Furthermore, rivers that receive wastewater effluents and discharge their water to these dams may introduce steroids and hormones into the dams. In summation, the highest level of the emerging contaminants in dams was recorded in the autumn season (Figure 4.4). It was mostly contributed by 17-alpha-ethinylestradiol, simazine and carbamazepine, which make the, contaminants of concern in this catchment.

Table 4.4 Occurrence of emerging contaminants in dams

Compound	Concentration (mg/ℓ)											
	Spring (n = 5)			Summer (n = 5)			Autumn (n = 5)			Winter (n = 5)		
	DF	Min-Max	Mean	DF	Min-Max	Mean	DF	Min-Max	Mean	DF	Min-Max	Mean
Pharmaceuticals and personal care products												
Acetaminophen	2	< LOQ to 0.12	0.07	0	< LOQ	-	1	< LOQ	-	0	< LOQ	-
Carbamazepine	5	0.01 to 0.63	0.29	5	0.01 to 0.21	0.12	5	0.03 to 0.19	0.08	4	< LOQ to 0.08	0.06
Ibuprofen	3	< LOQ to 0.81	0.3	0	< LOQ	-	2	< LOQ to 0.03	0.02	1	< LOQ to 0.10	-
Triclosan	0	< LOQ	-	0	< LOQ	-	0	< LOQ	-	0	< LOQ	-
Pesticides (herbicides)												
Atrazine	5	0.008 to 0.03	0.01	5	0.02 to 0.04	0.03	5	0.003 to 0.02	0.01	5	0.01 to 0.08	0.04
Metolachlor	5	0.002 to 0.03	0.01	5	0.01 to 0.04	0.03	5	0.01 to 0.02	0.01	5	0.003 to 0.02	0.01
Simazine	4	< LOQ to 0.20	0.09	4	< LOQ to 0.24	0.13	4	< LOQ to 0.29	0.12	2	< LOQ to 0.23	0.14
Terbuthylazine	5	0.01 to 0.06	0.03	5	0.02 to 0.08	0.05	5	0.003 to 0.03	0.01	5	0.01 to 0.03	0.02
Endocrine-disrupting compound (steroid hormones)												
17-alpha-ethinylestradiol	5	0.278 to 6.13	3.67	5	0.25 to 3.40	1.83	5	1.30 to 14.80	6.90	5	0.39 to 4.62	2.78
Estradiol	0	< LOQ	-	0	< LOQ	-	0	< LOQ	-	0	< LOQ	-
Progesterone	0	< LOQ	-	0	< LOQ	-	0	< LOQ	-	0	< LOQ	-
Testosterone	0	< LOQ	-	0	< LOQ	-	0	< LOQ	-	0	< LOQ	-

Notation: LOQ = limit of quantification, DF= detection frequency, n = number of samples, min = minimum concentration, max = maximum concentration, mg/ℓ = milligram per litre

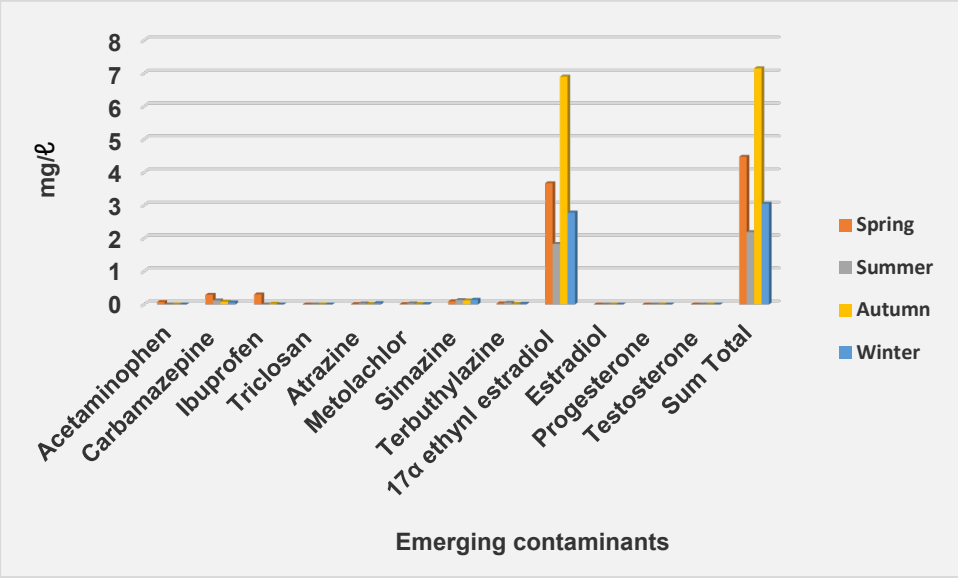


Figure 4.4 Occurrence of emerging contaminants in dams within the Modder River catchment

4.3.3 Emerging contaminants in treated drinking water

A few contaminants were detected in treated drinking water as shown in Table 4.5. Among the detected contaminants in treated drinking water, herbicides were the most detected contaminants. During the spring season, the mean concentrations of emerging contaminants were carbamazepine (0.13 mg/ℓ), atrazine (0.02 mg/ℓ), metolachlor (0.01 mg/ℓ), terbuthylazine (0.02 mg/ℓ), and 17-alpha-ethinylestradiol (1.46 mg/ℓ). During the summer season, the majority of the average concentrations of emerging contaminants were < LOQ, with only atrazine (0.07 mg/ℓ), metolachlor (0.05 mg/ℓ), terbuthylazine (0.09 mg/ℓ) and 17-alpha-ethinylestradiol (0.20 mg/ℓ) detected. In the autumn season, only atrazine (0.02 mg/ℓ), metolachlor (0.02 mg/ℓ), terbuthylazine (0.01 mg/ℓ) and 17-alpha-ethinylestradiol (0.73 mg/ℓ) were detected. Moreover, the winter season also showed the majority of emerging contaminants to be below limit of quantification (< LOQ), except for atrazine (0.02 mg/ℓ), metolachlor (0.01 mg/ℓ), terbuthylazine (0.01 mg/ℓ) and 17-alpha-ethinylestradiol (0.44 mg/ℓ).

The highest average concentrations of detected emerging contaminants in treated drinking water was recorded during the spring season. Their total average concentrations in treated water were trending as spring > autumn > winter > summer. The concentrations of 17-alpha-ethinylestradiol were the highest in all seasons. Their overall average concentrations were in the range of 17-alpha-ethinylestradiol > terbuthylazine = atrazine > metolachlor > carbamazepine. The situation of having pesticides as the most detected contaminants in treated drinking water within the Modder River catchment is comparable to the findings of other researchers who also reported the pesticides atrazine, and terbuthylazine as the most detected contaminants in treated drinking water (Machado et al., 2016; Odendaal et al., 2015). 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 high concentrations of herbicides in treated drinking water may be attributed to the use of herbicides to control weeds in dams used as a source of water in WWTPs. Rivers that recharge these dams may contain traces of herbicides and 17-alpha-ethinylestradiol as they mostly receive wastewater effluents. The high detection of atrazine in water sources may also be connected to their nature of being persistent. Herbicides such as atrazine are persistent in soil and their transport to water make it the most commonly detected pesticide in water sources (Almberg et al., 2018). Moreover, the presence of these compounds in treated drinking water reveals that the methods used in selected WWTPs are incapable of removing these compounds, which include abstraction, macro/micro sieving, coagulation, flocculation, sedimentation, filtration, and disinfection.

Table 4.5 Occurrence of emerging contaminants in treated drinking water

Compound	Concentration (mg/ℓ)											
	Spring (n = 2)			Summer (n = 2)			Autumn (n = 2)			Winter (n = 2)		
	DF	Min-Max	Mean	DF	Min-Max	Mean	DF	Min-Max	Mean	DF	Min-Max	Mean
Pharmaceuticals and personal care products												
Acetaminophen	1	< LOQ to 0.10	0	0	< LOQ	-	0	< LOQ	-	1	< LOQ to 0.28	-
Carbamazepine	2	0.01 to 0.25	0.13	0	< LOQ	-	0	< LOQ	-	0	< LOQ	-
Ibuprofen	1	< LOQ to 0.01	-	0	< LOQ	-	0	< LOQ	-	0	< LOQ	-
Triclosan	0	< LOQ	-	0	< LOQ	-	0	< LOQ	-	0	< LOQ	-
Pesticides (herbicides)												
Atrazine	2	0.015 to 0.019	0.02	2	0.02 to 0.12	0.07	2	0.01 to 0.03	0.02	2	0.008 to 0.03	0.02
Metolachlor	2	0.009 to 0.01	0.01	2	0.01 to 0.09	0.05	2	0.004 to 0.04	0.02	2	0.002 to 0.02	0.01
Simazine	1	< LOQ to 0.03	-	1	< LOQ to 0.04	-	0	< LOQ	-	0	< LOQ	-
Terbuthylazine	2	0.019 to 0.02	0.02	3	0.02 to 0.16	0.09	2	0.004 to 0.02	0.01	2	0.006 to 0.01	0.01
Endocrine-disrupting compound (steroid hormones)												
17-alpha-ethinylestradiol	2	0.15 to 2.78	1.46	2	0.14 to 0.26	0.2	2	0.42 to 1.04	0.73	2	0.16 to 0.01	0.01
Estradiol	0	< LOQ	-	0	< LOQ	-	0	< LOQ	-	0	< LOQ	-
Progesterone	0	< LOQ	-	0	< LOQ	-	0	< LOQ	-	0	< LOQ	-
Testosterone	0	< LOQ	-	0	< LOQ	-	0	< LOQ	-	0	< LOQ	-

Notation: LOQ = limit of quantification, DF = detection frequency, n = number of samples, min = minimum concentration, max = maximum concentration, mg/ℓ = milligram per litre

Moreover, as shown in Table 4.6, atrazine and terbuthylazine mean that the concentrations in this study were above the South African acceptable limit (Department of Water Affairs, 1996; Horak et al., 2021) and the corresponded with the World Health Organization guidelines (WHO, (2003; Hamilton et al., 2003) in all seasons, while metolachlor concentrations only exceeded those tolerable limits in the summer and autumn seasons. The outcomes of this study indicate a serious health concern for the community within Modder River catchment. Chronic pesticide exposure through water ingestion can mimic human hormones, lowering immunity, disrupting hormone balance, triggering reproductive issues, posing carcinogenic effects, and lowering intelligence, particularly in children at development stage of the body (Syafrudin et al., 2021). In summation, the sum concentration of emerging contaminants in treated drinking water was observed in the spring season (Figure 4.5). It was mostly contributed by 17-alpha-ethinylestradiol, terbuthylazine and atrazine. These compounds should be prioritised in pollution management campaigns.

Table 4.6 Concentration of pesticides in treated drinking water with guideline values

Contaminants	Spring	Summer	Autumn	Winter	Guideline values	
					DWAF	WHO
Atrazine	0.02	0.07	0.02	0.02	0.01	0.002
Metolachlor	0.01	0.05	0.02	0.01	-	0.01
Simazine	0.00	0.00	0.00	0.00	-	0.002
Terbuthylazine	0.02	0.09	0.01	0.01	-	0.007

Notation: DWAF = Department of Water Affairs and Forestry, South Africa (1996); WHO = World Health Organization (2003); Hamilton et al. (2003)

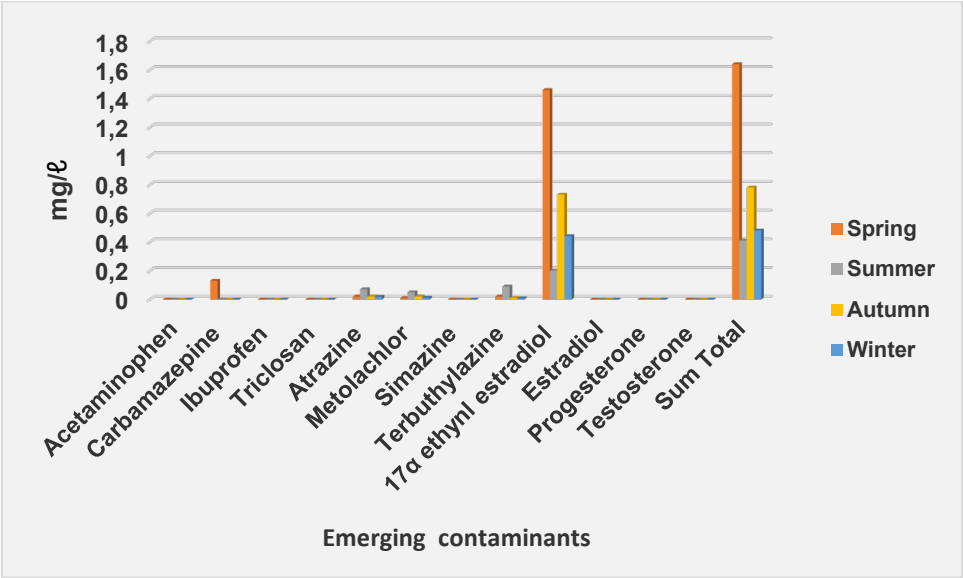


Figure 4.5 Occurrence of emerging contaminants in treated drinking water within the Modder River catchment

4.3.4 Emerging contaminants in wastewater influents

4.3.4.1 Pharmaceuticals and personal care products

In influents in the spring season, PPCPs, namely acetaminophen, carbamazepine, ibuprofen and triclosan, were detected as 2.73 to 8.81 mg/ℓ (5.63 mg/ℓ), 0.16 to 0.95 mg/ℓ (0.62 mg/ℓ), 3.32 to 11.10 mg/ℓ (6.34 mg/ℓ), and < LOQ to 0.31 mg/ℓ (0.30 mg/ℓ), respectively. Their respective concentrations during the summer season were 14.00 to 16.10 mg/ℓ (14.80 mg/ℓ), 0.54 to 0.83 mg/ℓ (0.64 mg/ℓ), 8.16 to 14.20 mg/ℓ (10.25 mg/ℓ), and 0.13 to 0.37 mg/ℓ (0.21 mg/ℓ). During the autumn season, their respective concentrations were < LOQ to 39.20 mg/ℓ (28.15 mg/ℓ), 0.25 to 0.48 mg/ℓ (0.35 mg/ℓ), 5.10 to 9.46 mg/ℓ (7.95 mg/ℓ) and 0.49 to 0.76 mg/ℓ (0.62 mg/ℓ). Moreover, in the winter season they were 5.28 to 18.10 mg/ℓ (11.16 mg/ℓ), 0.08 to 8.89 mg/ℓ (3.06 mg/ℓ), 5.74 to 7.80 mg/ℓ (7.04 mg/ℓ) and < LOQ, respectively (Table 4.7).

The highest total average concentration of PPCPs was detected in the autumn season, and their trend was autumn > summer > winter > spring. The total average concentration of acetaminophen was the highest in the influent samples. The overall average concentrations of the detected PPCPs in the influent sample were descending as acetaminophen > carbamazepine > ibuprofen > triclosan. Acetaminophen and ibuprofen are analgesics/non-steroid anti-inflammatory drugs that are commonly used alone or in combination with other formulations to treat a variety of ailments (Ekinci et al., 2020). In a related study, a concentration of acetaminophen and ibuprofen lower than the current findings were detected in WWTPs receiving inflows from health facilities in the North West province of South Africa (Kanama et al., 2018). Carbamazepine belongs to the anticonvulsant group of pharmaceuticals and is a prescription drug used to treat patients with seizures and bipolar disorders (Nannou et al., 2022). A lower concentration was observed for carbamazepine in wastewater influent of two sewage treatment plants in southern India (Subedi et al., 2017). Triclosan, as one of the PCPs detected in this study, is extensively used in a variety of consumer products because of their excellent antimicrobial and antifungal properties. Most of the consumer products such as soaps, disinfectants, toothpaste, body washes, and medical disinfectants, may have a concentration of triclosan ranging from 0.1 to 2% (Kanama et al., 2018). A very low concentration of triclosan than the present study was observed by Lin et al. (2020) in wastewater influents in China. The WWTPs in this study receive wastewater from the industry, households and hospitals. Consequently, the occurrence of these PPCPs in WWTPs may be attributed to the excretion from patients suffering from pain, fever, seizures, headaches, menstrual periods, toothaches,

backaches, osteoarthritis, or cold/flu aches and bipolar disorders. Moreover, the presence of triclosan reveals its constant use in households, industries, or hospitals, mostly in the spring season.

4.3.4.2 Pesticides

The concentrations of atrazine, metolachlor, simazine, and terbuthylazine during the spring season were 0.02 to 0.07 mg/ℓ (0.04 mg/ℓ), 0.003 to 0.01 mg/ℓ (0.01 mg/ℓ), 0.04 to 0.58 mg/ℓ (0.37 mg/ℓ), and 0.01 to 0.05 mg/ℓ (0.03 mg/ℓ), respectively. During the summer season, their respective concentrations were 0.02 to 0.07 mg/ℓ (0.04 mg/ℓ), 0.02 to 0.09 mg/ℓ (0.05 mg/ℓ), 0.11 to 0.45 mg/ℓ (0.32 mg/ℓ) and 0.02 to 0.11 mg/ℓ (0.08 mg/ℓ). In the autumn season, their concentrations were 0.02 to 0.07 mg/ℓ (0.04 mg/ℓ), 0.01 to 0.07 mg/ℓ (0.03 mg/ℓ), < LOQ to 0.19 mg/ℓ (0.15 mg/ℓ) and 0.02 to 0.08 mg/ℓ (0.04 mg/ℓ), respectively. Moreover, in the winter season their concentrations were 0.01 to 0.15 mg/ℓ (0.07 mg/ℓ), 0.002 to 0.21 mg/ℓ (0.07 mg/ℓ), 0.05 to 0.54 mg/ℓ (0.23 mg/ℓ) and 0.01 to 0.28 mg/ℓ (0.10 mg/ℓ), respectively (Table 4.7).

Among the herbicides detected in influent samples, the highest total average concentration was observed during the summer season and their trend was summer > spring > winter > autumn. The total average concentration of simazine was the highest in influent samples and their overall mean concentrations were descending as simazine > terbuthylazine > atrazine > metolachlor. Different trend of herbicides in wastewater influent was reported in a study conducted in a WWTP located in the Baoding city of China, showing atrazine with the highest concentration among the herbicides detected (Wang et al., 2022). Wastewater treatment plants receive municipal domestic wastewater from all residents, including fruit and vegetable cleaning, atmospheric sedimentation adsorption, and other irregular uses (Wang et al., 2022). The dominance of these herbicides in WWTPs clearly shows their abundant use in the city, households, agricultural areas, or pesticide production factories.

4.3.4.3 Steroid hormones

The concentrations of steroid hormones (Table 4.7), such as 17-alpha-ethinylestradiol, estradiol, progesterone and testosterone in wastewater influents during spring were 19.90 to 47 mg/ℓ (31.2 mg/ℓ), < LOQ, < LOQ to 0.03 mg/ℓ (0.02 mg/ℓ), and 0.006 to 0.009 mg/ℓ (0.01 mg/ℓ), respectively. During the summer season their respective concentrations were 23.10 to 46.10 mg/ℓ (32.77 mg/ℓ), < LOQ, < LOQ and < LOQ to 0.003 mg/ℓ (0.002 mg/ℓ). During the autumn season they were 17.30 to 62.10 mg/ℓ (37.53 mg/ℓ), < LOQ, < LOQ to 0.05 mg/ℓ (0.04 mg/ℓ), and < LOQ to 0.04 mg/ℓ (0.03 mg/ℓ), respectively. Moreover, their respective concentrations in the winter season were 6.43 to 32.80 mg/ℓ (21.68 mg/ℓ), < LOQ, < LOQ to 0.02 mg/ℓ (0.01 mg/ℓ), and < LOQ to 0.01 mg/ℓ (< LOQ).

The highest total average concentration was observed during the autumn season and their trend was autumn > summer > spring > winter. The total average concentration of 17-alpha-ethinylestradiol was the highest in influent samples and their overall mean concentrations were descending as 17-alpha-ethinylestradiol > progesterone > testosterone > estradiol. A concentration of 17-alpha-ethinylestradiol, which was lower than the present study, was reported in WWTPs receiving inflows from health facilities in the North West province of South Africa (Kanama et al., 2018). Another study by Manickum and John (2014) in WWTPs in Pietermaritzburg, South Africa, detected maximum concentrations of estradiol, 17-alpha-ethinylestradiol, progesterone, and testosterone, which were below the concentrations in this study, except for estradiol which was above. Synthetic estrogens such as 17-alpha-ethinylestradiol are frequently used as the main ingredient in many oral contraceptives (Kanama et al., 2018). Progesterone is a progestogens, regarded as a female pregnancy hormone, while testosterone is a major androgen compound necessary for normal spermatogenesis, and decreases the risk of osteoporosis (Hu et al., 2010; Prior, 2019). The presence of these hormones in wastewater influent could be attributed to the high excretion rates in humans (Kanama et al., 2018). According to Forghani et al. (2018), even without the use of hormonal drugs, every human excretes estrogens through their bodies. Women excrete approximately 2.3 to 259 g per day, and Triazine men 1.6 g per day of estradiol hormones, which explains their presence in WWTPs in the study area (Forghani et al.,

2018). In summation, high levels of the emerging contaminants in influent samples were recorded in the autumn season. It was mostly contributed by 17-alpha-ethinylestradiol, acetaminophen, which make them contaminants of concern in this catchment (Figure 4.6).

Table 4.7 Occurrence of emerging contaminants in influent

Compound	Concentration (mg/ℓ)											
	Spring (n = 3)			Summer (n = 3)			Autumn (n = 3)			Winter (n = 3)		
	DF	Min-Max	Mean	DF	Min-Max	Mean	DF	Min-Max	Mean	DF	Min-Max	Mean
Pharmaceuticals and personal care products												
Acetaminophen	3	2.73 to 8.81	5.63	3	14.00 to 16.10	14.8	2	< LOQ to 39.20	28.15	3	5.28 to 18.10	11.16
Carbamazepine	3	0.16 to 0.95	0.62	3	0.54 to 0.83	0.64	3	0.25 to 0.48	0.35	3	0.08 to 8.89	3.06
Ibuprofen	3	3.32 to 11.10	6.34	3	8.16 to 14.20	10.25	3	5.10 to 9.46	7.95	3	5.74 to 7.80	7.04
Triclosan	2	< LOQ to 0.31	0.3	3	0.13 to 0.37	0.21	3	0.49 to 0.76	0.62	0	< LOQ	-
Pesticides (herbicides)												
Atrazine	3	0.02 to 0.07	0.04	3	0.02 to 0.07	0.04	3	0.02 to 0.07	0.04	3	0.01 to 0.15	0.07
Metolachlor	3	0.003 to 0.01	0.01	3	0.02 to 0.09	0.05	3	0.01 to 0.07	0.03	3	0.002 to 0.21	0.07
Simazine	3	0.04 to 0.58	0.37	3	0.11 to 0.45	0.32	2	< LOQ to 0.19	0.15	3	0.05 to 0.54	0.23
Terbuthylazine	3	0.01 to 0.05	0.03	3	0.02 to 0.11	0.08	3	0.02 to 0.08	0.04	3	0.01 to 0.28	0.10
Endocrine-disrupting compound (steroid hormones)												
17-alpha-ethinylestradiol	3	19.90-47	31.2	3	23.10-46.10	32.77	3	17.30 to 62.10	37.53	3	6.43-32.8	21.68
Estradiol	0	< LOQ	-	0	< LOQ	-	0	< LOQ	-	0	< LOQ	-
Progesterone	2	< LOQ to 0.03	0.02	0	< LOQ	-	2	< LOQ to 0.05	0.04	2	< LOQ to 0.02	0.01
Testosterone	3	0.006 to 0.009	0.01	2	< LOQ to 0.003	0.002	2	< LOQ to 0.04	0.03	1	< LOQ to 0.01	-

Notation: LOQ = limit of quantification, DF = detection frequency, n = number of samples, min = minimum concentration, max = maximum concentration, mg/ℓ = milligram per litre

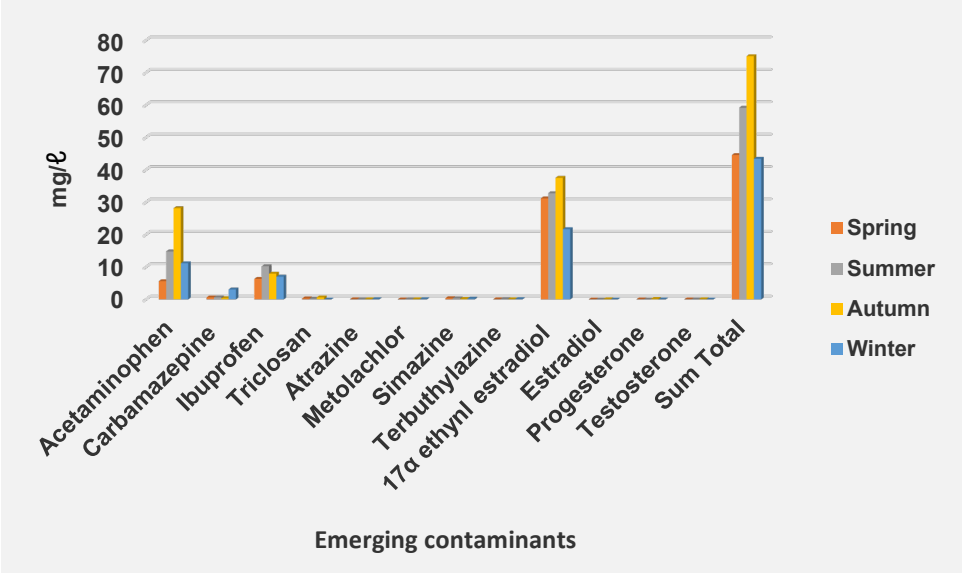


Figure 4.6 Occurrence of emerging contaminants in wastewater influent

4.3.5 Emerging contaminants in wastewater effluents

4.3.5.1 Pharmaceuticals and personal care products

The targeted compounds, acetaminophen, carbamazepine, ibuprofen and triclosan, showed different concentrations in effluent samples (Table 4.8). In the spring season, their respective concentrations were < LOQ, 0.51 to 1.20 mg/ℓ (0.93 mg/ℓ), 2.86 to 6.22 mg/ℓ (4.30 mg/ℓ) and < LOQ to 0.17 mg/ℓ (0.13 mg/ℓ). During the summer season their concentrations were < LOQ to 8.70 mg/ℓ (< LOQ), 0.57 to 2.82 (1.68 mg/ℓ), 0.22 to 7.67 mg/ℓ (3.72 mg/ℓ) and < LOQ to 0.14 mg/ℓ (< LOQ), respectively. In the autumn season, their respective

concentrations were < LOQ to 11.80 mg/ℓ (< LOQ), 0.51 to 0.81 mg/ℓ (0.63 mg/ℓ), 0.07 to 4.08 mg/ℓ (2.07 mg/ℓ) and < LOQ. They were also detected as < LOQ, 0.16 to 0.60 mg/ℓ (0.36 mg/ℓ), 0.42 to 5.58 mg/ℓ (2.19 mg/ℓ), and < LOQ, respectively.

The highest total average concentration was observed during the summer season and their trend was summer > spring > autumn > winter. The total average concentration of ibuprofen was the highest in effluent samples and their overall mean concentrations were descending as ibuprofen > carbamazepine > triclosan > acetaminophen. Other researchers also reported the occurrence of ibuprofen and acetaminophen in the North West province, South Africa (Kanama et al., 2018), carbamazepine in Msunduzi, KwaZulu-Natal (Matongo et al., 2015), and triclosan in the Eastern Cape province, South Africa (Ademoyegun, 2017). The occurrence of PPCPs in effluent samples shows poor removal efficiency of these contaminants in WWTPs.

4.3.5.2 Pesticides

Various concentrations of atrazine, metolachlor, simazine, and terbuthylazine herbicides in wastewater effluents were observed, as presented in Table 4.8. The concentrations of these contaminants in the spring season were 0.02 to 0.13 mg/ℓ (0.06 mg/ℓ), 0.003 to 0.03 mg/ℓ (0.02 mg/ℓ), 0.03 to 0.32 mg/ℓ (0.21 mg/ℓ), and 0.01 to 0.10 mg/ℓ (0.06 mg/ℓ), respectively. In the summer season, their respective concentrations were 0.02 to 0.07 mg/ℓ (0.04 mg/ℓ), 0.03 to 0.12 mg/ℓ (0.07 mg/ℓ), 0.13 to 0.72 mg/ℓ (0.44 mg/ℓ), and 0.03 to 0.11 mg/ℓ (0.07 mg/ℓ). In the autumn season, their concentrations were 0.01 to 0.11 mg/ℓ (0.05 mg/ℓ), 0.01 to 0.14 mg/ℓ (0.06 mg/ℓ), 0.05 to 0.38 mg/ℓ (0.24 mg/ℓ) and 0.01 to 0.05 mg/ℓ (0.02 mg/ℓ), respectively. Moreover, in the winter season, their respective concentrations were 0.02 to 0.05 mg/ℓ (0.03 mg/ℓ), 0.003 to 0.03 mg/ℓ (0.02 mg/ℓ), < LOQ to 8.45 mg/ℓ (4.32 mg/ℓ) and 0.01 to 0.02 mg/ℓ (0.02 mg/ℓ).

The highest total average concentration was observed during the winter season and their trend was winter > summer > autumn > spring. The total average concentration of simazine was the highest among the herbicides in effluent samples and their overall mean concentrations were descending as simazine > atrazine > metolachlor = terbuthylazine. A study conducted in Darvill in the KwaZulu-Natal province of South Africa reported average concentrations of simazine, and atrazine in effluent samples (Kunene, 2019), which were lower than the findings of this study. They also detected terbuthylazine in effluent samples around Amanzimtoti at concentrations lower than this study (Kunene, 2019).

4.3.5.3 Steroid hormones

The descriptive statistics for 17-alpha-ethinylestradiol, estradiol, progesterone and testosterone are presented in Table 4.8. During the spring season, their respective concentrations were 11.20 to 20.30 mg/ℓ (16.60 mg/ℓ), < LOQ to 0.03 mg/ℓ (< LOQ), < LOQ to 0.006 mg/ℓ (0.01 mg/ℓ), and < LOQ to 0.003 mg/ℓ (< LOQ). During the summer season, their respective concentrations were 2.64 to 26.40 mg/ℓ (13.58 mg/ℓ), < LOQ, < LOQ, and < LOQ to 0.002 mg/ℓ (< LOQ). In the autumn season, they were 26.20 to 52.80 mg/ℓ (41.40 mg/ℓ), < LOQ, < LOQ and < LOQ, respectively. Moreover, only 17-alpha-ethinylestradiol was detected among the steroid hormones during the winter season as 14.70 to 20.10 mg/ℓ (17.90 mg/ℓ).

The highest total average concentration was observed during the autumn season and they were trending as autumn > winter > spring > summer. The total average concentration of 17-alpha-ethinylestradiol was the highest among the detected steroid hormone samples and their overall mean concentrations were descending as 17-alpha-ethinylestradiol > progesterone > testosterone = estradiol. The occurrence of 17-alpha-ethinyl-estradiol and estradiol in effluent samples were also reported in a study conducted in China (Lin et al., 2020). In Pietermaritzburg, South Africa, wastewater treatment effluents also showed occurrences of progesterone and testosterone (Manickum and John, 2014). In summation, high levels of the emerging contaminants in effluent samples were recorded in the autumn season (Figure 4.7). It was mostly contributed by 17-alpha-ethinylestradiol, simazine and ibuprofen. Generally, in this study, the concentration of the emerging contaminants in effluent samples can be described as reduced, not reduced or higher than the influent

concentration. Noteworthy was a negative removal of other emerging contaminants. The negative removal efficiency observed for some emerging contaminants was in accordance with previous literature (Nannou et al., 2022; Ofrydopoulou et al., 2021). All emerging contaminants quantified at lower concentrations in the effluent than in the influent samples clearly indicate that these WWTPs have a significant removal efficiency.

Table 4.8 Occurrence of emerging contaminants in effluent

Compound	Concentration (mg/ℓ)											
	Spring (n = 3)			Summer (n = 3)			Autumn (n = 3)			Winter (n = 3)		
	DF	Min-Max	Mean	DF	Min-Max	Mean	DF	Min-Max	Mean	DF	Min-Max	Mean
Pharmaceuticals and personal care products												
Acetaminophen	0	< LOQ	-	1	< LOQ to 8.7	-	1	< LOQ to 11.80	-	0	< LOQ	-
Carbamazepine	3	0.51 to 1.20	0.93	3	0.57 to 2.82	1.68	3	0.51 to 0.81	0.63	3	0.16 to 0.60	0.36
Ibuprofen	3	2.86 to 6.22	4.3	3	0.22 to 7.67	3.72	3	0.07-4.08	2.07	3	0.42 to 5.58	2.19
Triclosan	2	< LOQ to 0.17	0.13	1	< LOQ to 0.14	-	0	< LOQ	-	0	< LOQ	-
Pesticides (herbicides)												
Atrazine	3	0.02 to 0.13	0.06	3	0.02 to 0.07	0.04	3	0.01 to 0.11	0.05	3	0.02 to 0.05	0.03
Metolachlor	3	0.003 to 0.03	0.02	3	0.03 to 0.12	0.07	3	0.01 to 0.14	0.06	3	0.003 to 0.03	0.02
Simazine	3	0.03 to 0.32	0.21	3	0.13 to 0.72	0.44	3	0.05 to 0.38	0.24	2	< LOQ to 8.45	4.32
Terbuthylazine	3	0.01 to 0.10	0.06	3	0.03 to 0.11	0.07	3	0.01 to 0.05	0.02	3	0.01 to 0.02	0.02
Endocrine-disrupting compound (steroid hormones)												
17-alpha-ethinylestradiol	3	11.20-20.30	16.6	3	2.64-26.40	13.580	3	26.20-52.80	41.4	3	14.7-20.10	17.90
Estradiol	1	< LOQ to 0.03	-	0	< LOQ	-	0	< LOQ	-	0	< LOQ	-
Progesterone	2	< LOQ to 0.006	0.01	0	< LOQ	-	0	< LOQ	-	0	< LOQ	-
Testosterone	1	< LOQ to 0.003	-	1	< LOQ to 0.002	-	1	< LOQ	-	0	< LOQ	-

Notation: LOQ = limit of quantification, DF = detection frequency, n = number of samples, min = minimum concentration, max = maximum concentration, mg/ℓ = milligram per litre

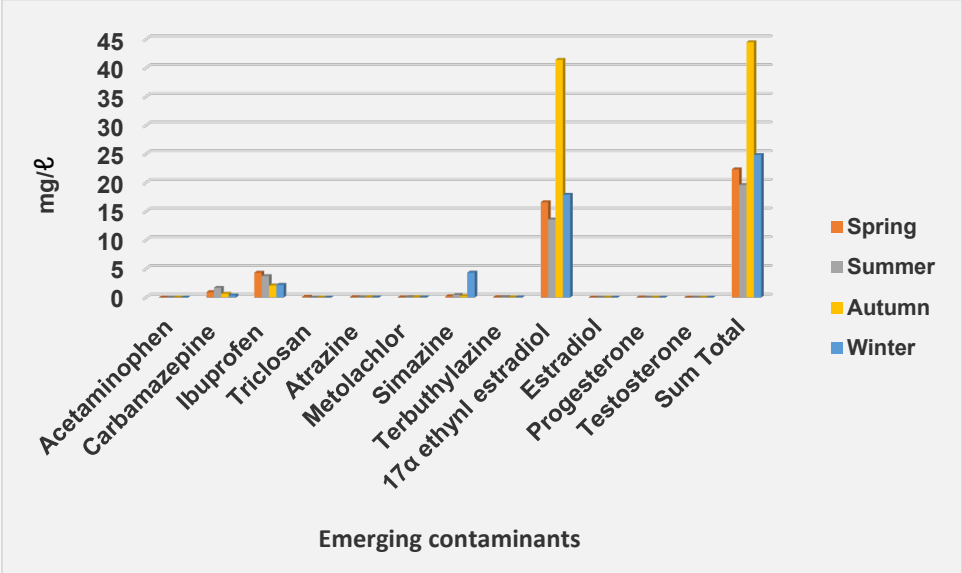


Figure 4.7 Occurrence of emerging contaminants in wastewater effluent

4.3.6 Removal efficiency of emerging contaminants in wastewater treatment plants

The removal rate of pollutants in wastewater can be used to assess the performance of WWTPs. Solubility, volatility, adsorption to solids, and other factors in WWTPs contribute to the removal and persistence of PPCPs, herbicides, and steroid hormones (Kanama et al., 2018). The removal efficiency (%) expresses the decrease in the concentration in a compound during treatment and is based on comparison of the average influent and

effluent concentrations (Nannou et al., 2022). The removal efficiencies of all the targeted emerging contaminants detected in three WWTPs were assessed using Equation 5:

$$RF\ (\%) = \frac{influent\ concentration - effluent\ concentration}{influent\ concentration} \times 100 \quad (5)$$

In this study, the removal efficiency of emerging contaminants in WWTPs were rated as complete (100%), efficient (70 to 99%), moderate (50 to 69%), poor (0 to 49%) as presented in Table 4.9. There was a poor removal rate of compounds such as ibuprofen, simazine and terbuthylazine during the spring season. During the summer season, there was poor a removal rate of metolachlor, and terbuthylazine while in the winter season, there was a poor removal rate of 17-alpha-ethinylestradiol. Furthermore, WWTPs also showed a negative removal rate of carbamazepine in the spring, summer, and autumn seasons. There was also a negative removal rate during the spring and autumn seasons for atrazine and metolachlor. A negative removal rate for terbuthylazine was only observed during the spring season, while for 17-alpha-ethinylestradiol it was observed during the autumn season. Moreover, a negative removal rate for simazine was observed during summer, autumn and winter. All emerging contaminants quantified at lower concentrations in the effluent than in the influent samples clearly indicate that these WWTPs had a significant removal efficiency (Figure 4.8). From the removal efficiency results, there was complete removal (100%) of acetaminophen and testosterone in all seasons. Other compounds such as progesterone (autumn and winter) and triclosan (summer and autumn) also showed complete removal. High removal rates of acetaminophen in WWTPs was also reported by other researchers (Kanama et al., 2018; Nantou et al., 2022). There was also poor and negative removal rates of the majority of pesticides. These outcomes are similar to the works conducted in WWTPs of four Mediterranean river basins (Campo et al., 2013), and in Baoding city, China (Wang et al., 2022). The low or negative removal rates of emerging contaminants can be attributed to particulate matter desorption and hydrolysis, as well as the degradation and transformation of emerging contaminants during the biochemical process (Köck-Schulmeyer et al., 2013; Wang et al., 2022). According to Kortesmäki et al. (2020), non-removal and the presence of higher concentrations of some analytes in effluent than in influent may be attributed to factors such as wastewater composition, structure of the analytes and conversion of the conjugated metabolites to the parent compound by enzymatic processes in the WWTPs.

The WWTPs chosen in this study were not built with the intention of removing emerging contaminants received from domestic, industrial, and hospital wastewater. All of the WWTPs use primary treatment, which involves removal of suspended solids by flotation, settling, and screening mechanisms and secondary treatment for removal of remaining organic matter via trickling filters utilising bacteria-coated stones and bacterial activated sludge. Therefore, it can be said that the processes employed in this treatment works were unable to remove some of the emerging contaminants and need improvement. In order to limit emerging contaminant pollution, according to Morin-Crini et al. (2022), tertiary treatment systems should be added in WWTPs. In South Africa, wastewater effluent is typically discharged into nearby streams, introducing pollutants into the aqueous environment. As a result, monitoring studies is critical to prioritise these chemicals in pollution. Not only will this protect aquatic life, but it will also preserve or sustain South Africa's water resources.

Table 4.9 Removal efficiency of emerging contaminants in wastewater treatment plants

	Removal efficiency (%)			
Analytes	**Spring**	**Summer**	**Autumn**	**Winter**
Acetaminophen	100	100	100	100
Carbamazepine	-50	-163	-80	88
Ibuprofen	32	64	74	69
Triclosan	57	100	100	< LOQ
Atrazine	-50	0	-25	57
Metolachlor	-100	40	-100	71
Simazine	43	-38	-60	-1 778
Terbuthylazine	-100	13	50	80
17-alpha-ethinylestradiol	47	59	-10	17
Estradiol	< LOQ	< LOQ	< LOQ	100
Progesterone	< LOQ	< LOQ	100	100
Testosterone	100	100	100	100

Notation: Complete: 100 >; efficient: 70 to 99%; moderate: 50 to 69%; poor: 0 to 49%

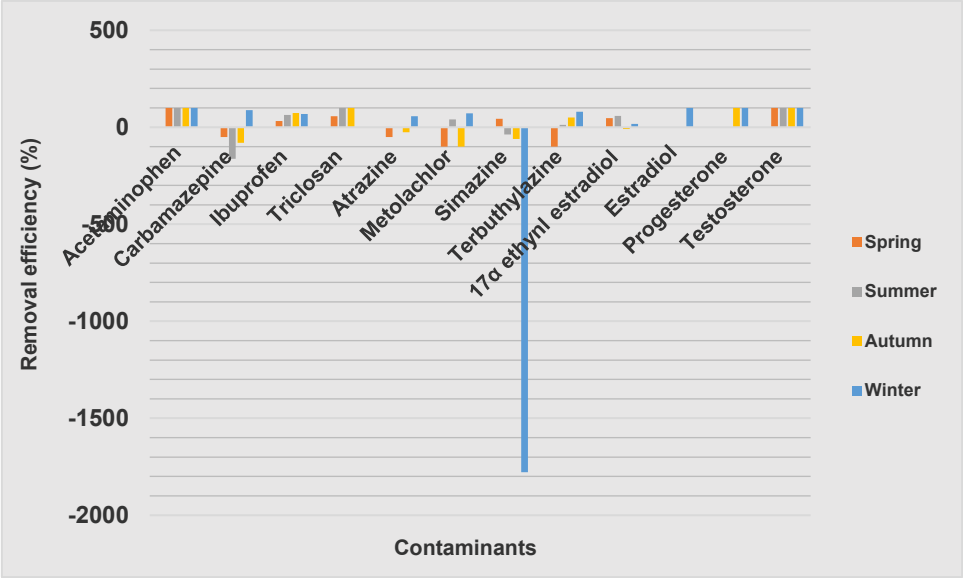


Figure 4.8 Efficiency of wastewater treatment plants in removing emerging contaminants

4.4 ENVIRONMENTAL RISK ASSESSMENT OF EMERGING CONTAMINANTS

4.4.1 Individual risk assessment

The individual environmental risk assessment was performed for emerging contaminants such as acetaminophen, carbamazepine, ibuprofen, triclosan, atrazine, metolachlor, simazine, terbuthylazine, 17-alpha-ethinylestradiol, estradiol, testosterone, and progesterone in water sources based on both acute and chronic toxicity on algae, daphnids and fish. The environmental risks of these emerging contaminants to sensitive aquatic species (algae, daphnids and fish) were carried out by using the RQ method. RQs of emerging contaminants on aquatic organisms were calculated from the MEC, and the PNEC. In this study, the mean concentrations of emerging contaminants in rivers, dams, wastewater effluent and treated drinking water were used to calculate the environmental risks of contaminants. The RQ approach was applied for the individual emerging contaminants detected at concentrations exceeding the quantification limits and with available toxicity data as reported by others (Nannou et al., 2022; Styszko et al., 2021).

In the absence of mean effective concentration (EC_{50}), the median lethal concentration (LC_{50}) were used. Even in cases where NOEC was unavailable, the lowest observed effect concentration values were used. Moreover,

in the event of data gaps, different species and endpoints were included. In this study, few contaminants had no toxicity data. For acute toxicity, there was no toxicity data for terbuthylazine on fish. For chronic toxicity, no data were available for terbuthylazine (algae), 17-alpha-ethinylestradiol (algae and daphnids), estradiol (algae and daphnids), testosterone (algae, daphnids and fish), and progesterone (algae and daphnids). The reason why there is a lack of chronic toxicity data for many of these compounds is due to the fact that most of these compounds have been only recently considered as emerging contaminants. Thus, this is a crucial disadvantage for the determination of the risk assessment, since chronic effects are much more likely to be induced rather than acute ones (Liu et al., 2023; Nannou et al., 2015, 2022; Pei et al., 2022). The risks covered four seasons of the year. They are discussed in the following subsections based on their presence in water sources.

4.4.1.1 Individual risk assessment in rivers

The ecological risk assessment of emerging contaminants in rivers, based on acute toxicity on sensitive aquatic species (algae, daphnids and fish), were assessed in all seasons as presented in Table 4.10. During the spring season, carbamazepine, ibuprofen, triclosan, atrazine, simazine, terbuthylazine, 17-alpha-ethinylestradiol and estradiol posed high risks to algae. Regarding daphnia, acetaminophen, carbamazepine, ibuprofen, triclosan, atrazine, simazine, terbuthylazine, 17-alpha-ethinylestradiol and estradiol posed high risks during the spring season. For fish, carbamazepine, ibuprofen, triclosan, atrazine, metolachlor, simazine, terbuthylazine, 17-alpha-ethinylestradiol and estradiol posed high risks. During the summer season, carbamazepine, ibuprofen, atrazine, simazine, terbuthylazine, and 17-alpha-ethinylestradiol posed high ecological risks to algae. Carbamazepine, ibuprofen, atrazine, metolachlor, simazine, terbuthylazine, and 17-alpha-ethinylestradiol posed high ecological risks to daphnids. Carbamazepine, ibuprofen, atrazine, metolachlor, simazine, terbuthylazine, and 17-alpha-ethinylestradiol posed high ecological risks to fish. During the autumn season, carbamazepine, ibuprofen, atrazine, simazine, terbuthylazine and 17-alpha-ethinylestradiol posed high acute risks to algae. For daphnids, carbamazepine, ibuprofen, atrazine, simazine, and 17-alpha-ethinylestradiol showed high acute ecological risks. It was carbamazepine, ibuprofen, atrazine, metolachlor, simazine, terbuthylazine and 17-alpha-ethinylestradiol that posed high acute risk to fish. Furthermore, during the winter season, high acute ecological risks to algae, daphnids and fish were posed by carbamazepine, ibuprofen, atrazine, metolachlor, simazine, terbuthylazine, and 17-alpha-ethinylestradiol.

The chronic toxicity risk results of emerging contaminants to algae, daphnids and fish are presented in Table 4.10. During the spring season, algae were likely to suffer high risks as a result of exposure to carbamazepine, ibuprofen, triclosan, atrazine, and simazine. Daphnids were likely to suffer high risks from exposure to carbamazepine, ibuprofen, atrazine and simazine. Fish were likely to suffer high ecological risks from exposure to ibuprofen, simazine, terbuthylazine, 17-alpha-ethinylestradiol and estradiol. In the summer season, algae were likely to suffer high risks from exposure to ibuprofen, atrazine, metolachlor, and simazine. Daphnids were likely to suffer high risks from exposure to carbamazepine, ibuprofen, atrazine, simazine and terbuthylazine. Fish were likely to suffer high chronic risks from exposure to ibuprofen, simazine, terbuthylazine, and 17-alpha-ethinylestradiol. During the autumn season, algae were more likely to suffer high chronic risks from exposure to carbamazepine, ibuprofen, atrazine, and simazine. Daphnids were more likely to suffer high risks from exposure to carbamazepine, ibuprofen, atrazine, simazine and 17-alpha-ethinylestradiol while fish were more likely to suffer high risks from ibuprofen, atrazine, simazine and 17-alpha-ethinylestradiol. Moreover, during the winter season, algae and daphnids were likely to suffer high ecological risks from exposure to carbamazepine, ibuprofen, atrazine, metolachlor, and simazine, while fish were more likely to suffer high chronic risks from exposure to ibuprofen, metolachlor, terbuthylazine and 17-alpha-ethinylestradiol.

From the results of individual ecological risks in rivers, high ecological risks were generally posed by acetaminophen, carbamazepine, ibuprofen, triclosan, atrazine, simazine, terbuthylazine, metolachlor, 17-alpha-ethinylestradiol and estradiol. The majority (83%) of targeted emerging contaminants showed the possibility of high acute risks, while 75% of them showed high chronic ecological risks. Most notable for acute

risks was the high risks of carbamazepine, ibuprofen, atrazine, simazine and 17-alpha-ethinylestradiol which occurred on all species in all seasons, while for chronic risks only ibuprofen and simazine posed high risks to all species in all seasons. The assessed high ecological risks of carbamazepine, ibuprofen, triclosan, terbuthylazine, and 17-alpha-ethinylestradiol in this study are in good accordance with other studies around the world (Čelić et al., 2021; Duarte et al., 2022; Grung et al., 2008; Guruge et al., 2019; Hernando et al., 2006; Jiang et al., 2015; Nannou et al., 2015). The observation of high ecological risks in river water clearly indicates that the rivers are not safe and these contaminants may have improper environmental health effects to the ecosystem and surrounding communities that may be exposed to rivers contaminated by these compounds. Domestic animals such as cows and goats were seen during site visits and drinking water from some of the rivers may also suffer some health effects. Most concerning in this study is the high risks of contaminants such as carbamazepine, ibuprofen, atrazine, simazine and 17-alpha-ethinylestradiol that were observed in all species in all seasons. There is an evidence that ibuprofen entering the body for a long time may lead to renal failure (Wu et al., 2020). Wanda et al. (2017) reported that carbamazepine has the virtue of disrupting the production of red blood cells, white blood cells, and platelets in humans and animals, even at lower concentrations. Atrazine and simazine are very important herbicides for maintenance of decent value and protection of agricultural produces or raw products. They are of serious concern in human health as they may gather in the human cell membrane and interfere with the normal body functions (Syafrudin et al., 2021). Exposure to these triazine herbicides may lead to irritation, carcinogenic and teratogenic effects (Sathiakumar et al., 2011). Moreover, exposure to low levels of estrogen, 17-alpha-ethinylestradiol may expand fish livers and affect the sexual characteristics of male fish in surface water (Ngqwala and Muchesa, 2020).

Table 4.10 Acute and chronic toxicity of individual emerging contaminants in rivers

Contaminant	Species	Spring		Summer		Autumn		Winter	
		HQ* mean	Risk	HQ mean	Risk	HQ mean	Risk	HQ mean	Risk
Acute toxicity of contaminants in rivers									
Acetaminophen	Algae	0.92	Medium	–	–	–	–	–	–
	Daphnids	13	High	–	–	–	–	–	–
	Fish	0.32	Medium	–	–	–	–	–	–
Carbamazepine	Algae	15.8	High	22	High	7.81	High	9.81	High
	Daphnids	95	High	117	High	41.67	High	48.74	High
	Fish	16.3	High	20	High	7.14	High	8.76	High
Ibuprofen	Algae	16.4	High	4	High	2.92	High	6.98	High
	Daphnids	69 375	High	38 667	High	30 667	High	68 750	High
	Fish	22.2	High	12	High	9.2	High	22	High
Triclosan	Algae	160.7	High	–	–	–	–	–	–
	Daphnids	230.7	High	–	–	–	–	–	–
	Fish	34.6	High	–	–	–	–	–	–
Atrazine	Algae	508.47	High	833	High	11 695	High	1 356	High
	Daphnids	4.35	High	7	High	100	High	11.59	High
	Fish	6.67	High	11	High	153	High	17.78	High
Metolachlor	Algae	0.17	Medium	1	High	0.35	Medium	2	High
	Daphnids	0.5	Medium	3	High	0.83	Medium	5	High
	Fish	2.5	High	15	High	5.13	High	31	High
Simazine	Algae	45 500	High	26 000	High	17 250	High	9 250	High
	Daphnids	1 820	High	1 040	High	627	High	336	High
	Fish	202	High	104	High	77	High	41	High
Terbuthylazine	Algae	3 000	High	4 000	High	500	High	2 500	High
	Daphnids	1.54	High	2	High	0.26	Medium	1.27	High
	Fish	16.67	High	20	High	2.78	High	14	High
17-alpha-ethinylestradiol	Algae	16 000 000	High	97 375 000	High	39 437 500	High	15 425 000	High
	Daphnids	10 666 666	High	6 491 667	High	26 291 667	High	10 283 333	High
	Fish	6 400 000	High	3 895 000	High	15 775 000	High	617 000	High
Estradiol	Algae	43 750	High	–	–	–	–	–	–
	Daphnids	2 333	High	–	–	–	–	–	–
	Fish	2 333	High	–	–	–	–	–	–
Progesterone	Algae	–	–	–	–	–	–	–	–

Contaminant	Species	Spring		Summer		Autumn		Winter	
		HQ* mean	Risk	HQ mean	Risk	HQ mean	Risk	HQ mean	Risk
Acute toxicity of contaminants in rivers									
	Daphnids	–	–	–	–	–	–	–	–
	Fish	–	–	–	–	–	–	–	–
Testosterone	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	–	–	–	–	–	–	–	–
Chronic toxicity of contaminants in rivers									
Acetaminophen	Algae	0.26	Medium	–	–	–	–	–	–
	Daphnids	1	Medium	–	–	–	–	–	–
	Fish	0.1	Medium	–	–	–	–	–	–
Carbamazepine	Algae	5.7	High	0.7	Medium	2.5	High	3	High
	Daphnids	1 140	High	140	High	500	High	620	High
	Fish	0.2	Medium	0.14	Medium	0.1	Medium	0.1	Medium
Ibuprofen	Algae	22 200	High	11 600	High	9 200	High	22 000	High
	Daphnids	111	High	47	High	36.8	High	89	High
	Fish	22 200	High	464	High	9 200	High	22 000	High
Triclosan	Algae	450	High	–	–	–	–	–	–
	Daphnids	0.02	Low	–	–	–	–	–	–
	Fish	0.01	Low	–	–	–	–	–	–
Atrazine	Algae	30	High	50	High	690	High	80	High
	Daphnids	15	High	25	High	345	High	40	High
	Fish	0.15	Medium	0.25	Medium	3.45	High	0.4	Medium
Metolachlor	Algae	0.33	Medium	2	High	0.67	Medium	4	High
	Daphnids	0.17	Medium	1	Medium	0.33	Medium	2	High
	Fish	0.1	Medium	0.6	Medium	0.2	Medium	1.2	High
Simazine	Algae	303	High	173	High	115	High	62	High
	Daphnids	182	High	87	High	57.5	High	31	High
	Fish	26	High	15	High	9.86	High	5	High
Terbuthylazine	Algae	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
	Daphnids	14.28	Medium	19	High	2.38	High	0.001	Low
	Fish	46.15	High	6	High	0.77	Medium	4	High
17-alpha-ethinylestradiol	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	4 060	High	2 597	High	10 517	High	4 113	High
Estradiol	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	1.66	High	–	–	–	–	–	–
Progesterone	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	–	–	–	–	–	–	–	–
Testosterone	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	–	–	–	–	–	–	–	–

Notation: HQ=Hazard quotient

4.4.1.2 Individual risk assessment in dams

The ecological risk assessment of emerging contaminants in dams are presented in Table 4.11. The risk assessment was based on acute and chronic toxicity on algae, daphnids, and fish. During the spring season, acute toxicity results showed that exposure to carbamazepine, atrazine, simazine, terbuthylazine, and 17-alpha-ethinylestradiol may possibly pose high risks to algae. Exposure to acetaminophen, carbamazepine, ibuprofen, atrazine, simazine and 17-alpha-ethinylestradiol showed possibilities of high risks to daphnids. Exposure to carbamazepine, ibuprofen, atrazine, metolachlor, simazine, terbuthylazine, and 17-alpha-ethinylestradiol showed possibilities of high ecological risks to fish. During the summer season, the risk results revealed that exposure to carbamazepine, atrazine, simazine, terbuthylazine, and 17-alpha-ethinylestradiol may cause high acute ecological risks to algae. For daphnids, the results showed possibilities of high ecological risks from exposure to carbamazepine, atrazine, metolachlor, simazine, terbuthylazine and

17-alpha-ethinylestradiol. For fish, the results showed high acute ecological risks from exposure to carbamazepine, metolachlor, simazine, terbuthylazine and 17-alpha-ethinylestradiol. During the autumn season, the possibility of high acute risks to algae was posed by carbamazepine, atrazine, simazine, terbuthylazine, and 17-alpha-ethinylestradiol. For daphnids, only carbamazepine, atrazine, simazine, and 17-alpha-ethinylestadiol showed the possibility of high risks, while exposure to carbamazepine, atrazine, metolachlor, simazine, terbuthylazine, and 17-alpha-ethinylestradiol showed the possibility of high risks to fish. Moreover, acute toxicity results during the winter season showed the possibility of carbamazepine, atrazine, simazine, terbuthylazine and 17-alpha-ethinylestradiol to pose high risks to fish. For daphnids, carbamazepine, atrazine, simazine, and 17-alpha-ethinylestradiol showed the possibility of high risks, while on fish the possibility of high ecological risks were likely to occur as a result of exposure to carbamazepine, atrazine, metolachlor, simazine, terbuthylazine and 17-alpha-ethinylestradiol.

The chronic toxicity risk results of emerging contaminants on algae, daphnids and fish are presented in Table 4.11. During the spring season, exposure to carbamazepine, ibuprofen, atrazine, and simazine showed the possibility of high risks to algae. For daphnids, exposure to carbamazepine, ibuprofen, atrazine and simazine showed the possibility of high risks. For fish, exposure to ibuprofen, simazine, terbuthylazine, and 17-alpha-ethinylestradiol showed the possibility of high risks. During the summer season, exposure to carbamazepine, atrazine, and simazine showed the possibility of high risks to algae. Exposure to carbamazepine, atrazine, simazine, and terbuthylazine showed the possibility of high risks to daphnids, while on exposure to simazine, terbuthylazine, and 17-alpha-ethinylestradiol showed the possibility of high risks to fish. During the autumn season, there was a possibility of high risks to algae as a result of exposure to ibuprofen, atrazine and simazine. Exposure to carbamazepine, atrazine, simazine and terbuthylazine showed the possibility of high risks to daphnids, while exposure to ibuprofen, simazine, terbuthylazine, and 17-alpha-ethinylestradiol posed high risks to fish. During the winter season, there was a possibility of high risks to algae from exposure to atrazine and simazine. Exposure to carbamazepine, atrazine, simazine and terbuthylazine posed high risks to daphnids. Moreover, exposure to terbuthylazine, simazine and 17-alpha-ethinylestradiol posed high risks to fish.

In dams, the results of individual ecological risks showed high ecological risks generally from carbamazepine, atrazine, simazine, terbuthylazine, acetaminophen, 17-alpha-ethinylestradiol, ibuprofen, and metolachlor. The majority (67%) of emerging contaminants in dams showed the possibility of high acute risks, while 50% of them showed high chronic ecological risks. Most notable for acute risks was the high risks of carbamazepine, simazine and 17-alpha-ethinylestradiol, which occurred on all species in all seasons, while for chronic risks only simazine posed high risks to all species in all seasons. High acute ecological risks and chronic ecological risks of these compounds may affect the survival of aquatic organisms (Pei et al., 2022) and the health of the local population through the food chain. Some of the dams are used as a fishing spot, which present a potential threat to human health via consumption due to the bioaccumulation of these compounds (Chen et al., 2020; Wang et al., 2018). In addition to these contaminants with high acute and chronic toxicity risks in dams, it should be noted that more compounds may be present at risk-inducing levels than screened during this study, and their mixture can result in additive, synergistic, or antagonistic effects (Abera et al., 2022).

Table 4.11 Acute and chronic toxicity of individual emerging contaminants in dams

Contaminant	Species	Spring		Summer		Autumn		Winter	
		HQ* mean	Risk	HQ mean	Risk	HQ mean	Risk	HQ mean	Risk
Acute toxicity of contaminants in dams									
Acetaminophen	Algae	0.52	Medium	–	–	–	–	–	–
	Daphnids	7.6	High	–	–	–	–	–	–
	Fish	0.2	Medium	–	–	–	–	–	–
Carbamazepine	Algae	8	High	3.75	High	2.5	High	1.9	High
	Daphnids	48.3	High	20	High	12.5	High	9	High
	Fish	8.3	High	3.43	High	2.26	High	1.67	High
Ibuprofen	Algae	0.9	Medium	–	–	0.06	Low	–	–

Contaminant	Species	Spring		Summer		Autumn		Winter	
		HQ* mean	Risk	HQ mean	Risk	HQ mean	Risk	HQ mean	Risk
	Daphnids	9 375	High	–	–	625	High	–	–
	Fish	3	High	–	–	0.2	Medium	-	-
Triclosan	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	–	–	–	–	–	–	–	–
Atrazine	Algae	338.98	High	500	High	169	High	678	High
	Daphnids	2.9	High	4.29	High	1.45	High	6	High
	Fish	4.44	High	0.6	Medium	2.22	High	9	High
Metolachlor	Algae	0.17	Medium	0.5	Medium	0.18	Medium	0.18	Medium
	Daphnids	0.5	Medium	1.5	High	0.43	Medium	0.43	Medium
	Fish	2.5	High	7.5	High	2.53	High	3	High
Simazine	Algae	2 500	High	3 250	High	3 000	High	3 500	High
	Daphnids	100	High	130	High	109	High	127	High
	Fish	11.11	High	14.44	High	13.33	High	16	High
Terbuthylazine	Algae	1 500	High	2 500	High	500	High	1 000	High
	Daphnids	0.77	Medium	1.25	High	0.25	Medium	0.51	Medium
	Fish	8.33	High	12.5	High	2.56	High	6	High
17-alpha-ethinylestradiol	Algae	4 587 500	High	2 287 500	High	8 625 000	High	3 475 000	High
	Daphnids	3 058 333	High	1 525 000	High	5 750 000	High	231 667	High
	Fish	1 835 000	High	91 500	High	3 450 000	High	1 390 000	High
Estradiol	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	–	–	–	–	–	–	–	–
Progesterone	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	–	–	–	–	–	–	–	–
Testosterone	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	–	–	–	–	–	–	–	–
Chronic toxicity of contaminants in dams									
Acetaminophen	Algae	0.1	Medium	–	–	–	–	–	–
	Daphnids	0.6	Medium	–	–	–	–	–	–
	Fish	0.07	Low	–	–	–	–	–	–
Carbamazepine	Algae	2.9	High	1.2	High	0.8	Medium	0.6	Medium
	Daphnids	580	High	240	High	16	High	120	High
	Fish	0.1	Medium	0.05	Low	0.03	Low	0.024	Low
Ibuprofen	Algae	3 000	High	–	–	200	High	–	–
	Daphnids	15	High	–	–	0.8	Medium	–	–
	Fish	3 000	High	–	–	2	High	–	–
Triclosan	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	–	–	–	–	–	–	–	–
Atrazine	Algae	20	High	3	High	10	High	40	High
	Daphnids	10	High	15	High	5	High	20	High
	Fish	0.1	Medium	0.15	Medium	0.005	Low	0.2	Medium
Metolachlor	Algae	0.33	Medium	1	Medium	0.33	Medium	0.33	Medium
	Daphnids	0.17	Medium	0.5	Medium	0.17	Medium	0.17	Medium
	Fish	0.1	Medium	0.3	Medium	0.1	Medium	0.10	Medium
Simazine	Algae	16.67	High	22	High	20	High	23	High
	Daphnids	10	High	11	High	10	High	100	High
	Fish	1.43	High	2	High	1.71	High	117	High
Terbuthylazine	Algae	–	–	–	–	–	–	–	–
	Daphnids	0.71	Medium	12	High	2.38	High	4.76	High
	Fish	2.3	High	4	High	0.77	Medium	1.54	High
17-alpha-ethinylestradiol	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	1 223	High	610	High	1 150	High	927	High

Contaminant	Species	Spring		Summer		Autumn		Winter	
		HQ* mean	Risk	HQ mean	Risk	HQ mean	Risk	HQ mean	Risk
Estradiol	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	–	–	–	–	–	–	–	–
Progesterone	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	–	–	–	–	–	–	–	–
Testosterone	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	–	–	–	–	–	–	–	–

Notation: HQ=Hazard quotient

4.4.1.3 Individual risk assessment in treated drinking water

As presented in Table 4.12, the assessment of ecological risks of emerging contaminants in treated drinking water was based on acute and chronic toxicity on algae, daphnids and fish. The acute toxicity of emerging contaminants in treated drinking water during the spring season showed carbamazepine, atrazine, simazine, terbuthylazine, and 17-alpha-ethinylestradiol to have a possibility of high risks to algae. On daphnids, high ecological risks were contributed by acetaminophen, carbamazepine, ibuprofen, atrazine, simazine, and 17-alpha-ethinylestradiol. On fish, high ecological risks were contributed by carbamazepine, atrazine, metolachlor, simazine, terbuthylazine, and 17-alphaethinylestradiol. During the summer season, high acute risks to algae were contributed by atrazine, terbuthylazine and 17-alpha-ethinylestradiol. On daphnids, high ecological risks were contributed by atrazine, metolachlor, terbuthylazine and 17-alpha-ethinylestradiol. On fish, high ecological risks were contributed by atrazine, metolachlor, terbuthylazine and 17-alpha-ethinylestradiol. During the autumn season, high acute risks to algae were contributed by atrazine, terbuthylazine, and 17-alpha-ethinylestradiol. On daphnids high risks were contributed by atrazine and 17-alpha-ethinylestradiol, while on fish it was contributed by atrazine, metolachlor and 17-alpha-ethinylestradiol. Moreover, during the winter season, the acute risks to algae were contributed by atrazine, terbuthylazine, and 17-alpha-ethinylestradiol. On daphnids, high risks were contributed by atrazine and 17-alpha-ethinylestradiol, while on fish it was contributed by atrazine, metolachlor, terbuthylazine and 17-alpha-ethinylestradiol.

The chronic toxicity risk assessment of emerging contaminants in treated drinking water are presented in Table 4.12. For acute toxicity on algae, the high risks were presented by carbamazepine, ibuprofen, atrazine, and simazine. On daphnids, high risks were presented by carbamazepine, atrazine, simazine, and terbuthylazine. On fish, ibuprofen, and 17-alpha-ethinylestradiol presented high risks. During the summer season, high acute toxicity on algae were posed by atrazine, and metolachlor. On daphnids, the high risks were presented by atrazine, and terbuthylazine. On fish, the high risks were presented by terbuthylazine and 17-alpha-ethinylestradiol. During the autumn and winter season, only atrazine posed high risks to algae. On daphnids, atrazine and terbuthylazine presented high risks, while 17-alpha-ethinylestradiol presented high risks to fish.

Generally, in treated drinking water, individual ecological risk assessments showed high ecological risks mostly from carbamazepine, acetaminophen, ibuprofen, atrazine, simazine, terbuthylazine, metolachlor and 17-alpha-ethinylestradiol. A total of 67% of the targeted emerging contaminants showed the possibility of high acute risks, while 58% showed the possibility of high chronic risks. Most notable for acute risks in drinking water were high risks of atrazine and 17-alpha-ethinylestradiol which occurred in all species in all seasons. In South Africa, there are no reported guidelines for emerging contaminants (carbamazepine, acetaminophen, ibuprofen, atrazine, simazine, terbuthylazine, metolachlor and 17-alpha-ethinylestradiol), which showed high ecological risks in this study, except for atrazine. The high ecological risks of these compounds in treated drinking water may put serious risks on the water consumers (Shipingana et al., 2022). Residues of pesticides is often suspected of being carcinogens or disrupting endocrine activities in drinking water (Kumar et al., 2013). Exposure to ibuprofen may increase vetellogenin production in male fish; decrease reproduction rate in fish; rise estradiol hormone levels and aromatase enzyme activity; and decreased testosterone hormone levels

(Veldhoen et al., 2014). The 17-alpha-ethinylestradiol may cause embryo deformation and mortality, impaired reproduction and growth in fish. Studies showed that progesterone at pollutant levels can cause oocyte maturation in female and sperm motility in male fish (Yazdan et al., 2022). Triazine herbicides are another class of chemical pesticides that have been related to endocrine-disrupting effects and reproductive toxicity (Jin et al., 2014). Studies have also shown the possible statistical relationship between triazine herbicides and the incidence of breast cancer (Nicolopoulou-Stamati et al., 2016). It worth noting that the combined effect of these emerging contaminants may further threaten the safety of drinking water in the area (Pei et al., 2022).

Table 4.12 Acute and chronic toxicity of individual emerging contaminants in treated drinking water

Contaminant	Species	Spring		Summer		Autumn		Winter	
		HQ* mean	Risk	HQ mean	Risk	HQ mean	Risk	HQ mean	Risk
Acute toxicity of contaminants in treated drinking water									
Acetaminophen	Algae	0.75	Medium	–	–	–	–	–	–
	Daphnids	11	High	–	–	–	–	–	–
	Fish	0.26	Medium	–	–	–	–	–	–
Carbamazepine	Algae	3.6	High	–	–	–	–	–	–
	Daphnids	21.6	High	–	–	–	–	–	–
	Fish	3.7	High	–	–	–	–	–	–
Ibuprofen	Algae	0.03	Low	–	–	–	–	–	–
	Daphnids	312	High	–	–	–	–	–	–
	Fish	0.1	Medium	–	–	–	–	–	–
Triclosan	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	–	–	–	–	–	–	–	–
Atrazine	Algae	338.98	High	1 186	High	339	High	339	High
	Daphnids	2.89	High	10	High	2.9	High	3	High
	Fish	4.44	High	16	High	4.44	High	4	High
Metolachlor	Algae	0.17	Medium	0.87	Medium	0.35	Medium	0.18	Medium
	Daphnids	0.5	Medium	2.13	High	0.85	Medium	0.43	Medium
	Fish	2.5	High	12.82	High	5.13	High	2.56	High
Simazine	Algae	750	High	–	–	–	–	–	–
	Daphnids	30	High	–	–	–	–	–	–
	Fish	3.33	High	–	–	–	–	–	–
Terbuthylazine	Algae	1 000	High	4 500	High	500	High	500	High
	Daphnids	0.51	Medium	2.28	High	0.25	Medium	0.25	Medium
	Fish	5.55	High	25	High	2.78	Medium	3	High
17-alpha-ethinylestradiol	Algae	1 825 000	High	250 000	High	912 500	High	55 000	High
	Daphnids	1 216 666	High	166 667	High	608 333	High	366 667	High
	Fish	730 000	High	100 000	High	365 000	High	220 000	High
Estradiol	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	–	–	–	–	–	–	–	–
Progesterone	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	–	–	–	–	–	–	–	–
Testosterone	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	–	–	–	–	–	–	–	–
Chronic toxicity of contaminants in treated drinking water									
Acetaminophen	Algae	0.22	Medium	–	–	–	–	–	–
	Daphnids	0.91	Medium	–	–	–	–	–	–
	Fish	0.1	Medium	–	–	–	–	–	–
Carbamazepine	Algae	1.3	High	–	–	–	–	–	–
	Daphnids	260	High	–	–	–	–	–	–
	Fish	0.05	Low	–	–	–	–	–	–
Ibuprofen	Algae	10	High	–	–	–	–	–	–
	Daphnids	0.5	Medium	–	–	–	–	–	–
	Fish	10	High	–	–	–	–	–	–
Triclosan	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	–	–	–	–	–	–	–	–
Atrazine	Algae	20	High	70	High	2	High	20	High

Contaminant	Species	Spring		Summer		Autumn		Winter	
		HQ* mean	Risk	HQ mean	Risk	HQ mean	Risk	HQ mean	Risk
	Daphnids	10	High	35	High	10	High	10	High
	Fish	0.1	Medium	0.35	Medium	0.1	Medium	0.25	Medium
Metolachlor	Algae	0.33	Medium	1.67	High	0.67	Medium	0.33	Medium
	Daphnids	0.17	Medium	0.83	Medium	0.33	Medium	0.17	Medium
	Fish	0.1	Medium	0.5	Medium	0.2	Medium	0.10	Medium
Simazine	Algae	5	High	–	–	–	–	–	–
	Daphnids	3	High	–	–	–	–	–	–
	Fish	0.43	Medium	–	–	–	–	–	–
Terbuthylazine	Algae	n/a	n/a	–	–	–	–	–	–
	Daphnids	4.76	High	21	High	2.38	High	2.34	High
	Fish	0.15	Medium	7	High	0.77	Medium	0.77	Medium
17-alpha-ethinylestradiol	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	487	High	67	High	243	High	147	High
Estradiol	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	–	–	–	–	–	–	–	–
Progesterone	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	–	–	–	–	–	–	–	–
Testosterone	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	–	–	–	–	–	–	–	–

Notation: HQ=Hazard quotient

4.4.1.4 Individual risk assessment in wastewater effluent

As presented in Table 4.13, the risk assessment of emerging contaminants in effluents was based on acute and chronic toxicity on algae, daphnids and fish. During the spring season, the high acute risks to algae were presented by acetaminophen, ibuprofen, triclosan, atrazine, simazine, terbuthylazine, estradiol, 17-alpha-ethinylestradiol, and progesterone. On daphnids, the high risks were presented by acetaminophen, ibuprofen, triclosan, atrazine, simazine, terbuthylazine, estradiol, 17-alpha-ethinylestradiol, and progesterone. On fish, the high risks were presented by acetaminophen, ibuprofen, triclosan, atrazine, metolachlor, simazine, terbuthylazine, estradiol, and 17-alpha-ethinylestradiol. During the summer season, high acute risks to algae were presented by carbamazepine, ibuprofen, atrazine, metolachlor, simazine, terbuthylazine, and 17-alpha-ethinylestradiol. On daphnids, the high risks were presented by carbamazepine, ibuprofen, atrazine, metolachlor, simazine, terbuthylazine, and 17-alpha-ethinylestradiol. On fish, the high risks were posed by carbamazepine, ibuprofen, atrazine, metolachlor, simazine, terbuthylazine, and 17-alpha-ethinylestradiol. During the autumn season, the high acute risks to algae were presented by carbamazepine, ibuprofen, atrazine, metolachlor, simazine, terbuthylazine and 17-alpha-ethinylestradiol. On daphnids, the high risks were presented by carbamazepine, ibuprofen, atrazine, metolachlor, simazine, and 17-alpha-ethinylestradiol. On fish, the high risks were presented by carbamazepine, ibuprofen, atrazine, metolachlor, simazine, terbuthylazine and 17-alpha-ethinylestradiol. Moreover, the high acute risks to algae during the winter season were presented by carbamazepine, ibuprofen, atrazine, simazine, terbuthylazine, and 17-alpha-ethinylestradiol. On daphnids, the high risks were presented by carbamazepine, ibuprofen, atrazine, metolachlor, simazine and 17-alpha-ethinylestradiol, while on fish it they were presented by carbamazepine, ibuprofen, atrazine, metolachlor, simazine, terbuthylazine and 17-alpha-ethinylestradiol.

The results of chronic toxicity risks to algae, daphnids and fish are presented in Table 4.13. During the spring season, the high chronic risks to algae were presented by carbamazepine, ibuprofen, triclosan, atrazine, and simazine. On daphnids, the high risks were presented by carbamazepine, ibuprofen, atrazine, simazine, and terbuthylazine. On fish, the high risks were presented by ibuprofen, simazine, terbuthylazine, and 17-alpha-ethinylestradiol. During the summer season, the high chronic risks to algae were presented by carbamazepine, ibuprofen, atrazine, metolachlor, and simazine. On daphnids, the high risks were presented by carbamazepine, ibuprofen, atrazine, simazine, and terbuthylazine. On fish, the high risks were presented by ibuprofen,

simazine, terbuthylazine and 17-alpha-ethinylestradiol. The high chronic risks to algae during the autumn season were presented by carbamazepine, ibuprofen, atrazine, metolachlor and simazine. On daphnids, the high risks were presented by carbamazepine, ibuprofen, atrazine, simazine and terbuthylazine. On fish, the high chronic risks were presented by ibuprofen, simazine, terbuthylazine and 17-alpha-ethinylestradiol. During the winter season, the high chronic risks to algae were presented by carbamazepine, ibuprofen, atrazine and simazine. On daphnids, the high risks were presented by carbamazepine, ibuprofen, atrazine, simazine and terbuthylazine. On fish, the high risks were presented by ibuprofen, simazine, terbuthylazine and 17-alpha-ethinylestradiol.

In wastewater effluent, individual ecological risk assessments in general showed high ecological risks mostly from acetaminophen, carbamazepine, ibuprofen, triclosan, atrazine, metolachlor, simazine, terbuthylazine, estradiol, 17-alpha-ethinylestradiol, and progesterone. The majority (92%) of the targeted emerging contaminants showed the possibility of high acute risks, while 67% showed the possibility of high chronic risks. Most notable for acute risks in wastewater effluents were high risks of carbamazepine, ibuprofen, atrazine, simazine, and 17-alpha-ethinylestradiol, which occurred on all species in all seasons. Moreover, only ibuprofen and simazine high risks were observed on all species in all seasons. The high ecological risks of acetaminophen, ibuprofen, triclosan, atrazine, simazine, terbuthylazine, estradiol, 17-alpha-ethinylestradiol, progesterone, and metolachlor in effluent were also reported in other studies (Cardini et al., 2021; Lin et al., 2020; Santos et al., 2007; Shao et al., 2019; Ying et al., 2009). The high ecological risks of these contaminants may be attributed to their low removal rate in WWTPs (Cardini et al., 2021). Moreover, their high RQ values may be caused by some working faults of the WWTPs and current electricity load shedding problems in the country. This factors may cause the composition of influent wastewater not to change much in effluent samples. Most of the time, wastewater effluent is discharged into downstream rivers after being treated by WWTPs. The release of effluents with unremoved pollutants into nearby water streams may contribute to the river contamination, which may lead to detrimental effects to aquatic organisms and human beings. At the same time, the combined effect of multiple emerging contaminants may further increase the level of ecological risk, which will affect and persecute the survival of aquatic organisms (Pei et al., 2022). Exposure to PPCPs such as ibuprofen and triclosan may decrease the reproduction rate in fish, increase the level of estradiol hormones (Veldhoen et al., 2014), reduce sperm counts in male fish and reduce the time of producing eggs in fish (Olujimi et al., 2010). Exposure to steroid hormones such as estradiol, progesterone and 17-alpha-ethinylestradiol is associated with serious medical conditions in both aquatic and terrestrial animals (Olujimi et al., 2010). Their exposure is associated with the development of vaginal and breast cancers in humans and uterine cancers in animals (Birnbaum and Fenton, 2003). Moreover, they cause embryo deformation and mortality, impaired reproduction and growth in fish (Yazdan et al., 2022). Triazine herbicides are another class of chemical pesticides that have been related to endocrine-disrupting effects and reproductive toxicity (Jin et al., 2014). During fieldwork, it was noticed that wastewater effluents were being used by small-scale farmers for irrigating vegetables. Therefore, the threats of these compounds are not only limited to aquatic organisms but also to human beings as the consumption of such vegetables entail a potential threat to human health due to bioaccumulation (Wang et al., 2018). Continuous monitoring and improvement of the treatment methods should be implemented in this catchment in order to decrease the high ecological risks of these compounds for safer reuse in the future.

Table 4.13 Acute and chronic toxicity of individual emerging contaminants in effluent

Contaminant	Species	Spring		Summer		Autumn		Winter	
		HQ* mean	Risk	HQ mean	Risk	HQ mean	Risk	HQ mean	Risk
Acute toxicity of contaminants in effluent									
Acetaminophen	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	–	–	–	–	–	–	–	–
Carbamazepine	Algae	25.8	High	52.5	High	19.69	High	11	High
	Daphnids	155	High	255	High	99.05	High	57	High
	Fish	26.5	High	48	High	17.8	High	7	High
Ibuprofen	Algae	13.6	High	11.81	High	6.57	High	7	High
	Daphnids	134 375	High	116 250	High	64 688	High	68 438	High
	Fish	43	High	37	High	20.7	High	22	High
Triclosan	Algae	214	High	–	–	–	–	–	–
	Daphnids	308	High	–	–	–	–	–	–
	Fish	461	High	–	–	–	–	–	–
Atrazine	Algae	1017	High	678	High	847	High	508	High
	Daphnids	8.69	High	5.79	High	7.25	High	4	High
	Fish	13.33	High	8.89	High	11.11	High	7	High
Metolachlor	Algae	0.33	Medium	1.22	High	1.05	High	0.04	Low
	Daphnids	1	Medium	2.98	High	2.55	High	0.85	Medium
	Fish	5	High	17.95	High	15.38	High	5	High
Simazine	Algae	5 250	High	11 000	High	6 000	High	108 000	High
	Daphnids	210	High	400	High	218	High	3 927	High
	Fish	23.33	High	48.89	High	26.67	High	480	High
Terbuthylazine	Algae	3 000	High	3 500	High	1 000	High	1 000	High
	Daphnids	15.38	High	1.78	High	0.51	Medium	0.51	Medium
	Fish	16.66	High	19.44	High	5.56	High	6	High
17-alpha-ethinylestradiol	Algae	20 750 000	High	16 975 000	High	51 750 000	High	22 375 000	High
	Daphnids	13 833 333	High	11 316 667	High	34 500 000	High	14 916 667	High
	Fish	8 300 000	High	6 790 000	High	20 700 000	High	8 950 000	High
Estradiol	Algae	18 750	High	–	–	–	–	–	–
	Daphnids	1 000	High	–	–	–	–	–	–
	Fish	1 000	High	–	–	–	–	–	–
Progesterone	Algae	10 000	High	–	–	–	–	–	–
	Daphnids	1 428	High	–	–	–	–	–	–
	Fish	–	–	–	–	–	–	–	–
Testosterone	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	–	–	–	–	–	–	–	–
Chronic toxicity of contaminants in effluent									
Acetaminophen	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	–	–	–	–	–	–	–	–
Carbamazepine	Algae	9.3	High	17	High	6.3	High	3.6	High
	Daphnids	1 860	High	3 360	High	1 260	High	720	High
	Fish	0.4	Medium	0.67	Medium	0.25	Medium	0.144	Medium
Ibuprofen	Algae	43 000	High	37 200	High	20 700	High	21 900	High
	Daphnids	215	High	151	High	84.15	High	89	High
	Fish	43 000	High	37 200	High	20 700	High	21 900	High
Triclosan	Algae	60	High	–	–	–	–	–	–
	Daphnids	0.03	Medium	–	–	–	–	–	–
	Fish	0.02	Medium	–	–	–	–	–	–
Atrazine	Algae	60	High	40	High	50	High	30	High
	Daphnids	30	High	20	High	25	High	15	High
	Fish	0.3	Medium	1	Medium	0.25	Medium	0.15	Medium
Metolachlor	Algae	0.67	Medium	2	High	2	High	0.67	Medium
	Daphnids	0.33	Medium	1	Medium	1	Medium	0.33	Medium
	Fish	0.2	Medium	0.7	Medium	0.6	Medium	0.2	Medium
Simazine	Algae	35	High	73	High	40	High	720	High
	Daphnids	21	High	37	High	20	High	3 600	High
	Fish	3	High	6	High	3.43	High	62	High
Terbuthylazine	Algae	–	–	–	–	–	–	–	–
	Daphnids	14.28	High	17	High	4.76	High	4.80	High

Contaminant	Species	Spring		Summer		Autumn		Winter	
		HQ* mean	Risk	HQ mean	Risk	HQ mean	Risk	HQ mean	Risk
	Fish	4.61	High	5	High	1.54	High	1.54	High
17-alpha-ethinylestradiol	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	5 533	High	4 527	High	13 800	High	5 967	High
Estradiol	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	0.7	Medium	-	-	-	-	-	-
Progesterone	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	–	–	–	–	–	–	–	–
Testosterone	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	–	–	–	–	–	–	–	–

Notation HQ=High quotient

4.4.2 Mixture risk assessment

Ecological risk assessment of emerging contaminants in water sources is still frequently done, substance by substance, ignoring mixture effects, which may underestimate the true risks to the ecosystem (Maasz et al., 2019). As the knowledge on the mixture toxicity of emerging contaminants towards various aquatic organisms within the Modder River catchment is still limited, the study used the concentration addition method to assess the mixture toxicity of emerging contaminants towards algae, daphnids, and fish. Concentration addition in this study was approximated by RQmix and TUsum approaches (Backhaus and Faust, 2012; Backhaus and Karlsson, 2014; Backhaus et al., 2013; Białk-Bielińska et al., 2022; Kienzler et al., 2019; Maasz et al., 2019).

The mixture risk assessment consisted of either acetaminophen, carbamazepine, ibuprofen, triclosan, atrazine, metolachlor, simazine, terbuthylazine, 17-alpha-ethinylestradiol, estradiol, progesterone, or testosterone. The composition of each mixture was established based on the results obtained for single compounds. Their observed RQ values towards algae, daphnids, and fish were then summarised in order to predict mixture toxicity (RQmix). According to this approach, the environmental quality standard was exceeded when RQmix was above 1 (Backhaus and Faust, 2012; Backhaus and Karlsson, 2014; Backhaus et al., 2013; Białk-Bielińska et al., 2022).

Moreover, the risk mixture was also based on the TUsum applied for each trophic level. In order to apply the same threshold of 1 as for the other metrics, the specific assessment factor for selected organisms was applied to each toxic unit (Backhaus and Karlsson, 2014; Finckh et al., 2022; Malaj et al., 2014; Markert et al., 2020) for both acute and chronic toxicity. The highest TUsum (a worst-case risk scenario) between the three trophic levels such as algae, daphnids and fish was used to define the mixture risks of contaminants (Backhaus and Faust, 2012; Backhaus and Karlsson, 2014; Finckh et al., 2022; Kienzler et al., 2019). Mixture risk assessment for contaminants below limit of quantification and with no experimental toxicity data on algae, daphnids, and fish were not assessed.

4.4.2.1 Mixture risk assessment in rivers

The acute and chronic mixture toxicity estimates for various contaminants in rivers during the spring, summer, autumn, and winter seasons are presented in Table 4.14. Based on the RQmix, the acute mixture risk of contaminants on algae, daphnids, and fish far exceeded the threshold of 1 during all seasons. As presented in Figure 4.9, the highest mixture risks for algae were observed in the summer season, indicating that it is likely to suffer more acute risks in summer seasons. For daphnids and fish, the highest mixture risks were observed during the autumn season, indicating that these aquatic species are likely to suffer more acute risks in such seasons. The RQmix results, based on chronic toxicity in rivers, also exceeded the acceptable limit for all selected aquatic organisms (algae, daphnids, and fish) in all seasons as presented in Table 4.14. The highest chronic mixture risks for algae, daphnids, and fish in the Modder River catchment were observed during the

spring season, indicating that aquatic organisms are more likely to suffer chronic toxicity risks during the spring season. Furthermore, mixture risks were assessed using the TUsum based on acute and chronic toxicity on algae, daphnids, and fish (Table 4.14). For acute mixture risks, algae had the highest TUsum in all seasons, while for chronic risk for fish showed the highest mixture risks in summer, autumn, and winter and during the spring season it was algae that showed the highest mixture risks (Figure 4.9). Therefore, the TUsum results for both acute and chronic toxicity revealed high mixture risks (TUsum > 1) for algae, daphnids, and fish in all seasons.

Table 4.14 Acute and chronic mixture toxicity of emerging contaminants in rivers

Species	Risk quotient mixture (RQmix)				Toxic unit sum (TUsum)			
	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter
Acute mixture risks								
Algae	160 92 952	93 382 460	39 466 956	15 438 125	15 318 534	976 8874	39 470 510	15 438 125
Daphnids	10 740 539	6 531 503	26 323 104	10 352 486	10 244 105	6 529 067	26 304 771	10 352 153
Fish	6 402 634	3 895 182	15 775 254	617 135	6 113 265	3 895 205	15 765 267	6 170 134
Chronic mixture risks								
Algae	22 990	11 826	10 008	22 149	22 536	11 859	10 009	22 149
Daphnids	1 463	319	942	782	1 431	5 930	941	794
Fish	26 335	3 083	19 731	26 124	14 222	26 295	19 735	26 124

The findings of this study are comparable to those of Bouzas-Monroy et al. (2022), who discovered that the RQmix of emerging contaminants in rivers in Africa, Asia, Europe, South and North America were greater than one. Based on TUsum, the trophic level with the highest toxic unit sum should be used to assess the final mixture risks (Kienzler et al., 2019). Therefore, for the acute mixture risk, algae had the highest TUsum in all seasons (Figure 4.9), which is consistent with previous research (Kienzler et al., 2019). In the case studies from European rivers (Kienzler et al., 2019) and the Erft River in Germany (Markert et al., 2020,) risk mixtures based on sum of toxic units were also found to be above the acceptable limit. which support the findings of this study. The findings of this study proved that the majority of the rivers in the Modder River catchment were not safe and were likely to have acute and chronic effects on sensitive algae, daphnids, and fish, which is concerning. According to Thrupp et al. (2018), regardless of the chemical composition, the exposed organism, and the considered biological endpoint, a chemical mixture will always have a greater toxic effect than the individual effect of each of its constituents, which supports the findings of this study. There are evidence showing that mixtures of emerging contaminants often have unexpected toxicity when compared to individual chemicals, resulting in immobilisation, higher rates of death, and deformity in exposed organisms than predicted by the single pollutant (Heys et al., 2016; Shore et al., 2014).

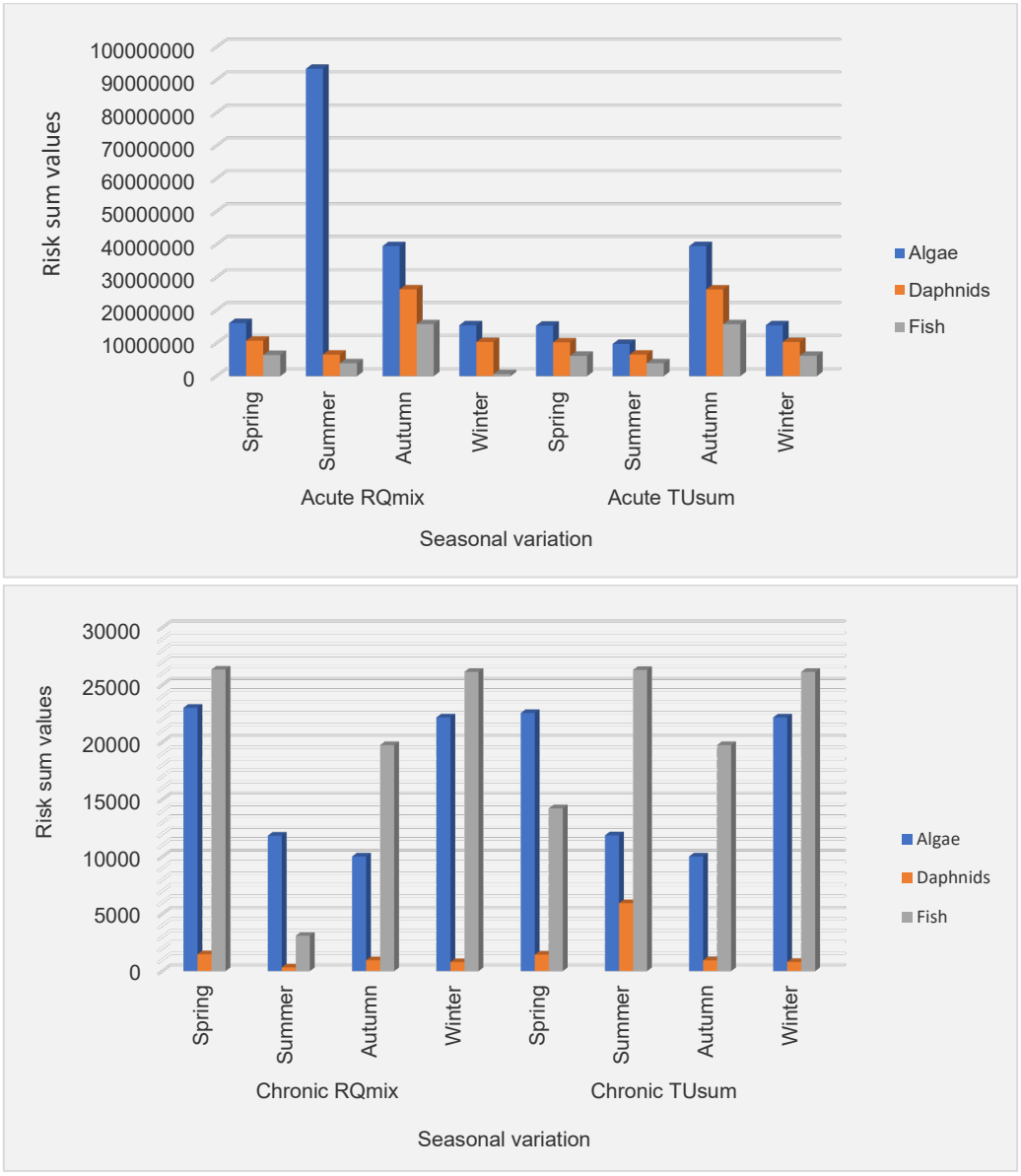


Figure 4.9 Mixture risk assessment of emerging contaminants in rivers within the Modder River catchment

4.4.2.2 Mixture risk assessment in dams

As shown in Table 4.15, the acute mixture risks based on RQmix on algae, daphnids, and fish exceeded the threshold of 1 by a wide margin in all seasons. The highest acute mixture risks to selected species in dams within the Modder River catchment were observed during the autumn season, indicating that these species are likely to suffer from high acute risks during the autumn season (Figure 4.10). For chronic risks to algae, daphnids, and fish, the RQmix values (Table 4.15) exceeded the acceptable limit in all seasons. The highest chronic mixture risks to all selected aquatic organisms were observed during the autumn season, indicating that aquatic organisms are more likely to suffer chronic risks during the autumn season (Figure 4.10). Furthermore, the results for both acute and chronic risks based on the TUsum in dams demonstrated high mixture risks (Tusum > 1) for algae, daphnids, and fish in all seasons (Table 4.15). The worst-case scenario on acute mixture risks was observed for algae in all seasons. The worst-case scenario for chronic risks was observed on fish in all seasons (Figure 4.10).

The TUsum results agreed with the RQmix that most of the dams in the Modder River catchments were unsafe. This situation is likely to endanger aquatic species both acutely and chronically. The dams in the Modder River catchment are constantly exposed to emerging contaminants introduced by rivers that discharge their water into them, as well as various anthropogenic activities. The high acute and chronic mixture risks of compounds detected in dams on aquatic organisms are alarming because they can have serious consequences for aquatic organisms and reach the top of the food chain via bioaccumulation and biomagnification processes (Paun et al., 2022). Because some of the dams are used as fishing spots, they may pose an indirect risk to human health. Exposure to such high-risk water and species ingestion by fish may result in chronic toxicity, endocrine-disruption in humans and aquatic wildlife, and the development of bacterial pathogen resistance (Paun et al., 2022). According to Bouzas-Monroy et al. (2022), contaminated sites with intolerable mixture risks may have unacceptable effects on algal growth, daphnia reproduction, and fish biochemistry and physiology. Furthermore, the degradation products of these compounds may be more toxic in the short and long-term than their parent compounds, and may contribute to the development of antibiotic resistance genes (Gozzo et al., 2023).

Table 4.15 Acute and chronic mixture toxicity of emerging contaminants in dams

Species	Risk quotient mixture (RQmix)				Toxic unit sum (TUsum)			
	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter
Acute mixture risks								
Algae	4 591 849	2 293 755	8 628 672	3 480 180	4 592 430	2 294 760	8 635 023	3 480 180
Daphnids	3 067 868	1 525 157	5 750 749	231 810	3 067 131	1 525 137	5 750 752	2 317 143
Fish	1 835 037	91 539	3 450 023	1 390 036	1 835 034	915 043	2 300 020	1 390 034
Chronic mixture risks								
Algae	3 040	26	231	64	3 030	54	231	64
Daphnids	617	279	34	245	633	288	179	161
Fish	4227	617	1 155	1 046	4 224	616	2 313	931

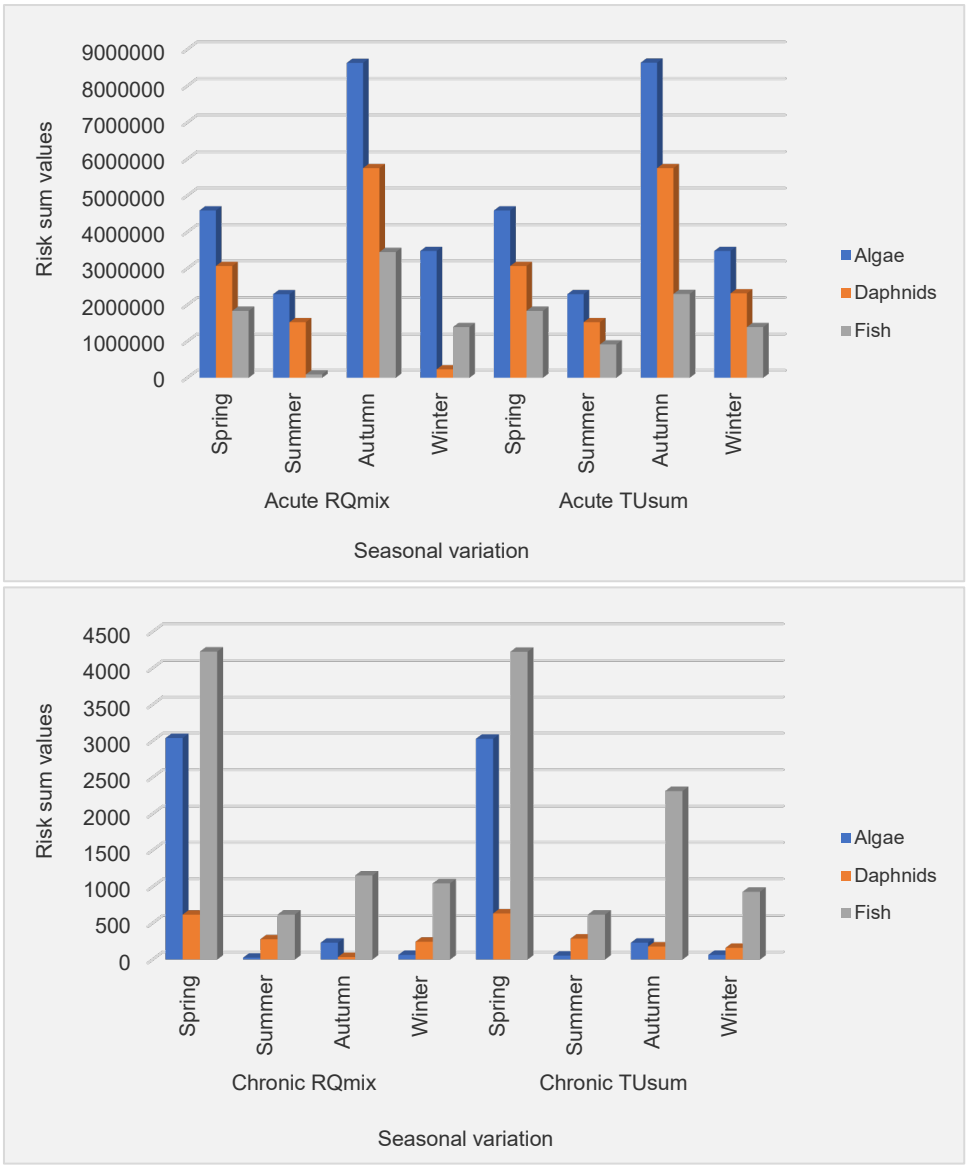


Figure 4.10 Mixture risk assessment of emerging contaminants in dams within the Modder River catchment

4.4.2.3 Mixture risk assessment in treated drinking water

The RQmix assessment, based on acute risks to algae, daphnids, and fish in treated drinking water revealed mixture risk values greater than one in all seasons, as shown in Table 4.16. The results of acute mixture risks revealed that the spring season had the highest mixture risk values for all aquatic organisms studied (Figure 4.11). The mixture risk values were also above the acceptable limit, based on chronic toxicity in algae, daphnids, and fish in all seasons, as presented in Table 4.16. The results of chronic mixture risks revealed that the spring season had the highest values of mixture risks to all aquatic organisms (Figure 4.11). Furthermore, acute and chronic mixture risks to algae, daphnids, and fish based on TUsum were investigated (Table 4.16). In all seasons, the TUsum results for both acute and chronic toxicity showed high mixture risks values (TUsum > 1) for algae, daphnids, and fish. Algae showed the worst-case scenario for acute mixture toxicity in all seasons. Fish had the highest toxic unit summation value for chronic mixture risks in all seasons (Figure 4.11).

Table 4.16 Acute and chronic mixture toxicity of emerging contaminants in treated drinking water

Species	Risk quotient mixture (RQmix)				Toxic unit sum (TUsum)			
	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter
Acute mixture risks								
Algae	1 827 094	255 687	913 339	55 839	18 26 343	256 001	913 840	550 839
Daphnids	1 217 045	16 6681	608 337	366 671	1 217 024	167 014	608 004	366 670
Fish	730 020	100 054	365 012	220 010	730 017	100 042	365 017	220 010
Chronic mixture risks								
Algae	37	72	3	20	22	72	94	20
Daphnids	280	57	13	13	265	57	13	13
Fish	498	75	244	148	492	77	241	148

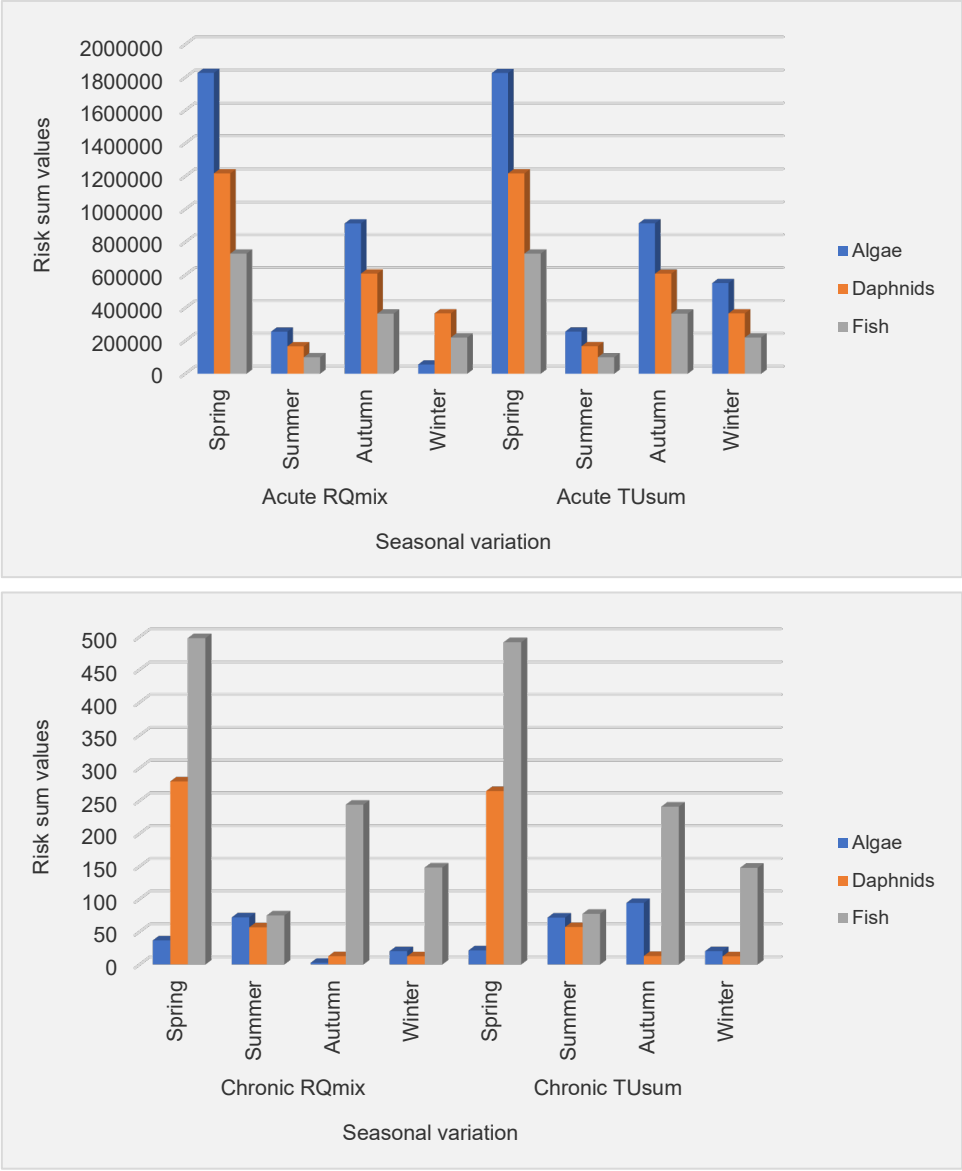


Figure 4.11 Mixture risk assessment of emerging contaminants in treated drinking water

These findings are concerning for water consumers because exposure to water contaminated by compounds with such high risks could have serious consequences as most of them are known toxins. Long-term exposure to contaminated water may have negative consequences for both water consumers and aquatic species. Once the various emerging contaminants are taken up by the organisms, biotransformation may occur with the

production of secondary metabolites, with possible interactions between chemicals in the mixture, such as synergism or antagonism (Ojemaye et al., 2022). The environmental health risks associated with the exposure to mixture of emerging contaminants for aquatic species and water consumers include damage to the olfactory tissues, lowering of the immune responses, alteration of steroidogenic pathways, thyroid disease, low sperm quality, and causing reproductive system disorders among women (Belden et al., 2007; Ferrari et al., 2017; Heys et al., 2016; Hunt et al., 2016; Ojemaye et al., 2022; Selvaraju et al., 2021). The outcomes of this study will play a significant role in raising awareness on cumulative effects of chemical mixtures and in protecting the public and environmental health.

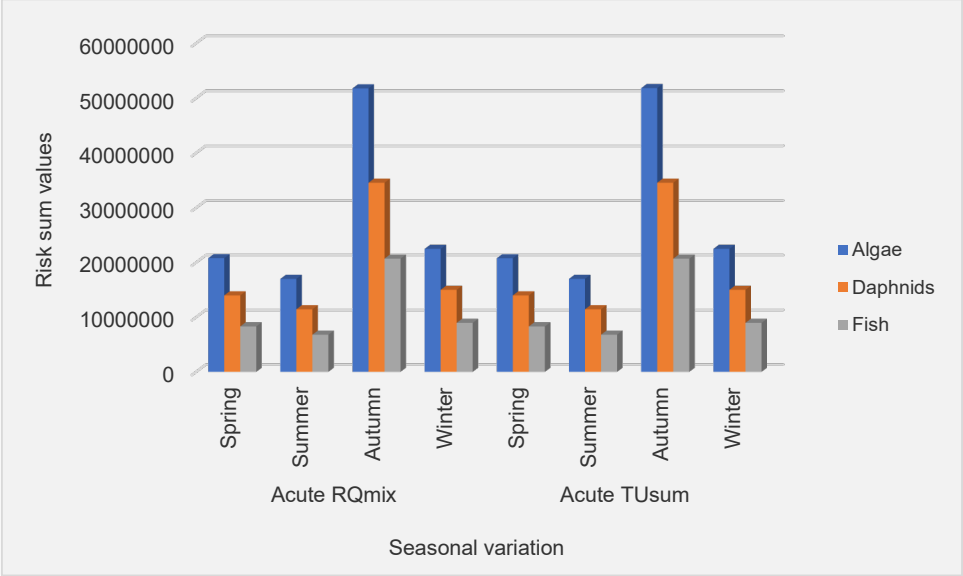
4.4.2.4 Mixture risk assessment in wastewater effluents

The RQmix assessment, based on acute toxicity on algae, daphnids, and fish in wastewater effluents revealed risk mixture values greater than one in all seasons, as presented in Table 4.17. The highest acute mixture risk values for contaminants in effluents for algae, daphnids, and fish were observed during the autumn season (Figure 4.12), indicating that these organisms are not safe in the autumn season. The mixture risk assessment based on chronic risks to algae, daphnids, and fish in effluents in all seasons were also above the acceptable limit. The highest chronic mixture risk of emerging contaminants was observed in fish in all seasons (Figure 4.12). Based on TUsum, the mixture risks for both acute and chronic toxicity on algae, daphnids, and fish exceeded the risk threshold limit (TUsum > 1) in all seasons (Table 4.17). The highest toxic unit summation values for acute toxicity were observed in algae in all seasons. Fish had the highest toxic unit summation value for chronic toxicity (Figure 4.12).

Table 4.17 Acute and chronic mixture toxicity of emerging contaminants in effluents

Species	Risk quotient mixture (RQmix)				Toxic unit sum (TUsum)			
	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter
Acute mixture risks								
Algae	20 788 271	16 990 244	51 757 874	22 484 526	20 764 817	16 990 744	51 811 881	22 484 527
Daphnids	13 970 834	11 433 583	34 565 015	14 989 094	13 969 110	11 433 675	34 565 348	14 989 427
Fish	8 301 589	6 790 180	20 700 097	8 950 527	8 300 627	6 790 179	20 700 110	8 95 0530
Chronic mixture risks								
Algae	43 165	37 322	20 798	22 654	43 097	162 433	20 798	22 654
Daphnids	2 141	3 586	1 395	4 429	408	3 574	1 385	1 189
Fish	48 542	41 740	34 506	27 931	48 535	41 827	34 506	27 930

The RQmix findings are comparable to those of a study conducted in European WWTPs (Finckh et al., 2022) and in wastewater effluent from the Republic of Ireland (Rapp-Wright et al., 2023), both of which reported that the mixture risk assessment of emerging contaminants in effluent samples were greater than one. Finckh et al. (2022) found that the TUsum value of contaminants in effluents exceeded the risk threshold, which is consistent with the findings of this study. From the results of both RQmix and TUsum it was clear that effluents in this study were not safe as they were significantly higher than the acceptable limit. The majority of wastewater effluents are discharged into nearby streams. This is concerning, given that environmental mixtures of emerging contaminants may unexpectedly have negative effects on aquatic ecosystems and, eventually, humans. The discharge of these wastewater effluents into natural water bodies, such as rivers, exposes aquatic organisms to emerging contaminants. Furthermore, rivers that receive effluent from treatment plants discharge their water in dams within the Modder River catchment, potentially endangering the water ecosystem. As a result, it causes morbidity and mortality in organisms by interfering with processes like reproduction and development (Heys et al., 2016). Advanced treatment should be implemented to remove these compounds. When treating wastewater, WWTPs should prioritise these contaminants as well. This will help to reduce their concentration and, as a result, their potential risks.



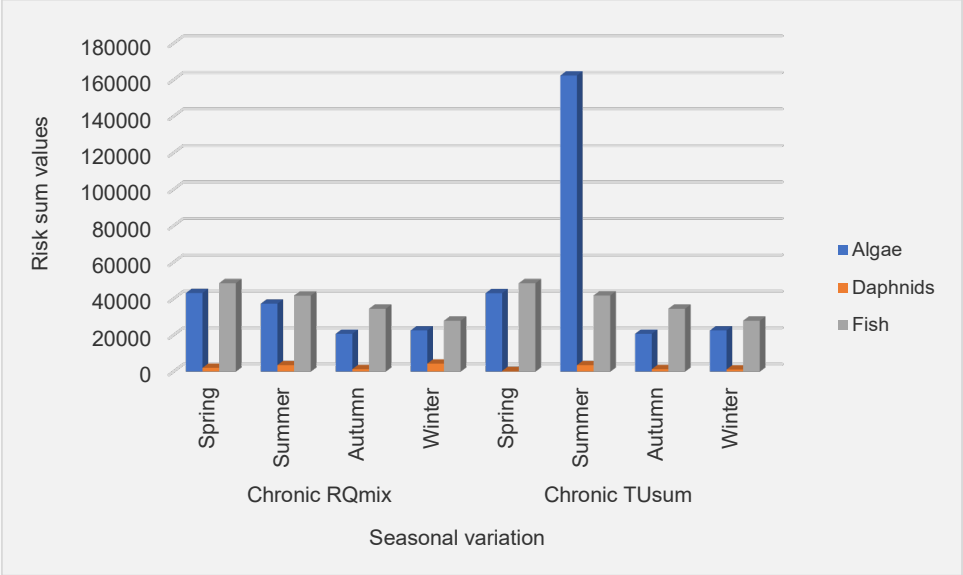


Figure 4.12 Mixture risks assessment of emerging contaminants in wastewater effluent

4.5 SOURCES OF EMERGING CONTAMINANTS IN THE MODDER RIVER CATCHMENT

4.5.1 Source identification with the Pearson correlation analysis

The Pearson correlation coefficient analysis was performed to establish the relationship 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). According to Mugudamani et al. (2022) and Zhao et al. (2019), a strong correlation between contaminants suggests a possible common source or similar chemical behaviour. The results of the Pearson correlation analysis in this study are presented and discussed in this section as per their sources.

4.5.1.1 Identification of pollution pathways in rivers

Table 4.18 shows the Pearson correlation matrix of the emerging contaminants in rivers in the spring and summer seasons. In the spring season, the strong correlation among the contaminants was between terbuthylazine and atrazine, carbamazepine and atrazine, metolachlor and atrazine, ibuprofen and carbamazepine, 17-alpha-ethinylestradiol and atrazine, 17-alpha-ethinylestradiol and carbamazepine, as well as between 17-alpha-ethinylestradiol and metolachlor. In the summer season, the analysis showed a strong positive correlation between atrazine and simazine, terbuthylazine and simazine, terbuthylazine and atrazine, metolachlor and simazine, metolachlor and atrazine, metolachlor and terbuthylazine, ibuprofen and carbamazepine, 17-alpha-ethinylestradiol and metolachlor, 17-alpha-ethinylestradiol and simazine, 17-alpha-ethinylestradiol and atrazine, 17-alpha-ethinylestradiol and terbuthylazine, 17-alpha-ethinylestradiol and metolachlor, as well as between 17-alpha-ethinylestradiol and ibuprofen.

Table 4.18 Correlation coefficients among emerging contaminants in the wet season in rivers

Contaminants	Aceta-minophen	Simazine	Atrazine	Terbu-thylazine	Carba-mazepine	Metola-chlor	Testos-terone	Proges-terone	Ibuprofen	Estradiol	Triclosan	17-alpha-ethinyl-estradiol
Spring												
Acetaminophen	1											
Simazine	-0.50	1										
Atrazine	-0.58	0.69	1									
Terbuthylazine	-0.51	1.00	**0.70**	1								
Carbamazepine	-0.40	0.58	**0.71**	0.60	1							
Metolachlor	-0.41	0.20	**0.84**	0.21	0.43	1						
Testosterone	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				
Ibuprofen	0.05	0.61	0.32	0.62	**0.77**	-0.11	0.00	0.00	1			
Estradiol	0.58	0.31	-0.01	0.29	-0.23	-0.18	0.00	0.00	0.24	1		
Triclosan	0.38	-0.97	-0.49	-0.96	-0.48	0.06	0.00	0.00	-0.67	-0.38	1	
17-alpha-ethinyl-esdradiol	-0.52	0.28	**0.84**	0.30	**0.77**	**0.88**	0.00	0.00	0.23	-0.42	-0.06	1
Summer												
Acetaminophen	1											
Simazine	0.00	1										
Atrazine	0.00	**0.98**	1									
Terbuthylazine	0.00	**0.84**	**0.73**	1								
Carbamazepine	0.00	-0.07	-0.03	-0.06	1							
Metolachlor	0.00	**0.91**	**0.86**	**0.90**	0.24	1						
Testosterone	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				
Ibuprofen	0.00	0.31	0.35	0.22	**0.92**	0.57	0.00	0.00	1			
Estradiol	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	0.0	1	
17-alpha-ethinyl-estradiol	0.00	**0.77**	**0.74**	**0.76**	0.54	**0.95**	0.00	0.00	**0.80**	0.0	0.00	1

Notation: Numbers in bold represent strong correlations

In the autumn season, there was a strong correlation between atrazine and simazine, terbuthylazine and simazine, terbuthylazine and atrazine, carbamazepine and simazine, carbamazepine and atrazine, carbamazine and terbuthylazine, metolachlor and atrazine, metolachlor and terbuthylazine, matolachlor and carbamazepine, 17-alpha-ethinylestradiol and simazine, 17-alpha-ethinylestradiol and atrazine, 17-alpha-ethinylestradiol and terbuthylazine, 17-alpha-ethinylestradiol and carbamazepine and 17-alpha-ethinyl-estradiol and metolachlor. In the winter season, the strong correlation was between terbuthylazine and atrazine, metolachlor and simazine, ibuprofen and simazine, ibuprofen and metolachlor, 17-alpha-ethinylestradiol and atrazine, 17-alpha-ethinylestradiol and terbuthylazine, and 17-alpha-ethinylestradiol and metolachor (Table 4.19).

Table 4.19 Correlation coefficients among emerging contaminants in the dry season in rivers

Contaminants	Aceta-minophen	Simazine	Atrazine	Terbu-thylazine	Carba-mazepine	Metola-chlor	Testos-terone	Proges-terone	Ibuprofe	Estradiol	Triclosan	17-alpha-ethinyl-estradiol
Autumn												
Acetaminophen	1											
Simazine	0.00	1										
Atrazine	0.00	**0.74**	1									
Terbuthylazine	0.00	**0.98**	**0.82**	1								
Carbamazepine	0.00	**0.74**	**0.86**	**0.85**	1							
Metolachlor	0.00	0.60	**0.93**	**0.71**	**0.93**	1						
Testosterone	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				
Ibuprofen	0.00	0.23	0.24	0.35	0.39	0.20	0.00	0.00	1			
Estradiol	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	1	
17-alpha-ethinyl-esdradiol	0.00	**0.91**	**0.78**	**0.95**	**0.93**	**0.78**	0.00	0.00	0.31	0.00	0.00	1
Winter												
Acetaminophen	1											
Simazine	-0.25	1										
Atrazine	-0.31	0.12	1									
Terbuthylazine	-0.36	0.32	**0.98**	1								
Carbamazepine	0.07	0.34	0.30	0.36	1							
Metolachlor	-0.38	**0.94**	0.46	0.63	0.43	1						
Testosterone	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				
Ibuprofen	0.29	**0.83**	0.15	0.31	0.52	**0.77**	0.00	0.00	1			
Estradiol	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	1	
17-alpha-ethinyl-estradiol	-0.30	0.53	**0.80**	**0.88**	**0.74**	**0.76**	0.00	0.00	0.54	0.00	0.00	1

Notation: Numbers in bold represent strong correlations

The strong positive correlations between emerging contaminants are an indication of the same sources of pollution, potentially from man-made activities. The Pearson correlation coefficient analysis revealed a strong positive correlation between the pesticides atrazine and simazine, terbuthylazine and atrazine, terbuthylazine and simazine, metolachlor and simazine, metolachlor and atrazine, and metolachlor and terbuthylazine, which may be attributed to agricultural activities, wastewater effluents, and stormwater runoff from roads, settlements and urban areas. Most of the rivers are surrounded by the agricultural activities producing maize, soybeans, wheat, sorghum, and sunflower, which necessitate the use of weed control herbicides before, during, and after farming. Moreover, the city of Bloemfontein is a developed area with well-developed roads, public parks, industrial areas, and golf courses. With all these noticeable areas, significant amounts of herbicides are applied to control weeds in paving, parks, golf courses, roadsides, buildings, and industrial areas. Therefore, runoff from agricultural fields, and stormwater from roads, public squares, golf courses, and industrial areas may be attributed as possible sources of these herbicides in nearby streams. The strong positive correlations between compounds such as ibuprofen and carbamazepine, 17-alpha-ethinylestradiol and ibuprofen, and 17-alpha-ethinylestradiol and carbamazepine also suggest similar sources of origin. These contaminants are medical drugs, and their origin can be linked to wastewater effluents and illegal dumping of household waste nearby the streams. Wastewater treatment plants receive domestic and industrial waste, as well as from hospitals, which contain loads of various pharmaceutical compounds used in our daily lives. As WWTPs are not designed to remove these organic 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, the strong positive correlations between contaminants such as carbamazepine and atrazine, carbamazepine and simazine, carbamazepine and terbuthylazine, metolachlor and carbamazepine, ibuprofen and metolachlor, ibuprofen and simazine, 17-alpha-ethinylestradiol and atrazine, 17-alpha-ethinylestradiol and simazine, 17-alpha-ethinylestradiol and terbuthylazine, and 17-alpha-ethinylestradiol and

metolachlor, are indications of similar sources of emissions. Some of the rivers run through townships and cities; hence, runoff from clogged sewage systems, or improper waste disposal may have introduced these contaminants in rivers. Additionally, because selected WWTPs receive wastewater from households, the industries and hospitals their wastewater effluents discharged into nearby streams may introduce traces of these emerging contaminants usually categorised as medical drugs and pesticides.

4.5.1.2 Identification of pollution ways in dams

From the correlation analysis in Table 4.20, the spring season showed the strong positive correlations between pairs of terbuthylazine and simazine, terbuthylazine and atrazine, carbamazepine and acetaminophen, metolachlor and simazine, metolachlor and atrazine, metolachlor and terbuthylazine, ibuprofen and acetaminophen, ibuprofen and carbamazepine, 17-alpha-ethinylestradiol and acetaminophen, and 17-alpha-ethinylestradiol and carbamazepine. During the summer season, the strong positive correlations were witnesses between pairs of atrazine and simazine, terbuthylazine and simazine, terbuthylazine and atrazine, carbamazepine and terbuthylazine, metolachlor and atrazine, as well as 17-alpha-ethinylestradiol (Table 4.20).

Table 4.20 Correlation coefficients among emerging contaminants during the wet season in dams

Contaminants	Aceta-minophen	Simazine	Atrazine	Terbu-thylazine	Carba-mazepine	Metola-chlor	Testos-terone	Proges-terone	Ibuprofen	Estradiol	Triclosan	17-alpha-ethinyl-estradiol
Spring												
Acetaminophen	1											
Simazine	0.44	1										
Atrazine	0.10	0.69	1									
Terbuthylazine	0.66	**0.93**	**0.73**	1								
Carbamazepine	**0.76**	0.10	-0.53	0.18	1							
Metolachlor	0.15	**0.89**	**0.92**	**0.84**	-0.35	1						
Testosterone	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				
Ibuprofen	**0.97**	0.22	-0.13	0.45	**0.84**	-0.10	0.00	0.00	1			
Estradiol	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	1	
17-alpha-ethinyl-esdradiol	**0.71**	0.60	-0.13	0.56	**0.82**	0.18	0.00	0.00	0.66	0.00	0.00	1
Summer												
Acetaminophen	1											
Simazine	0.00	1										
Atrazine	0.00	**0.85**	1									
Terbuthylazine	0.00	**0.86**	**0.81**	1								
Carbamazepine	0.00	0.37	0.56	**0.77**	1							
Metolachlor	0.00	0.46	**0.78**	0.34	0.21	1						
Testosterone	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				
Ibuprofen	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1			
Estradiol	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	1	
17-alpha-ethinyl-estradiol	0.00	0.13	0.56	0.37	**0.72**	0.47	0.00	0.00	0.00	0.00	0.00	1

Notation: Numbers in bold represent strong correlations

In the autumn season, the strong positive correlations between atrazine and simazine, terbuthylazine and simazine, terbuthylazine and atrazine, metolachlor and simazine, metolachlor and atrazine, metolachlor and terbuthylazine, ibuprofen and atrazine, 17-alpha-ethinylestradiol and carbamazepine, and 17-alpha-ethinyl-estradiol and ibuprofen were witnessed as indicated in bold in Table 4.21. The winter season had strong positive correlations between pairs of terbuthylazine and simazine, metolachlor and simazine, metolachlor and terbuthylazine, as well as 17-alpha-ethinylestradiol (Table 4.21).

Table 4.21 Correlation coefficients among emerging contaminants during the dry season in dams

Contaminants	Aceta-minophen	Simazine	Atrazine	Terbu-thylazine	Carba-mazepine	Metola-chlor	Testos-terone	Proges-terone	Ibuprofen	Estradiol	Triclosan	17-alpha-ethinyl-estradiol
Autumn												
Acetaminophen	1											
Simazine	-0.25	1										
Atrazine	-0.41	**0.89**	1									
Terbuthylazine	-0.27	**0.99**	**0.86**	1								
Carbamazepine	-0.45	-0.23	0.22	-0.24	1							
Metolachlor	-0.24	**0.81**	**0.83**	**0.86**	0.14	1						
Testosterone	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				
Ibuprofen	-0.49	0.41	**0.77**	0.33	0.67	0.41	0.00	0.00	1			
Estradiol	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	1	
17-alpha-ethinyl-esdradiol	-0.29	-0.20	0.27	-0.24	**0.96**	0.11	0.00	0.00	**0.76**	0.00	0.00	1
Winter												
Acetaminophen	1											
Simazine	0.00	1										
Atrazine	0.00	0.05	1									
Terbuthylazine	0.00	**0.84**	-0.24	1								
Carbamazepine	0.00	0.35	0.48	0.38	1							
Metolachlor	0.00	**0.97**	0.20	**0.76**	0.51	1						
Testosterone	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				
Ibuprofen	0.00	-0.08	-0.60	0.47	-0.06	-0.22	0.00	0.00	1			
Estradiol	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	1	
17-alpha-ethinyl-estradiol	0.00	0.61	-0.16	**0.87**	0.69	0.60	0.00	0.00	0.52	0.00	0.00	1

Notation: Numbers in bold represent strong correlations

Generally, the strong positive degree of correlations between herbicides such as terbuthylazine and simazine, metolachlor and atrazine, metolachlor and simazine, metolachlor and terbuthylazine, atrazine and simazine, and terbuthylazine and atrazine indicate a similar source of origin. According to Wang et al. (2022), herbicides can be applied before and after planting to control broadleaf and grassy weeds in agricultural fields. Given that the majority of the dams are surrounded by agricultural fields, runoff from those sites could be a contributing factor. Another strong positive correlation in dams was between ibuprofen and acetaminophen, carbamazepine and acetaminophen, ibuprofen and carbamazepine, 17-alpha-ethinylestradiol and carbamazepine, 17-alpha-ethinylestradiol and acetaminophen, and 17-alpha-ethinylestradiol and ibuprofen, which suggest a similar source of origin. These emerging contaminants are medical drugs used to control seizure (carbamazepine), treat inflammatory diseases, arthritis, fever, and dysmenorrhea (ibuprofen), pains, headaches, fever in humans and animals (acetaminophen), and used as the active ingredient in many oral contraceptives and postmenopausal hormone therapy (17-alpha-ethinylestradiol) around many communities (Ekinci et al., 2020, Nannou et al., 2022). Therefore, their strong positive correlations suggest that they are associated with similar sources such as domestic sewage runoff from nearby communities witnessed during a field visit. Illegal dumping of medical waste from nearby households, during aquatic sports activities, conferences or picnics may also be attributed as one of their possible sources. Moreover, the strong positive correlations between contaminants such as 17-alpha-ethinylestradiol and simazine, ibuprofen and atrazine, and carbamazepine and terbuthylazine, may be linked to sources such as agricultural runoff, and wastewater effluent discharged in rivers that recharge these dams.

4.5.1.3 Identification of pollution ways in treated drinking water

The Pearson correlation analysis (Table 4.22) revealed that most of the emerging contaminants had some strong positive correlations in the spring season. There were strong positive correlations between compounds

such as simazine and acetaminophen, terbuthylazine and atrazine, carbamazepine and acetaminophen, carbamazepine and simazine, metolachlor and acetaminophen, metolachlor and simazine, metolachlor and carbamazepine, ibuprofen and acetaminophen, ibuprofen and simazine, ibuprofen and carbamazepine, ibuprofen and metolachlor, 17-alpha-ethinylestradiol and acetaminophen, 17-alpha-ethinylestradiol and simazine, 17-alpha-ethinylestradiol and carbamazepine, 17-alpha-ethinylestradiol and metolachlor and 17-alpha-ethinylestradiol and ibuprofen. During the summer season, atrazine and simazine, terbuthylazine and simazine, terbuthylazine and atrazine, metolachlor and simazine, metolachlor and atrazine, metolachlor and terbuthylazine, 17-alpha-ethinylestradiol and simazine, 17-alpha-ethinylestradiol and atrazine, 17-alpha-ethinylestradiol and terbuthylazine, and 17-alpha-ethinylestradiol and metolachlor, showed strong positive correlations as shown in bold in Table 4.22.

Table 4.22 Correlation coefficients among emerging contaminants in the wet season in treated drinking water

Contaminants	Aceta-minophen	Simazine	Atrazine	Terbu-thylazine	Carba-mazepine	Metola-chlor	Testos-terone	Proges-terone	Ibuprofen	Estradiol	Triclosan	17-alpha-ethinyl-estradiol
Spring												
Acetaminophen	1											
Simazine	**1**	1										
Atrazine	-1	-1	1									
Terbuthylazine	-1	-1	**1**	1								
Carbamazepine	**1**	**1**	-1	-1	1							
Metolachlor	**1**	**1**	-1	-1	**1**	1						
Testosterone	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				
Ibuprofen	**1**	**1**	-1	-1	**1**	**1**	0.00	0.00	1			
Estradiol	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	1	
17-alpha-ethinyl-esdradiol	**1**	**1**	-1	-1	**1**	**1**	0.00	0.00	**1**	0.00	0.00	1
Summer												
Acetaminophen	1											
Simazine	0.0	1										
Atrazine	0.00	**1**	1									
Terbuthylazine	0.00	**1**	**1**	1								
Carbamazepine	0.00	0.00	0.00	0.00	1							
Metolachlor	0.00	**1**	**1**	**1**	0.00	1						
Testosterone	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				
Ibuprofen	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1			
Estradiol	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	1	
17-alpha-ethinyl-estradiol	0.00	**1**	**1**	**1**	0.00	**1**	0.00	0.00	0.00	0.00	0.00	1

Notation: Numbers in bold represent strong correlations

Both autumn and winter seasons showed the strong positive correlations between terbuthylazine and atrazine, metolachlor and atrazine, metolachlor and terbuthylazine, 17-alpha-ethinylestradiol and atrazine, 17-alpha-ethinylestradiol and terbuthylazine and 17-alpha-ethinylestradiol and metolachlor (Table 4.23).

Table 4.23 Correlation coefficients among emerging contaminants in the dry season in treated drinking water

Contaminants	Aceta-minophen	Simazine	Atrazine	Terbu-thylazine	Carba-mazepine	Metola-chlor	Testos-terone	Proges-terone	Ibuprofen	Estradiol	Triclosan	17-alpha-ethinyl-estradiol
Autumn												
Acetaminophen	1											
Simazine	0.00	1										
Atrazine	0.00	0.00	1									
Terbuthylazine	0.00	0.00	**1**	1								
Carbamazepine	0.00	0.00	0.00	0.00	1							
Metolachlor	0.00	0.00	**1**	**1**	0.00	1						
Testosterone	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				
Ibuprofen	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1			
Estradiol	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	1	
17-alpha-ethinyl-esdradiol	0.00	0.00	**1**	**1**	0.00	**1**	0.00	0.00	0.00	0.00	0.00	1
Winter												
Acetaminophen	1											
Simazine	0.00	1										
Atrazine	0.00	0.00	1									
Terbuthylazine	0.00	0.00	**1**	1								
Carbamazepine	0.00	0.00	0.00	0.00	1							
Metolachlor	0.00	0.00	**1**	**1**	0.00	1						
Testosterone	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				
Ibuprofen	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1			
Estradiol	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	1	
17-alpha-ethinyl-estradiol	0.00	0.00	**1**	**1**	0.00	**1**	0.00	0.00	0.00	0.00	0.00	1

Notation: Numbers in bold represent strong correlations

Generally, there were strong positive relationships between pairs of herbicides such as terbuthylazine and atrazine, terbuthylazine and simazine, atrazine and simazine, metolachlor and simazine, metolachlor and atrazine, and metolachlor and terbuthylazine, which indicate that they are probably derived from the same anthropogenic sources. Application of herbicides in surrounding agricultural fields, 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. The strong positive relationships between pairs of carbamazepine and acetaminophen, ibuprofen and acetaminophen, ibuprofen and carbamazepine, 17-alpha-ethinylestradiol and acetaminophen, 17-alpha-ethinylestradiol and carbamazepine and 17-alpha-ethinylestradiol and ibuprofen, which are medical drugs, 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 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. Moreover, the strong positive correlations between simazine and acetaminophen, carbamazepine and simazine, metolachlor and acetaminophen, metolachlor and carbamazepine, ibuprofen and simazine, ibuprofen and metolachlor, simazine and acetaminophen, 17-alpha-ethinylestradiol and simazine, 17-alpha-ethinylestradiol and metolachlor, 17-alpha-ethinylestradiol and atrazine, and 17-alpha-ethinylestradiol and terbuthylazine may be an indicative of similar man-made sources such as stormwater runoff, agricultural runoff, wastewater effluents, or illegal dumping of medical waste around some of the dams.

4.5.1.4 Identification of pollution ways in wastewater treatment plants

The analysis results of the Pearson correlation coefficients of targeted emerging contaminants in wastewater influent are presented in Table 4.24. During the spring season, influent samples showed a strong positive correlation between atrazine and simazine, terbuthylazine and atrazine, carbamazepine and simazine, carbamazepine and terbuthylazine, metolachlor and simazine, metalachlor and terbuthylazine, metolachlor and carbamazepine, progesterone and testosterone, ibuprofen and acetaminophen, ibuprofen and carbamazepine, ibuprofen and metolachlor, triclosan and simazine, triclosan and terbuthylazine, triclosan and carbamazepine, triclosan and metolachlor, triclosan and ibuprofen and 17-alpha-ethinylestradiol. In the summer season, the strong positive correlations were witnessed between atrazine and simazine, terbuthylazine and simazine, terbuthylazine and atrazine, metolachlor and atrazine, metolachlor and terbuthylazine, testosterone and acetaminophen, ibuprofen and atrazine, ibuprofen and terbuthylazine, ibuprofen and metolachlor, estradiol and progesterone, triclosan and carbamazepine, 17-alpha-ethinylestradiol and carbamazepine and 17-alpha-ethinylestradiol and triclosan as presented in Table 4.24.

Table 4.24 Correlation coefficients among emerging contaminants during the wet season in influents

Contaminants	Aceta-minophen	Simazine	Atrazine	Terbu-thylazine	Carba-mazepine	Metola-chlor	Testos-terone	Proges-terone	Ibuprofen	Estradiol	Triclosan	17-alpha-ethinyl-estradiol
Spring												
Acetaminophen	1											
Simazine	-0.08	1										
Atrazine	-0.66	**0.80**	1									
Terbuthylazine	-0.11	1.00	**0.82**	1								
Carbamazepine	0.33	**0.91**	0.50	**0.90**	1							
Metolachlor	0.61	**0.74**	0.19	**0.72**	**0.95**	1						
Testosterone	0.61	-0.84	-1.00	-0.85	-0.55	-0.25	1					
Progesterone	0.12	-1.00	-0.83	-1.00	-0.90	-0.71	**0.86**	1				
Ibuprofen	**0.83**	0.49	-0.12	0.47	**0.80**	**0.95**	0.06	-0.46	1			
Estradiol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1		
Triclosan	0.18	**0.97**	0.62	**0.96**	**0.99**	**0.89**	-0.67	-0.95	**0.70**	0.00	1	
17-alpha-ethinyl-esdradiol	0.16	-1.00	-0.85	-1.00	-0.88	-0.68	**0.88**	1.00	-0.42	0.00	-0.94	1
Summer												
Acetaminophen	1											
Simazine	0.52	1										
Atrazine	-0.01	**0.84**	1									
Terbuthylazine	0.13	**0.91**	**0.99**	1								
Carbamazepine	-0.34	-0.98	-0.94	-0.98	1							
Metolachlor	-0.36	0.60	**0.94**	**0.88**	-0.75	1						
Testosterone	**1**	0.47	-0.07	0.07	-0.28	-0.42	1					
Progesterone	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1				
Ibuprofen	-0.58	0.39	**0.82**	**0.73**	-0.57	**0.97**	-0.63	0.00	1			
Estradiol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	**1**	0.00	1		
Triclosan	-0.36	-0.98	-0.93	-0.97	**1**	-0.74	-0.30	0.00	-0.55	0.00	1	
17-alpha-ethinyl-estradiol	-0.60	-1	-0.79	-0.87	**0.96**	-0.52	-0.55	0.00	-0.30	0.00	**0.96**	1

Notation: Numbers in bold represent strong correlations

In the autumn season, the results showed the strong positive correlations between contaminants such as terbuthylazine and atrazine, carbamazepine and acetaminophen, metolachlor and atrazine, metolachlor/ terbuthylazine, testosterone and acetaminophen, testosterone and carbamazepine, progesterone and acetaminophen, progesterone and carbamazepine, progesterone and testosterone, ibuprofen and acetaminophen, ibuprofen and carbamazepine, ibuprofen and testosterone, ibuprofen and metolachlor progesterone, triclosan and acetaminophen, triclosan and carbamazepine, triclosan and testosterone, triclosan and progesterone, triclosan and ibuprofen, 17-alpha-ethinylestradiol and acetaminophen, 17-alpha-

ethinylestradiol and carbamazepine, 17-alpha-ethinylestradiol and testosterone, 17-alpha-ethinylestradiol and progesterone, 17-alpha-ethinylestradiol and ibuprofen and 17-alpha-ethinylestradiol and triclosan. The winter season revealed a strong positive correlations between atrazine and simazine, terbuthylazine and simazine, terbuthylazine and atrazine, metolachlor and simazine, metolachlor and atrazine, progesterone and acetaminophen, ibuprofen and acetaminophen, 17-alpha-ethinylestradiol and carbamazepine, 17-alpha-ethinylestradiol and testosterone as l as 17-alpha-ethinylestradiol and ibuprofen (Table 4.25).

Table 4.25 Correlation coefficients among emerging contaminants during the dry season in influents

Contaminants	Aceta-minophen	Simazine	Atrazine	Terbu-thylazine	Carba-mazepine	Metola-chlor	Testos-terone	Proges-terone	Ibuprofen	Estradiol	Triclosan	17-alpha-ethinyl-estradiol
Autumn												
Acetaminophen	1											
Simazine	-0.67	1										
Atrazine	-0.25	-0.56	1									
Terbuthylazine	-0.72	-0.03	**0.85**	1								
Carbamazepine	**0.97**	-0.82	-0.02	-0.54	1							
Metolachlor	-0.68	-0.09	**0.88**	**1.00**	-0.50	1						
Testosterone	**0.92**	-0.33	-0.61	-0.93	**0.81**	-0.91	1					
Progesterone	**0.96**	-0.43	-0.52	-0.89	**0.87**	-0.86	**0.99**	1				
Ibuprofen	**0.85**	-0.17	-0.72	-0.98	**0.70**	-0.97	**0.99**	**0.96**	1			
Estradiol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1		
Triclosan	**1**	-0.62	-0.31	-0.76	**0.96**	-0.72	**0.94**	**0.97**	**0.88**	0.00	1	
17-alpha-ethinyl-esdradiol	**1**	-0.73	-0.16	-0.65	**0.99**	-0.61	**0.88**	**0.93**	**0.79**	0.00	**0.99**	1
Winter												
Acetaminophen	1											
Simazine	-0.83	1										
Atrazine	-0.93	**0.98**	1									
Terbuthylazine	-0.80	**1**	**0.97**	1								
Carbamazepine	-0.13	-0.44	-0.25	-0.49	1							
Metolachlor	-0.79	**1**	**0.96**	1.00	-0.50	1						
Testosterone	-0.14	-0.43	-0.24	-0.48	1.00	-0.49	1					
Progesterone	**0.92**	-0.55	-0.71	-0.51	-0.50	-0.50	-0.51	1				
Ibuprofen	**0.72**	-0.98	-0.93	-0.99	0.59	-0.99	0.58	0.40	1			
Estradiol	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	1	
17-alpha-ethinyl-estradiol	0.60	-0.94	-0.86	-0.96	**0.71**	-0.96	**0.71**	0.25	**0.99**	0.00	0.00	1

Notation: Numbers in bold represent strong correlations

Generally, in wastewater influent, the strong positive correlations between atrazine and simazine, terbuthylazine and atrazine, terbuthylazine and simazine, metolachlor and simazine, metolachlor and terbuthylazine, and metolachlor and atrazine were witness which is an indication of similar man-made sources. These contaminants are herbicides mostly used in industrial areas, roadsides, and public squares to control weeds. Wastewater treatment works in this area receive municipal domestic wastewater from all residents, industrial areas including fruit and vegetable cleaning areas. Therefore, their sources may be linked to industrial wastewater, and stormwater runoff from roadside, industrial, residential, and public squares. There was also strong positive correlations between medical drugs such as carbamazepine and acetaminophen, testosterone and acetaminophen, progesterone and testosterone, pro-gesterone and acetaminophen, progesterone and carbamazepine, ibuprofen and acetaminophen, ibuprofen and carbamazepine, ibuprofen and testosterone, ibuprofen and progesterone, estradiol and progesterone, testosterone and carbamazepine, 17-alpha-ethinylestradiol and testosterone, 17-alpha-ethinylestradiol and carbamazepine, 17-alpha-ethinylestradiol and ibuprofen, 17-alpha-ethinylestradiol and acetaminophen, and 17-alpha-ethinylestradiol and progesterone. These correlations indicate that these contaminants are probably derived from the same anthropogenic sources such as hospital, and domestic wastewaters. The strong positive correlations between

compounds under PPCPs groups such as triclosan and carbamazepine, triclosan and acetaminophen, triclosan and ibuprofen, triclosan and testosterone, triclosan and progesterone and 17-alpha-ethinylestradiol and triclosan may also be linked to hospital and domestic wastewaters that are received by these WWTPs. Other emerging contaminants such as carbamazepine and simazine, carbamazepine and terbuthylazine, metolachlor and carbamazepine, ibuprofen and metolachlor, ibuprofen and atrazine, ibuprofen and terbuthylazine, triclosan and simazine, triclosan and terbuthylazine, and triclosan and metolachlor also showed the strong positive correlations. Their strong positive correlations is an indication of similar sources such as surface runoff, domestic, industrial, and hospital wastewater.

In effluent samples, there was the strong positive correlations between terbuthylazine and simazine, terbuthylazine and atrazine, metolachlor and simazine, metolachlor and atrazine, metolachlor and terbuthylazine, testosterone and atrazine, testosterone and terbuthylazine, ibuprofen and atrazine, ibuprofen and testosterone, estradiol and ibuprofen, triclosan and carbamazepine, triclosan and progesterone, 17-alpha-ethinylestradiol and simazine, 17-alpha-ethinylestradiol and terbuthylazine, and 17-alpha-ethinylestradiol and metolachlor as presented in Table 4.26. The summer season revealed the strong positive correlations between atrazine and simazine, terbuthylazine and atrazine, carbamazepine and acetaminophen, testosterone and acetaminophen, testosterone and carbamazepine, testosterone and metolachlor, ibuprofen and acetaminophen, ibuprofen and testosterone, estradiol and progesterone, triclosan and acetaminophen, triclosan and carbamazepine, triclosan and metolaxchlor, triclosan and testosterone, triclosan and ibuprofen, 17-alpha-ethinylestradiol and acetaminophen, 17-alpha-ethinylestradiol and testosterone, 17-alpha-ethinylestradiol and ibuprofen, and 17-alpha-ethinylestradiol and triclosan.

Table 4.26 The correlation coefficients among emerging contaminants during the wet season in effluents

Contaminants	Aceta-minophen	Simazine	Atrazine	Terbu-thylazine	Carba-mazepine	Metola-chlor	Testos-terone	Proges-terone	Ibuprofen	Estradiol	Triclosan	17-alpha-ethinyl-estradiol
Spring												
Acetaminophen	1											
Simazine	0.00	1										
Atrazine	0.00	0.50	1									
Terbuthylazine	0.00	**0.82**	**0.91**	1								
Carbamazepine	0.00	-0.24	-0.96	-0.75	1							
Metolachlor	0.00	**0.93**	**0.78**	**0.97**	-0.57	1						
Testosterone	0.00	0.38	**0.99**	**0.84**	-0.99	0.69	1					
Progesterone	0.00	0.60	-0.39	0.04	0.63	0.28	-0.51	1				
Ibuprofen	0.00	0.11	**0.91**	0.66	-0.99	0.46	**0.96**	-0.73	1			
Estradiol	0.00	-0.61	0.38	-0.05	-0.62	-0.29	0.50	-1	**0.72**	1		
Triclosan	0.00	0.44	-0.55	-0.14	**0.76**	0.10	-0.66	**0.98**	-0.84	-0.98	1	
17-alpha-ethinyl-esdradiol	0.00	**1**	0.43	**0.77**	-0.16	**0.90**	0.31	0.66	0.03	-0.67	0.52	1
Summer												
Acetaminophen	1											
Simazine	-0.91	1										
Atrazine	-0.74	**0.95**	1									
Terbuthylazine	-0.88	**1**	**0.97**	1								
Carbamazepine	**0.88**	-0.61	-0.33	-0.54	1							
Metolachlor	**0.85**	-0.57	-0.28	-0.49	**1**	1						
Testosterone	**1**	-0.91	-0.74	-0.88	**0.88**	**0.85**	1					
Progesterone	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1				
Ibuprofen	**0.91**	-1	-0.95	-1	0.61	0.56	**0.91**	0.00	1			
Estradiol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	**1**	0.00	1		
Triclosan	**1**	-0.91	-0.74	-0.88	**0.88**	**0.85**	**1**	0.00	**0.91**	0.00	1	
17-alpha-ethinyl-estradiol	**0.93**	-1	-0.94	-0.99	0.63	0.59	**0.93**	0.00	**0.99**	0.00	**0.93**	1

Notation: Numbers in bold represent strong correlations

The autumn season showed the strong positive correlations between atrazine and simazine, terbuthylazine and simazine, terbuthylazine and atrazine, carbamazepine and atrazine, carbamazepine and terbuthylazine, metolachlor and simazine, metolachlor and atrazine, metolachlor and terbuthylazine, metolachlor and carbamazepine, testosterone and acetaminophen, ibuprofen and acetaminophen, ibuprofen and testosterone, 17-alpha-ethinylestradiol and simazeine (Table 4.27). In the winter season, the strong positive correlations were between carbamazepine and terbuthylazine, metolachlor and atrazine as well as ibuprofen and carbamazepine.

Table 4.27 Correlation coefficients among emerging contaminants during the dry season in effluents

Contaminants	Aceta-minophen	Simazine	Atrazine	Terbu-thylazine	Carba-mazepine	Metola-chlor	Testos-terone	Proges-terone	Ibuprofen	Estradiol	Triclosan	17-alpha-ethinyl-estradiol
Autumn												
Acetaminophen	1											
Simazine	-0.96	1										
Atrazine	-0.55	**0.76**	1									
Terbuthylazine	-0.52	**0.74**	**1**	1								
Carbamazepine	-0.29	0.54	**0.96**	**0.97**	1							
Metolachlor	-0.52	**0.73**	**1**	**1**	**0.97**	1						
Testosterone	**1**	-0.96	-0.55	-0.52	-0.29	-0.52	1					
Progesterone	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1				
Ibuprofen	**0.87**	-0.70	-0.06	-0.03	0.22	-0.03	**0.87**	0.00	1			
Estradiol	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	1	
17-alpha-ethinyl-esdradiol	-0.96	**0.85**	0.29	0.27	0.01	0.26	-0.96	0.00	-0.97	0.00	0.00	1
Winter												
Acetaminophen	1											
Simazine	0.00	1										
Atrazine	0.00	-0.05	1									
Terbuthylazine	0.00	0.52	-0.88	1								
Carbamazepine	0.00	-0.18	-0.97	**0.75**	1							
Metolachlor	0.00	0.65	**0.73**	-0.31	-0.86	1						
Testosterone	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				
Ibuprofen	0.00	-0.51	-0.84	0.48	**0.94**	-0.98	0.00	0.00	1			
Estradiol	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	1	
17-alpha-ethinyl-estradiol	0.00	-0.97	-0.18	-0.31	0.40	-0.81	0.00	0.00	0.69	0.00	0.00	1

Notation: Numbers in bold represent strong correlations

The occurrence of emerging contaminants in wastewater effluent may be attributed mainly to their inefficient removal in influents. General results of correlation matrix in effluent samples showed the strong positive correlations between terbuthylazine and simazine, terbuthylazine and atrazine, metolachlor and simazine, metolachlor and terbuthylazine, metolachlor and atrazine and atrazine and simazine which suggest similar sources. These contaminants are herbicides which possibly may be linked to wastewater form industrial and settlement areas. The strong positive correlations between ibuprofen and testosterone, estradiol and ibuprofen, progesterone and carbamazepine, ibuprofen and acetaminophen, ibuprofen and carbamazepine, carbamazepine and acetaminophen, testosterone and acetaminophen, testosterone and carbamazepine, 17-alpha-ethinylestradiol and acetaminophen, 17-alpha-ethinylestradiol and testosterone, and 17-alpha-ethinylestradiol and ibuprofen which are pharmaceutical products may be linked to domestic and hospital wastewater received in these WWTPs. This can be supported by the fact that these contaminants are medical drugs mostly found in hospitals and many homes for treatment of various diseases. The strong positive correlations between contaminants such as triclosan and carbamazepine, triclosan and acetaminophen, triclosan and ibuprofen, triclosan and carbamazepine, triclosan and testosterone, triclosan and progesterone,

and 17-alpha-ethinylestradiol and triclosan which are PPCPs may be linked to domestic and hospital wastewater received in this WWTPs. The strong positive relationships between other contaminants such as 17-alpha-ethinylestradiol and simazine, 17-alpha-ethinylestradiol and terbuthylazine, 17-alpha-ethinylestradiol and metolachlor, carbamazepine and terbuthylazine, carbamazepine and atrazine, carbamazepine and terbuthylazine, metolachlor and acetaminophen, metolachlor and carbamazepine, ibuprofen and atrazine, testosterone and atrazine, testosterone and terbuthylazine, and testosterone and metolachlor may also be linked to stormwater runoff, hospital, domestic and industrial wastewater entering these treatment works.

4.5.2 Source identification with principal component analysis

The hierarchical cluster analysis technique was also used to determine the sources of emerging contaminants in water sources such as rivers, dams, WWTPs and treated drinking water, during spring, summer, autumn, and winter. According to the hierarchical cluster technique, the most likely observations fell within the same class or category (Rashid et al., 2022). In this study, emerging contaminants within the same clusters were considered as emanating from the homogenous pollution sources.

Table 4.28 provides a simplified analysis of the clusters identified for emerging contaminants in water sources within the Modder River catchment.

Table 4.28 Simplified analysis of clusters identified for emerging contaminants in water sources within the Modder River catchment

Season	Cluster group	Nodes	Contaminants per cluster	Main potential pollution source
			Rivers	
Spring	C1	1	Simazine	Wastewater effluent, agricultural runoff, and urban surface runoff
	C2	7	Carbamazepine, atrazine, progesterone, testosterone, metolachlor, terbuthylazine, and estradiol	Wastewater treatment effluent, agricultural runoff, illegal dumping, and urban surface runoff
	C3	3	Acetaminophen, triclosan, and ibuprofen	Wastewater treatment effluent, and illegal dumping
	C4	1	17-alpha-ethinylestradiol	Wastewater treatment effluent, and illegal dumping
Summer	C1	1	Simazine	Wastewater effluent, agricultural runoff, and urban surface runoff
	C2	8	Acetaminophen, progesterone, testosterone, estradiol, metolachlor, atrazine, terbuthylazine, and triclosan	Wastewater treatment effluent, agricultural runoff, illegal dumping, and urban surface runoff
	C3	2	Ibuprofen, and carbamazepine	Wastewater treatment effluent, and illegal dumping
	C4	1	17-alpha-ethinylestradiol	Wastewater treatment effluent, and illegal dumping
Autumn	C1	6	Acetaminophen, metolachlor, progesterone, testosterone, atrazine, and terbuthylazine	Wastewater effluent, agricultural runoff, illegal dumping, and urban surface runoff
	C2	3	Estradiol, carbamazepine, and simazine	Wastewater effluent, agricultural runoff, illegal dumping, and urban surface runoff
	C3	2	Triclosan, and ibuprofen	Wastewater effluent and illegal dumping
	C4	1	17-alpha-ethinylestradiol	Wastewater effluent, and illegal dumping
Winter	C1	9	Atrazine, terbuthylazine, metolachlor, acetaminophen, progesterone, testosterone, estradiol, simazine, and carbamazepine	Wastewater effluent, illegal dumping, stormwater runoff, domestic sewage, and agricultural runoff
	C2	1	Triclosan	Wastewater effluent, and illegal dumping
	C3	1	Ibuprofen	Wastewater effluent, and illegal dumping
	C4	1	17-alpha-ethinylestradiol	Wastewater effluent, and illegal dumping
			Dams	

Season	Cluster group	Nodes	Contaminants per cluster	Main potential pollution source
Spring	C1	2	Ibuprofen, carbamazepine	Wastewater effluent, illegal dumping, and domestic sewage
	C2	6	Acetaminophen, testosterone, metolachlor, simazine, terbuthylazine, and atrazine	Wastewater effluent, illegal dumping, domestic sewage, and agricultural runoff
	C3	3	Estradiol, triclosan and progesterone	Wastewater effluent, domestic sewage, and illegal dumping
	C4	1	17-alpha-ethinylestradiol	Wastewater effluent, domestic sewage, and illegal dumping
Summer	C1	2	Simazine, and carbamazepine	Wastewater effluent, illegal dumping, agricultural runoff, and domestic sewage
	C2	7	Acetaminophen, progesterone, testosterone, estradiol, metolachlor, atrazine, and terbuthylazine	Wastewater effluent, illegal dumping, domestic sewage, agricultural runoff, and urban surface runoff
	C3	2	Triclosan, and ibuprofen	Wastewater effluent, illegal dumping, and domestic sewage
	C4	1	17-alpha-ethinylestradiol	Wastewater effluent, illegal dumping, and domestic sewage
Autumn	C1	9	Acetaminophen, testosterone, progesterone, atrazine, terbuthylazine, estradiol, metolachlor, ibuprofen, and carbamazepine	Wastewater effluent, illegal dumping, domestic sewage, and agricultural runoff
	C 2	1	Simazine	Wastewater effluent, and agricultural runoff
	C 3	1	Triclosan	Wastewater effluent
	C4	1	17-alpha-ethinylestradiol	Wastewater effluent, illegal dumping, and domestic sewage
Winter	C1	7	Simazine, acetaminophen, progesterone, testosterone, metolachlor, terbuthylazine, and estradiol	Wastewater effluent, illegal dumping, domestic sewage, and agricultural runoff
	C2	2	Carbamazepine, and atrazine	Wastewater effluent, illegal dumping and agricultural runoff
	C3	2	Triclosan, and ibuprofen	Wastewater effluent, illegal dumping, and domestic sewage
	C4	1	17-alpha-ethinylestradiol	Wastewater effluent, illegal dumping, and domestic sewage
Treated drinking water				
Spring	C1	1	Carbamazepine	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 of this contaminants in treated drinking water
	C2	7	Acetaminophen, testosterone, metolachlor, ibuprofen, simazine, atrazine, and terbuthylazine	
	C3	3	Estradiol, triclosan, and progesterone	
	C4	1	17-alpha-ethinylestradiol	
Summer	C1	6	Acetaminophen, progesterone, testosterone, estradiol, carbamazepine, and simazine	
	C2	3	Metolachlor, atrazine, and terbuthylazine	
	C3	2	Triclosan, and ibuprofen	
	C4	1	17-alpha-ethinylestradiol	
Autumn	C1	7	Acetaminophen, progesterone, testosterone, simazine, estradiol, carbamazepine, and terbuthylazine	
	C2	2	Atrazine, and metolachlor	
	C3	2	Ibuprofen, and triclosan	
	C4	1	17-alpha-ethinylestradiol	
Winter	C1	7	Acetaminophen, progesterone, testosterone, simazine, estradiol and terbuthylazine	
	C2	2	Metolachlor and atrazine	
	C3	2	Triclosan and ibuprofen	
	C4	1	17-alpha-ethinylestradiol	
Wastewater influent				

Season	Cluster group	Nodes	Contaminants per cluster	Main potential pollution source
Spring	C1	9	Progesterone, testosterone, metolachlor, terbuthylazine, atrazine, estradiol, triclosan, simazine and carbamazepine	Domestic, industrial, and hospital wastewater, urban stormwater
	C2	1	Acetaminophen	Domestic, industrial, and hospital wastewater
	C3	1	Ibuprofen	Domestic, industrial, and hospital wastewater
	C4	1	17-alpha-ethinylestradiol	Domestic, industrial, and hospital wastewater
Summer	C1	9	Testosterone, atrazine, metolachlor, terbuthylazine, estradiol, progesterone, triclosan, simazine and carbamazepine	Domestic, industrial, and hospital wastewater, urban stormwater
	C2	1	Ibuprofen	Domestic, industrial, and hospital wastewater
	C3	1	Acetaminophen	Domestic, industrial, and hospital wastewater
	C4	1	17-alpha-ethinylestradiol	Domestic, industrial, and hospital wastewater
Autumn	C1	9	Progesterone, testosterone, estradiol, metolachlor, atrazine, terbuthylazine, simazine, carbamazepine, and triclosan	Domestic, industrial, and hospital wastewater, urban stormwater
	C2	1	Ibuprofen	Domestic, industrial, and hospital wastewater
	C3	1	Acetaminophen	Domestic, industrial, and hospital wastewater
	C4	1	17-alpha-ethinylestradiol	Domestic, industrial, and hospital wastewater
Winter	C1	1	17-alpha-ethinylestradiol	Domestic, industrial, and hospital wastewater
	C2	1	Acetaminophen	Domestic, industrial, and hospital wastewater
	C3	1	Ibuprofen	Domestic, industrial, and hospital wastewater
	C4	9	Simazine, terbuthylazine, metolachlor, atrazine, triclosan, estradiol, progesterone, testosterone, and carbamazepine	Domestic, industrial, and hospital wastewater, and urban stormwater
Wastewater effluent				
Spring	C1	9	Progesterone, acetaminophen, testosterone, metolachlor, terbuthylazine, atrazine, estradiol, triclosan, and simazine	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	Carbamazepine	
	C3	1	Ibuprofen	
	C4	1	17-alpha-ethinylestradiol	
Summer	C1	1	Carbamazepine	
	C2	8	Simazine, terbuthylazine, progesterone, estradiol, triclosan, metolachlor, atrazine, and testosterone	
	C3	2	Acetaminophen, and ibuprofen	
	C4	1	17-alpha-ethinylestradiol	
Autumn	C1	1	17-alpha-ethinylestradiol	
	C2	1	Acetaminophen	
	C3	1	Ibuprofen	
	C4	9	Carbamazepine, simazine, triclosan, metolachlor, atrazine, terbuthylazine, estradiol, testosterone and progesterone	
Winter	C1	1	17-alpha-ethinylestradiol	
	C2	1	Simazine	
	C3	9	Acetaminophen, progesterone, testosterone, estradiol, terbuthylazine, metolachlor, atrazine, triclosan, and carbamazepine	
	C4	1	Ibuprofen	

4.5.2.1 Identification of pollution ways in rivers

The hierarchical cluster analysis in rivers clustered the 12 targeted emerging contaminants into four clusters in all seasons, as highlighted in Figure 4.13. In the spring season, Cluster 1 (C1) is characterised by one contaminant (simazine) that may be linked to wastewater effluent, agricultural runoff, and urban surface runoff. Cluster 2 is a combination of seven contaminants (carbamazepine, atrazine, progesterone, testosterone, metolachlor, terbuthylazine and estradiol) possibly from wastewater treatment effluent, agricultural runoff, illegal dumping, and urban surface runoff. Cluster 3 is made up of three contaminants (acetaminophen, triclosan, and ibuprofen) which may be liked to wastewater treatment effluent, and illegal dumping. Cluster 4 only has one contaminant (17-alpha-ethinylestradiol), which may be associated with wastewater treatment effluent and illegal dumping in the study area. In summer, C1 is characterised by one contaminant (simazine), which may be linked to wastewater effluent, agricultural runoff, and urban surface runoff. Cluster 2 is characterised by eight contaminants (acetaminophen, progesterone, testosterone, estradiol, metolachlor, atrazine, terbuthylazine, and triclosan), which may be linked to wastewater treatment effluent, agricultural runoff, illegal dumping, and urban surface runoff. Cluster 3 has two contaminants (ibuprofen and carbamazepine), which may be linked to wastewater treatment effluent, and illegal dumping. Cluster 4 has one contaminant (17-alpha-ethinylestradiol), which may be linked to wastewater treatment effluent and illegal dumping.

Moreover, as shown in Figure 4.13, sources of emerging contaminants were also identified during the autumn season, where C1 has six contaminants (acetaminophen, metolachlor, progesterone, testosterone, atrazine, and terbuthylazine), which may have been introduced by wastewater effluent, agricultural runoff, illegal dumping, and urban surface runoff. Cluster 2 is dominated by three contaminants (estradiol, carbamazepine, and simazine), which may have been introduced by wastewater effluent, agricultural runoff, illegal dumping, and urban surface runoff. Moreover, C3 has two contaminants (triclosan and ibuprofen), which are possibly a result of wastewater effluent, and C4 has one contaminant (17-alpha-ethinylestradiol), probably from wastewater effluent, and illegal dumping. During the winter season, C1 has nine contaminants (atrazine, terbuthylazine, metolachlor, acetaminophen, progesterone, testosterone, estradiol, simazine and carbamazepine), which link very well with wastewater effluent, illegal dumping, stormwater runoff, domestic sewage, and agricultural runoff. Cluster 2 is characterised by triclosan, which may have been introduced in rivers by wastewater effluent, and illegal dumping. The contaminants in C3 (ibuprofen) and C4 (17-alpha-ethinylestradiol) in rivers may also link very well to wastewater effluent and illegal dumping (Figure 4.13).

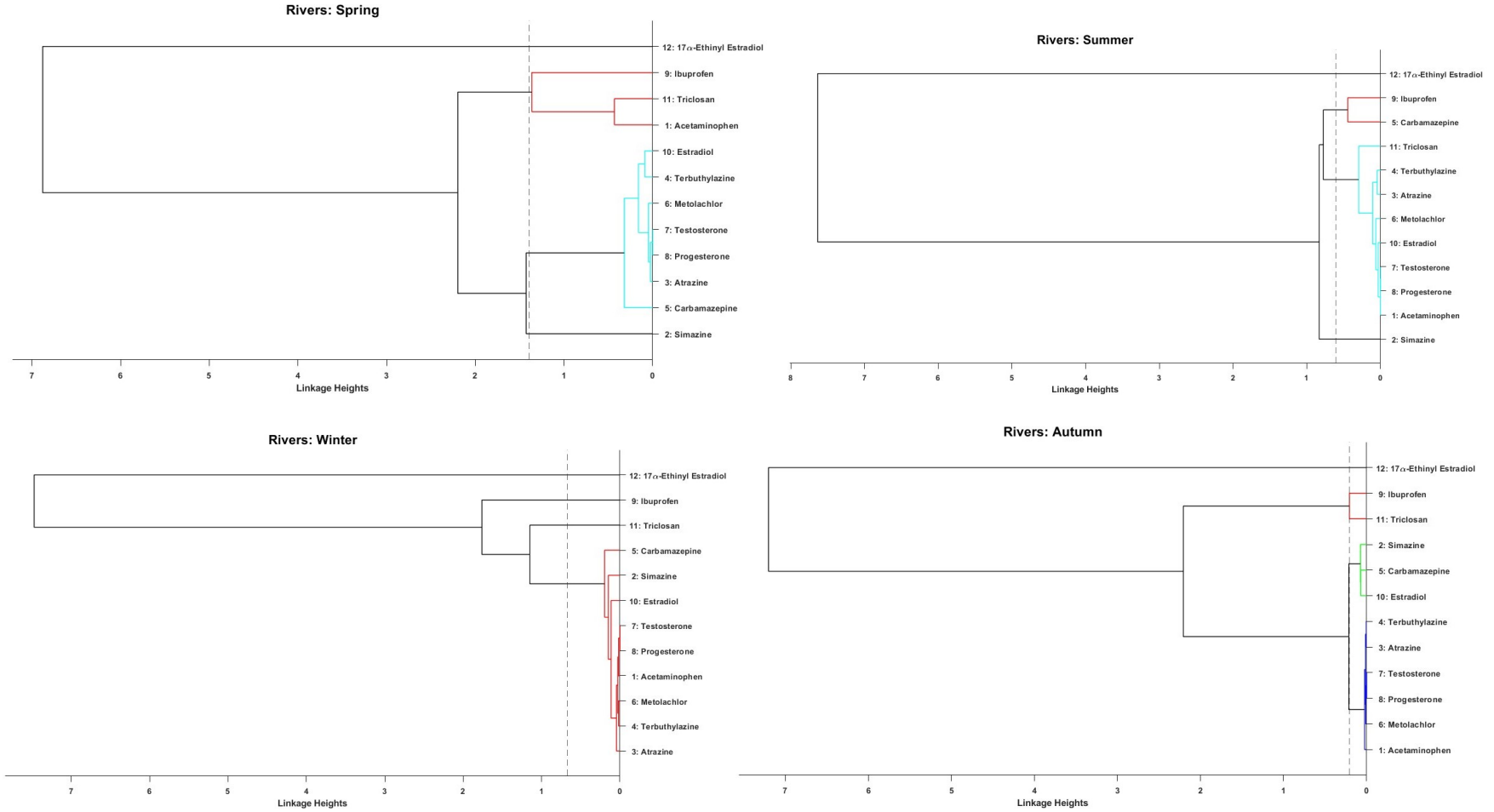


Figure 4.13 Cluster diagram showing similarities of emerging contaminants in rivers

Agricultural activities (specifically crop production) 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 use of herbicides to control weeds in paved areas, public parks, golf courts, and industrial areas in the city of Bloemfontein may also lead to the detection of traces of herbicides 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, Yang et al., 2020). 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 wastes from nearby settlements. Therefore, it is reasonable to link emerging contaminants such as acetaminophen, ibuprofen, carbamazepine, 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 pin-pointed as main potential sources of many organic chemical pollutants in water sources (Bella-Atangana et al., 2023; Das, 2022; Khan et al., 2021; Rashid et al., 2019, 2022).

4.5.2.2 Identification of pollution ways in dams

The hierarchical cluster analysis in dams produced dendrograms with four clusters in all seasons as highlighted in Figure 4.14 and presented in Table 4.28. During the spring season, two contaminants (ibuprofen and carbamazepine) are linked together in C1, which may be associated with wastewater effluent, domestic sewage, and illegal dumping. In C2, six contaminants (acetaminophen, testosterone, metolachlor, simazine, terbuthylazine and atrazine) are linked together, which may have originated from wastewater effluent, illegal dumping, domestic sewage, and agricultural runoff. In C3, there are three contaminants (estradiol, triclosan, and progesterone) linked together, possibly due to wastewater effluent, domestic sewage, and illegal dumping. Cluster 4 is seen with one contaminant (17-alpha-ethinylestradiol) due to discharge of wastewater effluent, domestic sewage, and illegal dumping around the area. In summer, C1 is linked with two contaminants (simazine and carbamazepine), which may be associated with wastewater effluent, illegal dumping, agricultural runoff, and domestic sewage. Cluster 2 is linked with seven contaminants (acetaminophen, progesterone, testosterone, estradiol, metolachlor, atrazine, and terbuthylazine), likely emanating from wastewater effluent, illegal dumping, domestic sewage, agricultural runoff, and urban surface runoff. Cluster 3 is linked with two contaminants (triclosan and ibuprofen), which may be associated with wastewater effluent, illegal dumping, and domestic sewage. Cluster 4 is linked with only one contaminant (17-alpha-ethinylestradiol), which may be associated with wastewater effluent, illegal dumping, and domestic sewage.

As shown in Figure 4.14, the hierarchical cluster analysis also produced four clusters in the autumn and winter seasons. During the autumn season, C1 is linked with nine contaminants (acetaminophen, testosterone, progesterone, atrazine, terbuthylazine, estradiol, metolachlor, ibuprofen and carbamazepine), which may be connected to wastewater effluent, illegal dumping, domestic sewage, and agricultural runoff. Cluster 2 is linked with one contaminant (simazine), most likely from wastewater effluent, and agricultural runoff. Cluster 3 is liked with one contaminant (triclosan) possibly from wastewater effluent, while C4 is also linked with one contaminant (17-alpha-ethinylestradiol), possibly from wastewater effluent, illegal dumping, and domestic sewage. During the winter season, C1 is linked with seven contaminants (simazine, acetaminophen, progesterone, testosterone, metolachlor, terbuthylazine and estradiol) as a result of wastewater effluent, illegal dumping, domestic sewage, and agricultural runoff. Cluster 2 is linked with two contaminants (carbamazepine and atrazine), which are likely a result of wastewater effluent, illegal dumping and agricultural runoff. Cluster 3 is also linked with two contaminants (triclosan and ibuprofen), which may be linked to wastewater effluent, illegal dumping, and domestic sewage. Cluster 4 is linked with only one contaminant (17-alpha-ethinylestradiol), which may be connected to wastewater effluent, illegal dumping, and domestic sewage.

Around the Modder River catchment, agricultural activities, namely crop production and animal husbandry, are the most prominent. Therefore, agricultural runoff may be a contributing factor to the occurrence of some emerging contaminants in surface water such as dams. Yang et al. (2020) and Hou et al. (2022) also reported agricultural runoff as one of the potential sources of organic contaminants in surface water sources. Illegal dumping of domestic wastes (unused or expired drugs), 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 one of the potential sources of chemical water pollution (Rashid et al., 2019, 2022). 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 pharmaceutical, steroid hormones and PCPs. Many studies have also reported urban sewage and domestic wastewater discharge as main potential sources of many chemical pollutants in water sources (Bella-Atangana et al., 2023, Das, 2022, Rashid et al., 2022). According to Gosset et al. (2021), emerging contaminants are continuously released in trace amounts into receiving streams due to inefficiency of WWTPs to remove them. Considering this case, these contaminants ended up being introduced into local reservoirs or dams during the recharging period.

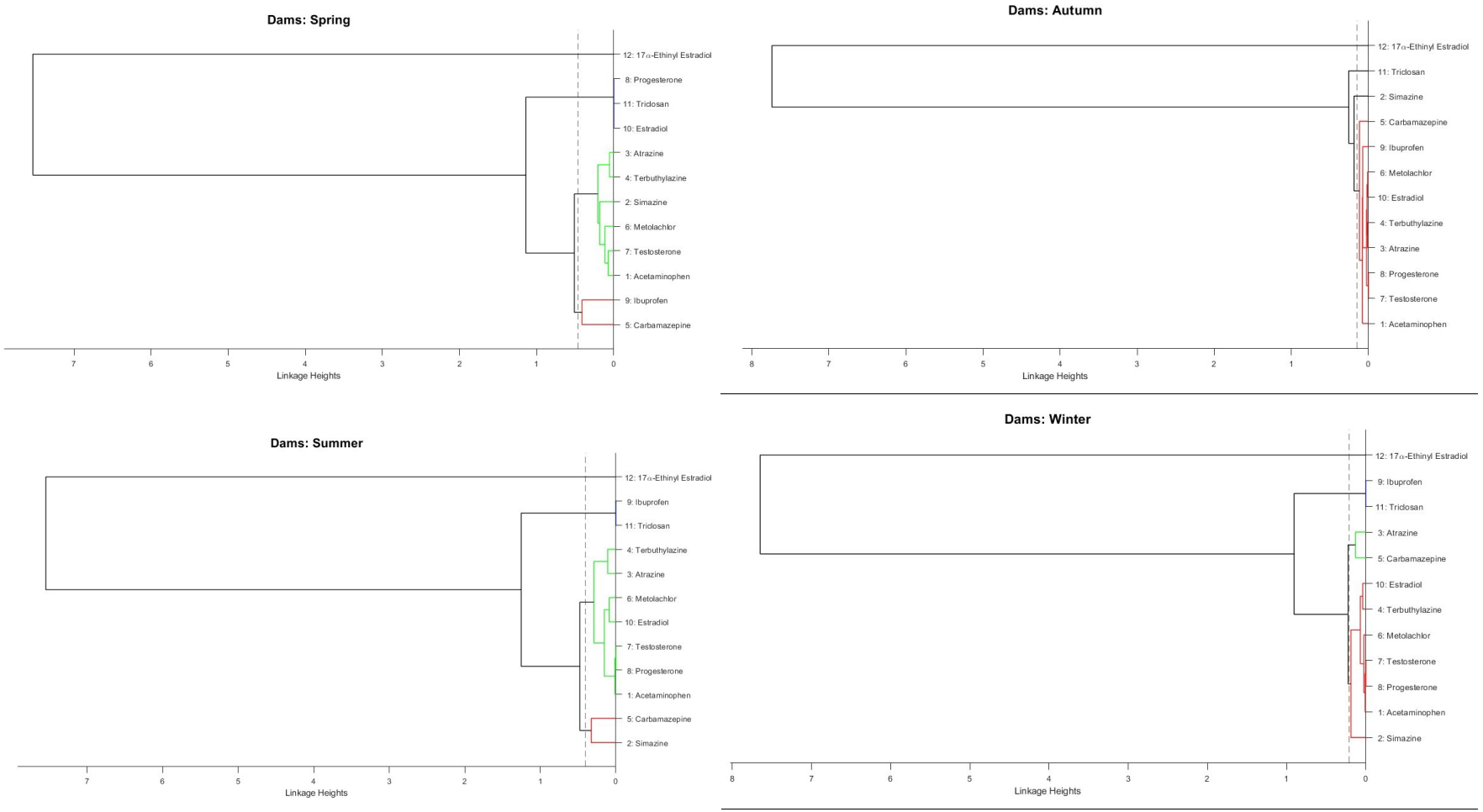


Figure 4.14 Cluster diagram showing similarities of emerging contaminants in dams

4.5.2.3 Identification of pollution ways in treated drinking water

The hierarchical cluster analysis in treated drinking water also generated four clusters in all seasons as highlighted in Figure 4.15 and presented in Table 4.28. In the spring season, C1 is characterised by one contaminant (carbamazepine), C2 is characterised by seven contaminants (acetaminophen, terbuthylazine, metolachlor, ibuprofen, simazine, atrazine and terbuthylazine), C3 is characterised by three contaminants (estradiol, triclosan, and progesterone), whereas C4 is characterised by only one contaminant (17-alpha-ethinylestradiol). In summer, C1 is characterised by six contaminants (acetaminophen, progesterone, testosterone, estradiol, carbamazepine and simazine), C2 is characterised by three contaminants (metolachlor, atrazine, and terbuthylazine), C3 is characterised by two contaminants (triclosan and ibuprofen), and C4 is characterised by one contaminant (17-alpha-ethinylestradiol), as presented in Figure 4.15.

There were also four clusters in the autumn and winter seasons (Figure 4.15). During the autumn season, C1 was the host of seven contaminants (acetaminophen, testosterone, progesterone, simazine, estradiol, carbamazepine and terbuthylazine), C2 was the hosts of two contaminants (atrazine and metolachlor), C3 was the host of two contaminants (ibuprofen and triclosan) and C4 was the host of one contaminant (17-alpha-ethinylestradiol). In the winter season, C1 was the host of seven contaminants (acetaminophen, progesterone, testosterone, simazine, estradiol, carbamazepine, and terbuthylazine), C2 was the host of two contaminants (metolachlor and atrazine), C3 was the host of two contaminants (triclosan and ibuprofen) and C4 was the host of 17-alpha-ethinylestradiol only.

It is reasonable to conclude that dams or reservoirs used as a source of water for WWTPs are polluted by wastewater effluent, agricultural runoff, illegal dumping, urban surface runoff and domestic sewage. This status quo lead to the detection of emerging contaminants in treated drinking water as a result of inefficient removal by the treatment method employed in WWTPs. Therefore, managers of WWTPs should continuously monitor their reservoirs in order to implement advanced treatment methods that can remove the detected emerging contaminants.

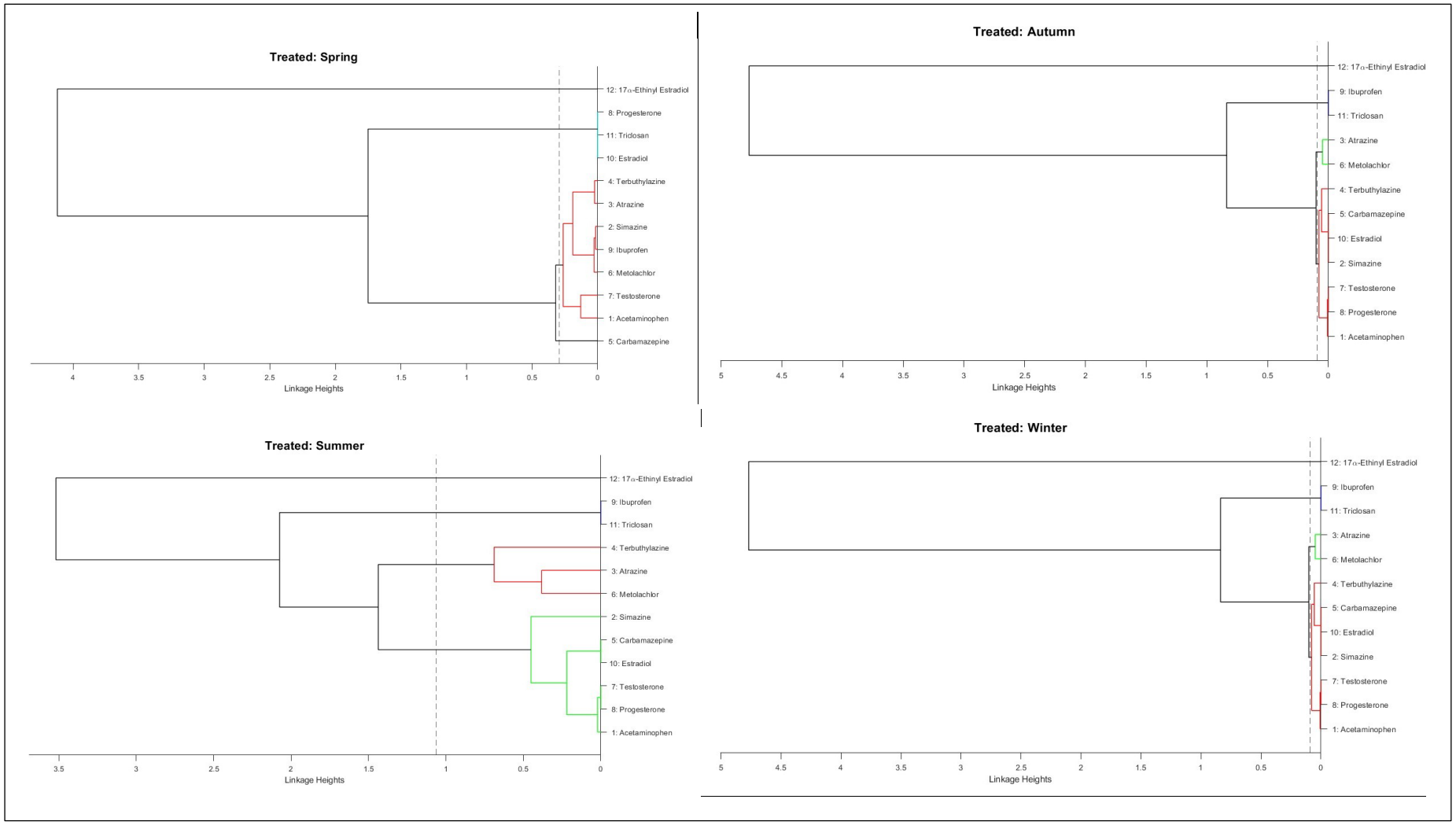


Figure 4.15 Cluster diagram showing similarities of emerging contaminants in treated drinking water

4.5.2.4 Identification of pollution ways in wastewater treatment plants

Sources of emerging contaminants in wastewater treatment influent were determined in all seasons of the year as shown in Figure 4.16 and summarised in Table 4.28. In the spring season, C1 was a host of nine contaminants (progesterone, testosterone, metolachlor, terbuthylazine, atrazine, estradiol, triclosan, simazine, and carbamazepine) indicating that they have been introduced by one source, which may be domestic, industrial, or hospital wastewater as well as urban stormwater. Cluster 2 was a host of one contaminant (acetaminophen), possibly from domestic, industrial, and hospital wastewater received by these WWTPs. Cluster 4 was a host of one contaminant (ibuprofen), which link well with wastewater from hospitals, industries and residential areas. Cluster 4 was also a host of one contaminant (17-alpha-ethinylestradiol), possibly from domestic, industrial, and hospital wastewater received in these WWTPs. In the summer season, C1 hosted nine contaminants (testosterone, atrazine, metolachlor, terbuthylazine, estradiol, progesterone, triclosan, simazine and carbamazepine), which clearly show similar pathways such as domestic, industrial, and hospital wastewater as well as urban stormwater. Cluster 2 hosted one contaminant (ibuprofen), which may be linked to wastewater from hospitals, industrial and residential areas, C3 hosted only one contaminant (acetaminophen) emanating from hospitals, industrial and domestic wastewater, while C4 also hosted one contaminant (17-alpha-ethinylestradiol) also from domestic, hospital and industrial wastewater.

The autumn season shows C1 connected to nine contaminants (progesterone, testosterone, estradiol, metolachlor, atrazine, terbuthylazine, simazine, carbamazepine and triclosan) connoting a similar source of origin, possibly domestic, industrial, and hospital wastewater as well as urban stormwater. C2 is connected to one contaminant (ibuprofen) from domestic, industrial, and hospital wastewater. Cluster 3 is connected to one contaminant (acetaminophen), possibly from domestic, industrial, and hospital wastewater, and C4 is connected to one contaminant (17-alpha-ethinylestradiol) also from domestic, industrial, and hospital wastewater. In the winter season, C1 is connected to one contaminant (17-alpha-ethinylestradiol), C2 is connected to one contaminant (acetaminophen), and C3 is connected to one contaminant (ibuprofen), which may all have been introduced by domestic, industrial, and hospital wastewater. Cluster 4 is connected to nine contaminants (simazine, terbuthylazine, atrazine, metolachlor, triclosan, estradiol, progesterone, testosterone and carbamazepine). The connection of these contaminants in C4 shows similar sources of origin, possibly domestic, industrial, and hospital wastewater as well as urban stormwater in this study.

In this area, WWTPs receive 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 emerging contaminants in wastewater influents in this study. Domestic and hospital wastewater are considered the major sources of PPCPs (Khan et al., 2021, Tormo-Budowski et al., 2021, Ulvi et al., 2022). Urban stormwater may also introduce PPCPs as a result of illegal dumping of unused or expired drugs in residential and industrial areas (Rodriguez-Mozaz et al., 2015). Moreover, urban stormwater may introduce traces of pesticides in WWTPs as a result of the application 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, C1 contained nine contaminants (progesterone, acetaminophen, testosterone, metolachlor, terbuthylazine, atrazine, estradiol, triclosan, and simazine). The following clusters all contained only one contaminant: C2 contained carbamazepine, C3 contained ibuprofen and C4 contained 17-alpha-ethinylestradiol. In the summer season, C1 contained one contaminant (carbamazepine), C2 eight contaminants (simazine, terbuthylazine, progesterone, estradiol, triclosan, metolachlor, atrazine, and testosterone), C3 two contaminants (acetaminophen and ibuprofen) and C4 one contaminant (17-alpha-ethinylestradiol).

The occurrence of contaminants in one cluster is an indication of a similar source of origin (Figure 2.4). During the autumn season, C1 contained one contaminant (17-alpha-ethinylestradiol), C2 contained acetaminophen, C3 contained 17-alpha-ethinylestradiol, while C4 contained nine contaminants (carbamazepine, simazine, triclosan, metolachlor, atrazine, terbuthylazine, estradiol, testosterone and progesterone). Furthermore, in the winter season, C1 contained one contaminant (17-alpha-ethinylestradiol), C2 contained simazine, C3 contained acetaminophen, progesterone, testosterone, estradiol, terbuthylazine, metolachlor, atrazine, triclosan, and carbamazepine, and C4 only contained ibuprofen, as shown in Figure 4.17. Having contaminants in one cluster suggest that they were emanating from the same source.

The occurrence of emerging contaminants in effluent samples may be first defined as the inability of WWTPs to remove them. According to Kuroda et al. (2021), commonly used conventional WWTPs that include primary and secondary treatment processes to remove pollutants such as organic matter and suspended solid matter, are not designed to eliminate emerging contaminants, which was also the case in this area. Therefore, many emerging contaminants go through conventional WWTPs without adequate 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 discharged into nearby streams that introduces emerging contaminants in surface water receiving rivers (Lim et al., 2017). Their introduction into receiving water bodies eventually poses a high risk for aquatic organisms (Ulvi et al., 2022). Therefore, emerging contaminants in wastewater effluent around this area must be quantified and their environmental risk should be evaluated before discharge.

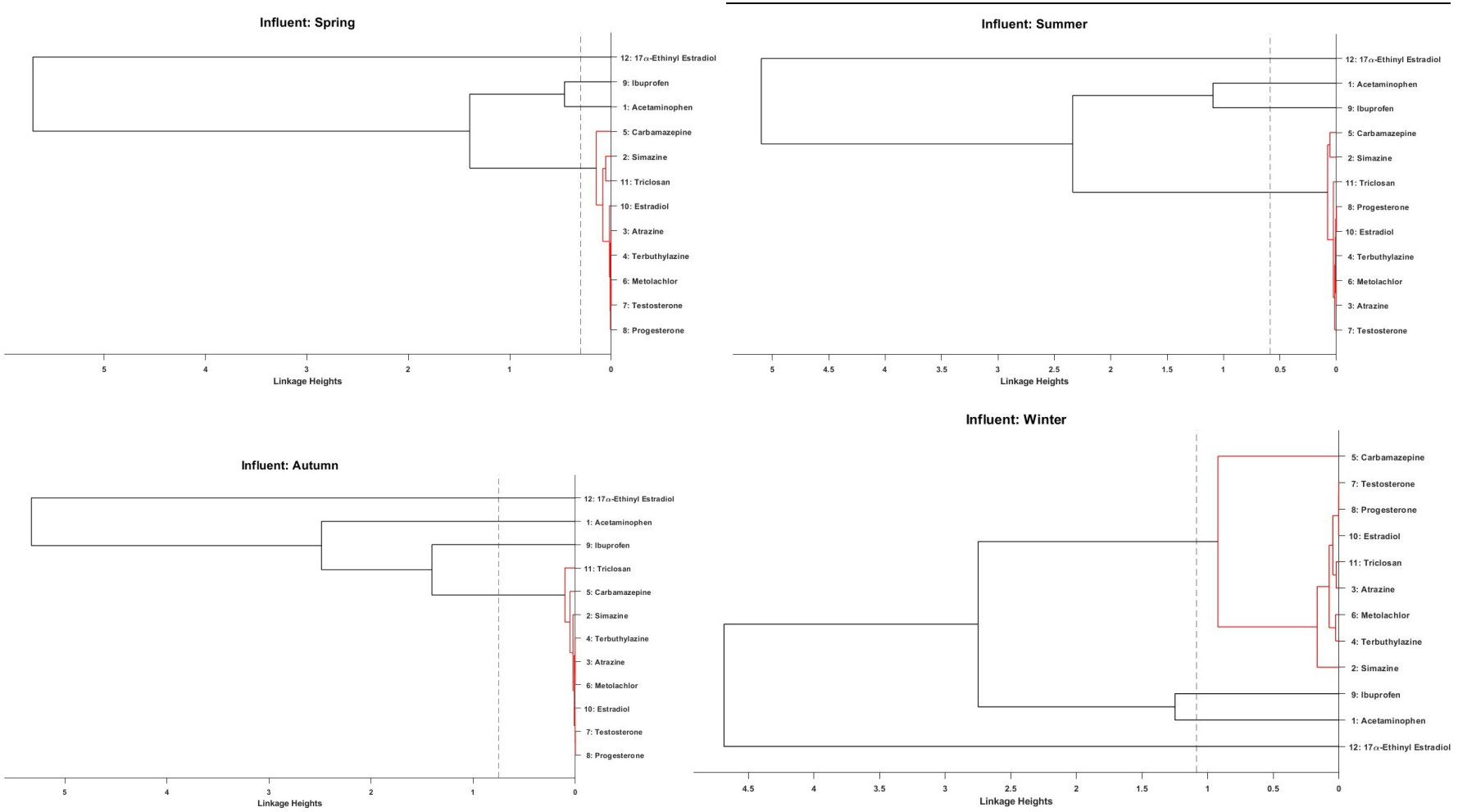


Figure 4.16 Cluster diagram showing similarities of emerging contaminants in wastewater influent

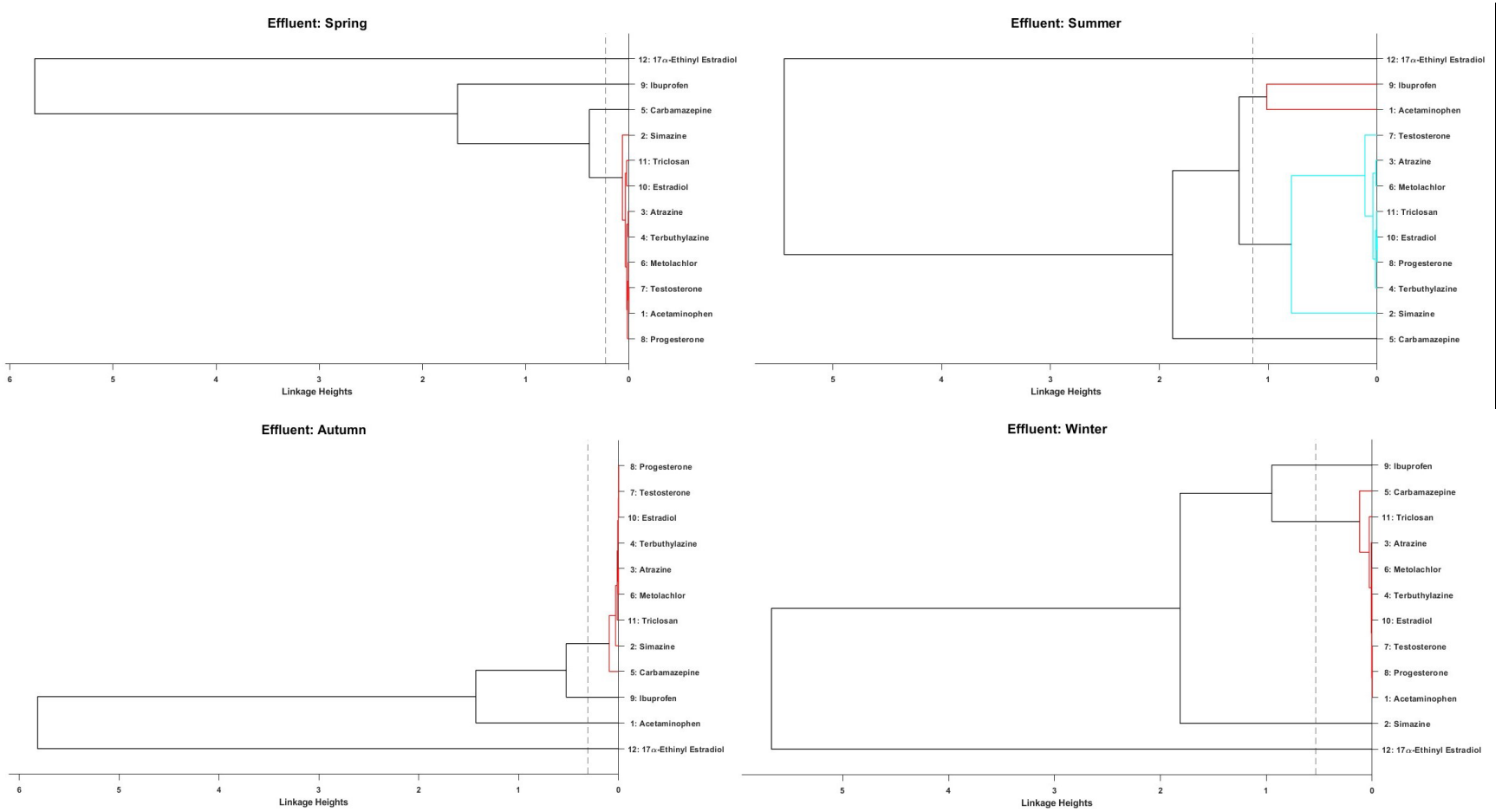


Figure 4.17 Cluster diagram showing similarities of emerging contaminants in wastewater effluent

4.5.3 Source identification with cluster analysis

The individual association of emerging contaminants in water sources within the Modder River catchment was also determined by the PCA method as presented in Tables 4.29, 4.30, 4.31, 4.32 and 4.33. Their overall loading factors and the correlation are also presented in the figures included in Appendix E of this report. Using PCA, unobserved pollution sources can be identified (Hou et al., 2022). To identify the possible sources of origin, the factor loadings are classified as strong (> 0.75), moderate (0.75 to 0.50) and week (0.50 to 0.30) in this study (Chen et al., 2016, Hou et al., 2022, Zhang et al., 2015).

4.5.3.1 Identification of pollution source in rivers

In the spring, summer, autumn and winter seasons, three principal components (PCs) were obtained in rivers (Table 4.29). The overall loading factors and the correlation between the first and second loading factors are also described in Figures included in Appendix D. In the spring season, the first PC (PC1) had a weak positive loading of simazine, atrazine, terbuthylazine, carbamazepine and 17-alpha-ethinylestradiol, which explains 52.53% of the total variance. The loading in PC1 indicates that they may have originated from the same sources, such as wastewater effluents, agricultural runoff, urban stormwater, and illegal dumping. The second PC (PC2) accounting for 30.79% of the total variance, showed a moderate positive loading of estradiol and weak positive loading of metolachlor, triclosan, as well as 17-alpha-ethinylestradiol. These contaminants may be linked to agricultural runoff, urban stormwater, wastewater effluent, and illegal dumping. Principal component 3, accounting for 10.67% of the total variance, showed a moderate positive loading of acetaminophen and ibuprofen, together with a weak positive loading of carbamazepine. The contaminants in PC3 may be linked to wastewater effluent, illegal dumping and urban stormwater runoff. In the summer season, PC1, accounting for 67.55% of the total variance, showed a weak positive loading of simazine, atrazine, terbuthylazine, metolachlor and 17-alpha-ethinylestradiol. The sources of these contaminants may be interpreted as pollution from agricultural runoff, urban stormwater and wastewater effluent. Principal component 2 had 27.56% of the total variance, with a moderate positive loading of carbamazepine and ibuprofen. Therefore, PC2 may be interpreted as pollution from wastewater effluent and illegal dumping. Principal component 3 exhibits 4.67% of total variance, with a moderate positive loading of atrazine and terbuthylazine and a weak positive loading of simazine, possibly from agricultural runoff and urban stormwater.

During the autumn season, PC1 had 75.56% of the total variance, dominated by a weak positive loading of simazine, atrazine, terbuthylazine, carbamazepine, and metolachlor. The loading in PC1 may be associated with agricultural runoff, urban stormwater runoff, wastewater effluent, and illegal dumping. Principal component 2 had 13.03% of the total variance, with a strong positive loading of ibuprofen, which may be linked to wastewater effluent and illegal dumping. Principal component 3 had 8.71% of the total variance, with a moderate positive loading of simazine and terbuthylazine, relating very well to agricultural runoff and urban stormwater. In the winter season, PC1 had 56.09% of the total variance, with a weak positive loading of simazine, atrazine, terbuthylazine, carbamazepine, metolachlor, and ibuprofen. The introduction of these contaminants in rivers may be linked to wastewater effluent, agricultural runoff, urban stormwater and illegal dumping. In PC2, a weak positive loading of acetaminophen, simazine, atrazine, terbuthylazine, and ibuprofen was observed, which explains 22% of the total variance. These observations may be explained as a pollution from wastewater effluent, agricultural runoff, urban stormwater runoff, and illegal dumping.

The above results from the PCA indicate that the major pollution sources threating the rivers within the Modder River catchment are anthropogenic pollution from agricultural runoff, urban stormwater runoff, illegal dumping and wastewater effluent. Similarly, the contamination of rivers by agricultural runoff, and wastewater effluent discharge was reported by other authors in the Sinos River, Brazil (Alves et al., 2018), Nag River, India (Dutta et al., 2018), Kinta River, Malaysia (Isiyaka et al., 2018), Jhelum River, Pakinstan (Mir and Gani, 2019), Akaki River, Ethiopia (Yilma et al., 2018) and Qinhuai River, China (Ma et al., 2020). Some of the rivers in the study area run through townships and cities; hence, improper waste disposal witnessed during the field visit may

have introduced these contaminants in rivers. The selected WWTPs receive wastewater from households, industrial areas and hospitals, which are the carriers of various organic chemicals. Consequently, their wastewater effluents discharged into these rivers may introduce traces of these emerging contaminants. Urban stormwater may also introduce these contaminants due to illegal dumping of unused or expired drugs (in residential areas), application of sewage sludge to ensure soil fertility (in community gardens, recreational parks, golf courses and other public areas) in this study area (Čelić et al., 2019, Rodriguez-Mozaz et al., 2015).

Table 4.29 Principal component analysis of emerging contaminants in rivers

Contaminants	Spring			Summer			Autumn			Winter		
	PC1	PC2	PC3	PC1	PC2	PC3	PC1	PC2	PC3	PC1	PC2	PC3
Acetaminophen	-0.28	-0.18	0.56	0.00	0.00	0.00	0.00	0.00	0.00	-0.15	0.42	0.64
Simazine	0.37	-0.26	-0.22	0.42	-0.27	-0.30	0.39	-0.08	0.57	0.35	0.37	-0.42
Atrazine	0.40	0.15	-0.01	0.41	-0.23	-0.60	0.40	-0.15	-0.32	0.34	-0.46	0.23
Terbuthylazine	0.38	-0.26	-0.21	0.39	-0.27	0.67	0.42	0.01	0.37	0.39	-0.36	0.14
Carbamazepine	0.37	0.02	0.45	0.15	0.68	0.06	0.42	0.03	-0.25	0.30	0.17	0.45
Metolachlor	0.25	0.40	0.04	0.46	-0.06	0.17	0.38	-0.19	-0.56	0.43	0.16	-0.31
Testosterone	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Progesterone	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ibuprofen	0.25	-0.33	0.53	0.29	0.55	-0.19	0.16	0.97	-0.10	0.33	0.52	0.08
Estradiol	0.12	0.52	-0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Triclosan	-0.31	0.38	0.21	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
17-alpha-ethinylestradiol	0.32	0.35	0.26	0.44	0.17	0.17	0.42	-0.03	0.22	0.45	-0.13	0.18
Eigenvalue	5.25	3.08	1.07	4.73	1.93	0.33	5.29	0.91	0.61	4.49	1.76	1.15
Variability (%)	52.53	30.79	10.67	67.55	27.56	4.67	75.56	13.03	8.71	56.09	22.00	14.42
Cumulative (%)	52.53	83.32	93.99	67.55	95.11	99.79	75.56	88.59	97.30	56.09	78.09	92.50

Notation: PC = Principal component

4.5.3.2 Identification of pollution source in dams

As presented in Table 4.30, three PCs were obtained in samples collected from dams within the Modder River catchment during the spring, summer, autumn and winter seasons. The overall loading factors and the correlation between the first and second loading factors are also depicted in the figures included in Appendix D. In the spring season, PC1 accounting for 53.12% of the total variance, exhibited weak positive loadings for acetaminophen, simazine, terbuthylazine, ibuprofen and 17-alpha-ethinylestradiol, suggesting that they share a common source of origin such as domestic sewage, wastewater effluent, agricultural runoff, and illegal dumping. Principal component 2, with 39.36% of the total variance, showed weak positive loadings for atrazine and metolachlor, which are pesticides possibly originating from agricultural runoff and wastewater effluent. Principal component 3, accounting for 7.44% of total variance, exhibited a weak positive loading of simazine and moderate positive loading of 17-alpha-ethinylestradiol derived from domestic sewage, wastewater effluent and agricultural runoff. In the summer season, PC1 showed 63.63% of total variance with a weak positive loading of simazine, atrazine, terbuthylazine, carbamazepine, metolachlor, and 17-alpha-ethinylestradiol possibly from agricultural runoff, wastewater effluent, domestic sewage, and illegal dumping. Principal component 2 accounting for 18.48% of the total variance, had a weak positive loading of carbamazepine and a moderate loading of 17-alpha-ethinylestradiol. Principal component 2 loading suggests that these contaminants shared a common source of origin such as domestic sewage, illegal dumping and wastewater effluent.

In the autumn season, PC1 accounting for 52.31% of the total variance, had weak positive loadings for simazine, atrazine, terbuthylazine, metolachlor and ibuprofen that may be linked to wastewater effluent, domestic sewage, illegal dumping and agricultural runoff. Principal component 2, with 34.07% of the total variance, exhibited moderate positive loadings for carbamazepine and 17-alpha-ethinylestradiol, as well as a weak positive loading of ibuprofen. These contaminants in PC2 may have been introduced into dams by domestic sewage, illegal dumping and wastewater effluent. Principal component 3, accounting for 9.10% of total variance, had a strong positive loading of acetaminophen, which may be linked to domestic sewage, illegal dumping and wastewater effluent. In the winter season, PC1 accounting for 53.04% of the total variance, had a weak positive loading of simazine, terbuthylazine, carbamazepine, metolachlor, and 17-alpha-ethinylestradiol that may have originated from agricultural runoff, wastewater effluent, domestic sewage, and illegal dumping. Principal component 2, accounting for 29.05% of the total variance, had a positive loading of ibuprofen, possibly from domestic sewage, illegal dumping and wastewater effluent. Principal component 3, accounting for 14.20% of the total variance, had a weak positive loading of atrazine, ibuprofen, and 17-alpha-ethinylestradiol, and a moderate positive loading of carbamazepine. The loading in PC3 may be explained as pollution from domestic sewage, wastewater effluent, illegal dumping and agricultural runoff.

The major sources of emerging contaminants in dams are domestic sewage, illegal dumping, wastewater effluent and agricultural runoff. In many agricultural fields, pesticides are applied before and after planting to control broadleaf and grassy weeds (Wang et al., 2022). Given that the majority of the dams are surrounded by agricultural fields, runoff from those fields may introduce traces of pesticides in dams. Ma et al. (2020) also indicated agricultural activities as one of the sources of water pollution**.** During a field visit, clogged and running domestic sewage was channelled towards one of the dams, leading to the introduction of these emerging contaminants. Pollution of water sources by urban sewage overflow was also pin-pointed by other researchers (Hou et al., 2022, Zhang et al., 2015, Zhou et al., 2023). Moreover, some of the dams are open to the public for picnics and aquatic sports activities. Therefore, considering that some of the PPCPs are over-the-counter drugs used to treat various ailments such as inflammatory diseases, arthritis, fever, dysmenorrhea, pains, and headaches in many communities (Ekinci et al., 2020, Nannou et al., 2022), care should be taken as these activities may lead to their introduction in dams due to illegal dumping during aquatic sports activities, conferences and picnics.

Table 4.30 Principal component analysis of emerging contaminants in dams

Contaminants	Spring			Summer			Autumn			Winter		
	PC1	PC2	PC3	PC1	PC2	PC3	PC1	PC2	PC3	PC1	PC2	PC3
Acetaminophen	0.41	-0.24	-0.41	0.00	0.00	0.00	-0.25	-0.20	0.92	0.00	0.00	0.00
Simazine	0.41	0.25	0.35	0.41	-0.53	-0.16	0.41	-0.31	0.01	0.46	-0.12	-0.43
Atrazine	0.22	0.48	-0.35	0.49	-0.17	0.19	0.48	-0.04	0.10	0.01	-0.62	0.31
Terbuthylazine	0.45	0.20	-0.08	0.46	-0.15	-0.43	0.41	-0.33	-0.02	0.49	0.21	-0.12
Carbamazepine	0.25	-0.48	0.16	0.39	0.47	-0.41	0.15	0.56	0.05	0.33	-0.28	0.63
Metolachlor	0.29	0.45	0.11	0.34	-0.10	0.74	0.42	-0.15	0.23	0.46	-0.24	-0.32
Testosterone	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Progesterone	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ibuprofen	0.34	-0.35	-0.46	0.00	0.00	0.00	0.38	0.33	0.11	0.12	0.62	0.32
Estradiol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Triclosan	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
17-alpha-ethinylestradiol	0.38	-0.24	0.57	0.33	0.66	0.22	0.16	0.55	0.28	0.47	0.19	0.33
Eigenvalue	4.25	3.15	0.60	3.82	1.11	0.93	4.18	2.73	0.73	3.71	2.03	0.99
Variability (%)	53.12	39.36	7.44	63.63	18.48	15.46	52.31	34.07	9.10	53.04	29.05	14.20
Cumulative (%)	53.12	92.48	99.92	63.63	82.11	97.56	52.31	86.38	95.49	53.04	82.09	96.29

Notation: PC = Principal component

4.5.3.3 Identification of pollution source in treated drinking water

As presented in Table 4.31, only PC1 was generated in treated drinking water in all seasons. The overall loading factors and the correlation between the first and second loading factors are also described in the figures included in Appendix D. This may have been influenced by the low number of samples collected. In the spring season, PC1 exhibited weak positive loading of atrazine and terbuthylazine, suggesting that they shared a common source of origin. In the summer season, PC1 exhibited a weak positive loading of simazine, atrazine, terbuthylazine, metolachlor and 17-alpha-ethinylestradiol. In the autumn and winter seasons, the results of PCA exhibited weak positive loading of atrazine, terbuthylazine, metolachlor and 17-alpha-ethinylestradiol, connoting that they shared a similar source of origin. This relative analysis in treated drinking water may be connected to the reservoirs or dams used as a source of water for WWTPs in the area. The major sources of pollution in dams were domestic sewage, wastewater effluent, agricultural runoff, and illegal dumping. Therefore, the contamination of dams used as a source of water for WWTPs may eventually lead to the detection of emerging contaminants in treated drinking water as a result of inefficient removal by the treatment method employed in WWTPs. Most of the positive loadings in treated drinking water in all seasons were pesticides and steroid hormones. Therefore, their occurrence may be linked to wastewater effluent, domestic sewage and agricultural runoff. Agricultural activities are the major carriers of pesticides (Hou et al., 2022), while domestic sewage and wastewater effluents contain various emerging contaminants (Lim et al., 2017, Zhou et al., 2023).

Table 4.31 Principal component analysis of emerging contaminants in treated drinking water

Contaminants	Spring	Summer	Autumn	Winter
	PC1	PC1	PC1	PC1
Acetaminophen	-0.35	0.00	0.00	0.00
Simazine	-0.35	0.45	0.00	0.00
Atrazine	0.35	0.45	0.50	0.50
Terbuthylazine	0.35	0.45	0.50	0.50
Carbamazepine	-0.35	0.00	0.00	0.00
Metolachlor	-0.35	0.45	0.50	0.50
Testosterone	0.00	0.00	0.00	0.00
Progesterone	0.00	0.00	0.00	0.00
Ibuprofen	-0.35	0.00	0.00	0.00
Estradiol	0.00	0.00	0.00	0.00
Triclosan	0.00	0.00	0.00	0.00
17-alpha-ethinylestradiol	-0.35	0.45	0.50	0.50
Eigenvalue	8.00	5.00	4.00	4.00
Variability (%)	100.00	100.00	100.00	100
Cumulative (%)	100.00	100.00	100.00	100

Notation: PC = Principal component

4.5.3.4 Identification of pollution sources in wastewater treatment plants

Table 4.32 shows the results of PCA in influents during spring, summer, autumn and winter. The overall loading factors and the correlation between the first and second loading factors are also described in the figures included in Appendix D. Two PCs were generated in all seasons. During the spring season, PC1 exhibited a weak positive loading of simazine, terbuthylazine, carbamazepine, and triclosan, indicating that they may have originated from the same sources such as domestic, industrial, and hospital wastewater, as well as urban stormwater. Similarly, the weak positive loading of acetaminophen, metolachlor, testosterone and ibuprofen in PC2 may suggest that they shared a common source of origin. The possible sources of these contaminants in

PC2 may be linked to urban stormwater, industrial, domestic and hospital wastewater. In the summer season, PC1 exhibited a weak positive loading of simazine, atrazine, terbuthylazine, and metolachlor. The sources of these herbicides in PC1 may be urban stormwater received by these WWTPs. Furthermore, PC2 showed a moderate positive loading of acetaminophen and testosterone. Therefore, PC2 may be interpreted as pharmaceutical pollution from domestic, industrial, hospital wastewater.

In the autumn season, PC1 showed weak positive loadings of acetaminophen, carbamazepine, testosterone, progesterone, ibuprofen, triclosan, and 17-alpha-ethinylestradiol. The loading in PC1 may be linked to domestic, industrial, and hospital wastewater received by these WWTPs. Similarly, the moderate positive loading of simazine in PC2 may be interpreted as organic pollution from urban stormwater. In the winter season, the weak positive loading of simazine, atrazine, terbuthylazine, and metolachlor in PC1 may be interpreted as pesticide pollution from urban stormwater. The moderate positive loading of carbamazepine and testosterone in PC2 suggests that they shared a common source, which may be domestic, industrial, and hospital wastewater received in these WWTPs (Table 4.28).

From the PCA results in wastewater influents, the major sources of emerging contaminants were stormwater runoff, and domestic, industrial, and hospital wastewater. Domestic wastewater, industrial wastewater, and hospital wastewater have been reported as the major carriers of PPCPs in WWTPs (Khan et al., 2021, Tormo-Budowski et al., 2021, Ulvi et al., 2022). Considering that these WWTPs are located in the city and near a well-established settlement with easy access to medical drugs, therefore, urination, flushing of expired drugs, improper handling of pharmaceutical products in households and release of hospital and industrial wastewater may definitely introduce these compounds into the WWTPs. Urban stormwater may carry PPCPs as a result of illegal dumping of unused or expired drugs in residential and industrial areas (Rodriguez-Mozaz et al., 2015). Therefore, illegal dumping of domestic waste in the city centre and some residential settlements witnessed during the field survey, may also influence the occurrence of some medical drugs in WWTPs during rainy seasons. In some areas, sewage sludge, manures and pesticides are used to manage gardens, public parks, and golf courses, which may introduce traces of emerging contaminants in nearby WWTPs due to urban stormwater runoff. Čelić et al. (2019) also indicated that urban stormwater may introduce organic contaminants in WWTPs as a result of the application of sewage sludge to ensure soil fertility in community gardens, recreational parks, and other public areas (Čelić et al., 2019).

Table 4.32 Principal component analysis of emerging contaminants in wastewater influent

Contaminants	Spring		Summer		Autumn		Winter	
	PC1	PC2	PC1	PC2	PC1	PC2	PC1	PC2
Acetaminophen	0.00	0.57	0.09	0.55	0.33	-0.18	-0.30	-0.36
Simazine	0.35	-0.04	0.36	0.18	-0.15	0.56	0.37	0.04
Atrazine	0.27	-0.37	0.37	-0.14	-0.18	-0.53	0.36	0.16
Terbuthylazine	0.35	-0.06	0.38	-0.06	-0.31	-0.28	0.37	0.01
Carbamazepine	0.33	0.19	-0.38	-0.06	0.30	-0.31	-0.18	0.52
Metolachlor	0.28	0.35	0.31	-0.32	-0.30	-0.31	0.37	0.00
Testosterone	-0.28	0.35	0.07	0.55	0.34	0.07	-0.18	0.52
Progesterone	-0.35	0.07	0.00	0.00	0.35	0.00	-0.19	-0.52
Ibuprofen	0.20	0.47	0.25	-0.42	0.33	0.17	-0.37	0.07
Estradiol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Triclosan	0.35	0.10	-0.38	-0.08	0.34	-0.14	0.00	0.00
17-alpha-ethinylestradiol	-0.35	0.09	-0.35	-0.22	0.32	-0.23	-0.36	0.16
Eigenvalue	7.94	3.06	6.83	3.17	8.38	2.62	7.21	2.79
Variability (%)	72.15	27.85	68.29	31.71	76.16	23.84	72.07	27.93
Cumulative (%)	72.15	100.00	68.29	100.00	76.16	100.00	72.07	100.00

Notation: PC = Principal component

Moreover, PCA in wastewater effluents also generated two components in all seasons (Table 4.33). The overall loading factors and the correlation between the first and second loading factors are also described in the figures included in Appendix D. In the spring season, PC1 showed week positive loadings of atrazine, terbuthylazine, testosterone, and ibuprofen, indicating that they may have originated from the same sources. Similarly, the weak positive loadings of simazine, metolachlor, progesterone, triclosan, and 17-alpha-ethinylestradiol may suggest that they shared a common source of origin. In the summer season, there was a weak positive loading of acetaminophen, testosterone, ibuprofen, triclosan, and 17-alpha-ethinylestradiol in PC1, suggesting the same source of origin. Principal component 2 had a moderate loading of carbamazepine, metolachlor and weak loading of atrazine, which is an indication of a similar source of origin.

In the autumn season, PC1 showed a weak positive loading of simazine, atrazine, terbuthylazine, metolachlor, and 17-alpha-ethinylestradiol, whereas PC2 showed weak loadings of atrazine, terbuthylazine, carbamazepine, metolachlor, ibuprofen and 17-alpha-ethinylestradiol. In the winter season, PC1 had a weak positive loading of carbamazepine, ibuprofen, and 17-alpha-ethinylestradiol, while PC2 had moderate positive loadings of simazine and terbuthylazine (Table 4.33). The positive loadings of contaminants in the same PC indicates that they shared a common source of origin.

Therefore, the presence of PPCPs, herbicides and steroid hormones in wastewater effluent in this study may be interpreted, first, as the inability of the WWTPs to remove them. Kuroda et al. (2021) also supported this statement by stating that WWTPs are not designed to eliminate emerging contaminants, which lead to their detection in wastewater effluent. Moreover, the analysis of PCs in wastewater influent demonstrated domestic, industrial, and hospital wastewater, as well as urban stormwater as the major sources of emerging contaminants, which may also be the case of their occurrence in wastewater effluents.

Table 4.33 Principal component analysis of emerging contaminants in wastewater effluent

Contaminants	Spring		Summer		Autumn		Winter	
	PC1	PC2	PC1	PC2	PC1	PC2	PC1	PC2
Acetaminophen	0.00	0.00	0.34	0.14	-0.37	0.24	0.00	0.00
Simazine	0.14	0.43	-0.33	0.21	0.40	-0.09	-0.22	0.56
Atrazine	0.39	0.07	-0.29	0.45	0.34	0.31	-0.40	-0.32
Terbuthylazine	0.33	0.26	-0.32	0.27	0.34	0.33	0.24	0.54
Carbamazepine	-0.40	0.05	0.27	0.51	0.27	0.44	0.45	0.19
Metolachlor	0.27	0.34	0.26	0.54	0.34	0.33	-0.46	0.14
Testosterone	0.40	0.01	0.34	0.14	-0.37	0.24	0.00	0.00
Progesterone	-0.21	0.39	0.00	0.00	0.00	0.00	0.00	0.00
Ibuprofen	0.39	-0.11	0.33	-0.21	-0.24	0.47	0.47	-0.03
Estradiol	0.21	-0.39	0.00	0.00	0.00	0.00	0.00	0.00
Triclosan	-0.27	0.34	0.34	0.14	0.00	0.00	0.00	0.00
17-alpha-ethinylestradiol	0.11	0.44	0.33	-0.18	0.31	-0.38	0.31	-0.48
Eigenvalue	6.24	4.76	8.53	1.47	6.07	2.93	4.52	2.48
Variability (%)	56.76	43.24	85.33	14.67	67.47	32.53	64.53	35.47
Cumulative (%)	56.76	100.00	85.33	100.00	67.47	100.00	64.53	100.00

Notation: PC = Principal component

4.6 MITIGATION MEASURES FOR EMERGING CONTAMINANT POLLUTION IN THE MODDER RIVER CATCHMENT

Various types of interventions are necessary to inhibit or reduce the load of emerging contaminant pollution in water sources for environmental protection and sustainability of water resources within the Modder River catchment. Based on the source apportionment results in this study, emerging contaminants in the Modder

River catchment are generally released, mainly as a result of anthropogenic activities. The established potential anthropogenic sources of pollution include wastewater effluents, domestic sewage, urban surface runoff, agricultural runoff, and illegal dumping. Therefore, the following mitigation measures are suggested to help manage or remedy the situation.

4.6.1 Wastewater effluent discharged in nearby streams

Most wastewater effluents in the study area are discharged into nearby streams, thus introducing traces of emerging contaminants in those water bodies. According to Wang et al. (2015), conventional WWTPs were not 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. Therefore, relevant regulatory authorities should introduce proactive measures in the form of mandatory orders, and formulates proper guidelines for permissible limits for the discharge of effluent in streams to reduce emerging contaminant pollution (Caban and Stepnowski, 2021). Considering that WWTPs in this study receive industrial, domestic and hospital wastewater together, there should be implementation and application of monitoring schemes that are able to discriminate between the domestic, industrial, and hospital wastewater in the area. Governments should also financially support current WWTPs in developing and implementing advanced treatment technologies (such as powdered activated carbon treatment, ozonation, and peroxonation) for the removal of a broad spectrum of emerging contaminants with different properties (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. Moreover, WWTP operators or managers should assess the overall mixture toxicity of emerging contaminants in effluents before discharge in order to protect aquatic life (Bourgin et al., 2018).

4.6.2 Illegal dumping of domestic waste near water bodies

During the sampling campaign, illegal dumping of domestic waste (likely to contain unused or expired medical dugs) near some of the dams and rivers was witnessed. This situation may be due to lack of knowledge about the impact that organic contaminants may have on the environment. Moreover, the lack of proper disposal may also have intensified illegal dumping around the area. 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). Taking back unused or expired medications may help to mitigate their quantities in the aqueous environment and their possible health risks. However, the effectiveness of this strategy rests on teaching people the possible environmental implications of unused or expired medical drugs (Caban and Stepnowski, 2021). Therefore, local communities should be educated on the proper waste disposal methods and environmental implications of illegal dumping.

4.6.3 Emission from 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 observation, 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).

4.6.4 Emission from urban stormwater runoff

Stormwater is a cause of concern in urban areas due to the fact that urban areas are more polluted by a cocktail of anthropogenic emissions. The presence of emerging contaminants in stormwater may be a result of runoff, illegal dumping of wastewater and unsealed systems, and overflow in combined sewer systems. Moreover, the pollution of surface runoff by emerging contaminants is related to various activities such as the

use of solid sludge from WWTPs for soil amendments, the use of reclaimed wastewater for soil irrigation, the use of slurry and liquid manure as fertilisers, and urination and defecation of grazing animals and pets. Rainwater may carry pesticides from golf courses, parks, and residential properties through storm drains and then into rivers and local water reservoirs. Priority should also be placed on enhancing non-point source pollution control measures in the Modder River catchment, including the implementation of infrastructure improvements, such as rainwater and sewerage separation systems. These measures can effectively impede the entry of land-based emerging contaminants into water sources around the Modder River catchment (Caban and Stepnowski, 2021).

4.6.5 Emission from agricultural activities

The Modder River catchment is surrounded by various agricultural activities such as crop production and animal husbandry. Crop production may necessitate the use of herbicides (atrazine, simazine, metolachlor) for maintenance of various crops, while animal husbandry may require the use of medical drugs (fenbendazole, carprofen, estradiol) for the health of livestock. Emissions from these activities may introduce these compounds in nearby water bodies. According to Gozzo et al. (2023), one of the main causes of pharmaceutical pollution is intensive farming, excretion through faeces, urine during the free grazing of animals, manure spreading on land, and contamination via runoff. Therefore, reducing both intensive farming and the use of livestock drugs could be crucial to warrantee the quality of surface water in the Modder River catchment. Furthermore, improvements in agricultural practices may protect water bodies and also contribute to the reduction of risks associated with the presence of emerging contaminants. Changes in treatment timings and intensities, as well as manure application rates and timings, may help to reduce discharges of emerging contaminants in the Modder River catchment (Topp et al., 2008).

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

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

5.1.1 Investigation and monitoring of emerging contaminants in the Modder River catchment

Investigating and monitoring of emerging contaminants for the first time in the Modder River catchment brings to an end the dearth of data on the occurrence of emerging contaminants, environmental risk assessment and their possible sources in the Free State province. From the qualitative screening results, it can be concluded that water sources within the Modder River catchment are polluted or exposed to various groups of emerging contaminants. Notably, herbicides and stimulants were the leading class of emerging contaminants. The data from this study may be used directly for target-screening of these chemicals in future monitoring and risk assessment studies in the Free State region, where emerging contaminants research is limited. Furthermore, it will assist water managers and policymakers to assess water quality and manage pollution more effectively.

The quantification of targeted emerging contaminants such as acetaminophen, carbamazepine, ibuprofen, triclosan, atrazine, simazine, metolachlor, terbuthylazine, 17-alpha-ethinylestradiol, estradiol, progesterone and testosterone in water sources within the Modder River catchment provided a much-needed initial measurement of these contaminants. The majority of these contaminants have been found in quantifiable concentrations in all water sources. Among them, 17-alpha-ethinylestradiol, simazine and ibuprofen showed the highest concentrations in all water sources and should be listed as priority pollutants in future pollution monitoring and waste management programmes within the Modder River catchment. Most notable was the concentration of 17-alpha-ethinylestradiol which was far higher than found in most studies in South Africa. These findings will raise awareness on the occurrence of emerging contaminants in water sources and may 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.

Moreover, the WWTPs showed an insufficient removal efficiency of compounds such as carbamazepine, atrazine, metolachlor, simazine and 17-alpha-ethinylestradiol. Most notable was the inability of the WWTPs to remove pesticides. In South Africa, wastewater effluent is typically discharged into nearby streams, introducing pollutants into the aqueous environment. Therefore, based on the findings of their removal efficiency it can be concluded that the release of wastewater effluent to nearby streams will cause pollution, and ultimately adversely affect the aquatic species and human health.

5.1.2 Environmental health risk assessment of emerging contaminants in the Modder River catchment

Individual ecological risk assessments showed the possibility of some emerging contaminants to pose high ecological risks to aquatic organisms. Moreover, the result of mixture risk assessments in this study also confirmed that algae, daphnids, and fish were more sensitive to targeted compounds. It can be concluded that water sources within the Modder River catchment are not safe for aquatic species and public health. The presence of these emerging contaminants with high ecological risks in water sources within the Modder River catchment is concerning, considering that South Africa is a water-stressed country, and contaminants in water sources may pose a variety of risks, including developmental, growth, and reproductive effects. The outcomes of the risk assessment will serve as a cornerstone in the Free State province for developing a more complete

understanding of the environmental health risks linked to exposure to emerging contaminants. It will also aid in the development of municipal pollution management and risk reduction strategies for organic chemicals.

5.1.3 Sources and pathways of emerging contaminants within 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 anthropogenic activities such as wastewater effluents, domestic sewage, urban surface runoff, agricultural runoff, and illegal dumping. However, this study did not seek to implement any means of mitigation, but only to inform local inhabitants, WWTP managers, farmers and the relevant authorities of the sources of emerging contaminants to their water sources. The outcomes of the study may be relevant for the prioritisation of hazardous substances in order to address suitable monitoring campaigns and any necessary countermeasures to be adopted for environmental protection and the sustainability of water resources. Protecting raw water from pollution by emerging contaminants is an indicative premise of the water environment and ecosystem health. This work may also facilitate the management of existing and future sources of pollution by emerging contaminants within the Modder River catchment.

5.2 RECOMMENDATIONS

The following recommendations can be made:

- Monitoring of emerging contaminants should be expanded to groundwater sources.
- Additional groups of emerging contaminants should be targeted within the Modder River catchment.
- Wastewater treatment managers should conduct individual and mixture risks assessments before discharging effluent to nearby streams.
- Human health risk assessment studies of pesticide exposure through vegetables being irrigated by wastewater effluents and through ingestion of treated drinking water should be assessed.
- Development and implementation of advanced treatment technologies for the removal of a broad spectrum of emerging contaminants with different properties is recommended.
- Residents within the Modder River catchment should be educated on segregating wastes at the source.
- Taking back unused or expired medications may help to mitigate their quantities in the Modder River catchment and their possible health risks.
- Reducing both intensive farming and the use of livestock drugs could be crucial to guarantee the quality of surface water within the Modder River catchment.
- Guidelines of these group of chemicals – PPCPs, pesticides and steroid hormones – in freshwater and drinking water are required in this region.
- Considering that the WWTPs in this study receive industrial, domestic, and hospital wastewater together, there should be implementation and application of monitoring schemes capable to discriminating between the domestic, industrial, and hospital wastewater in the area.

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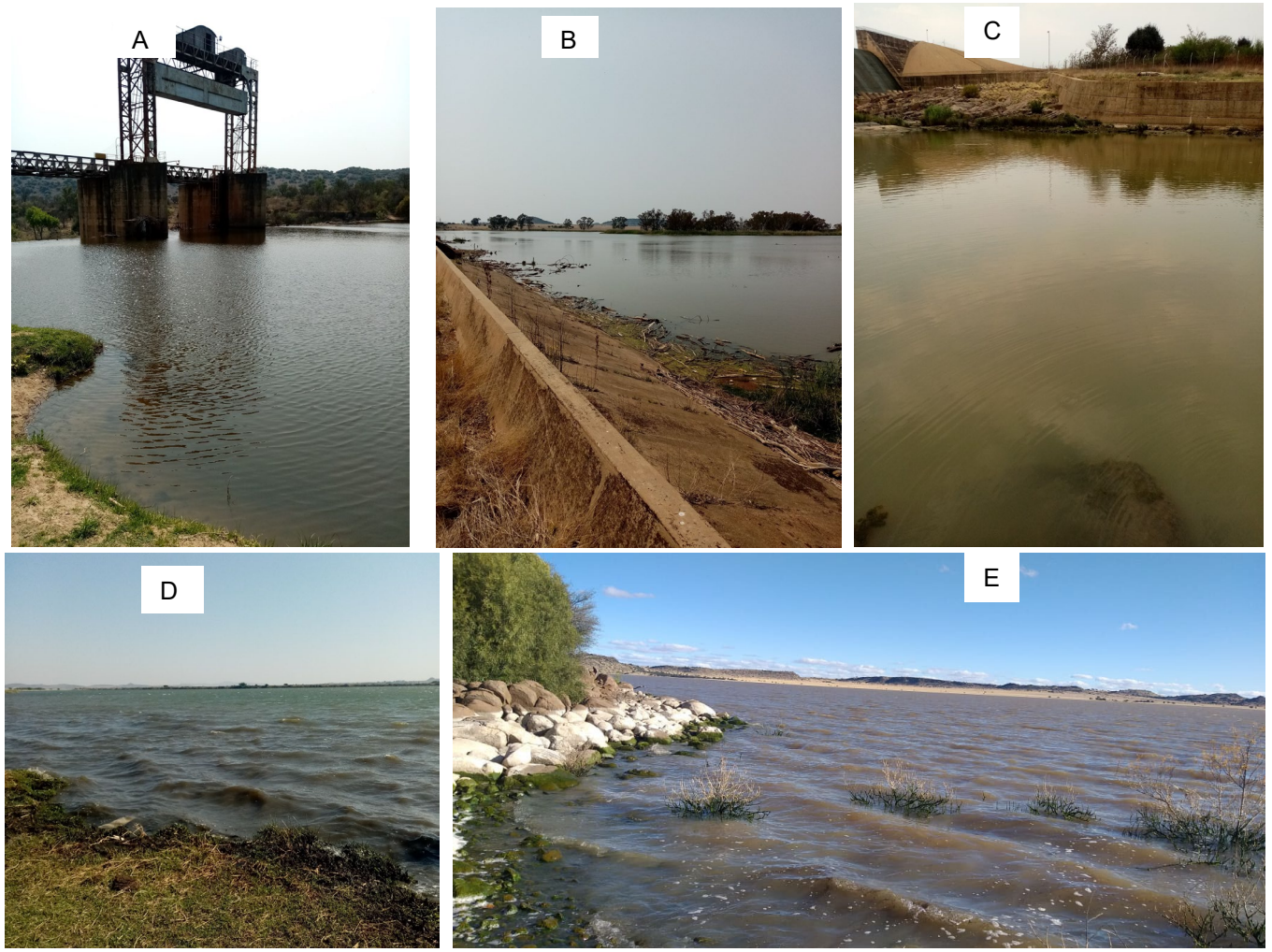
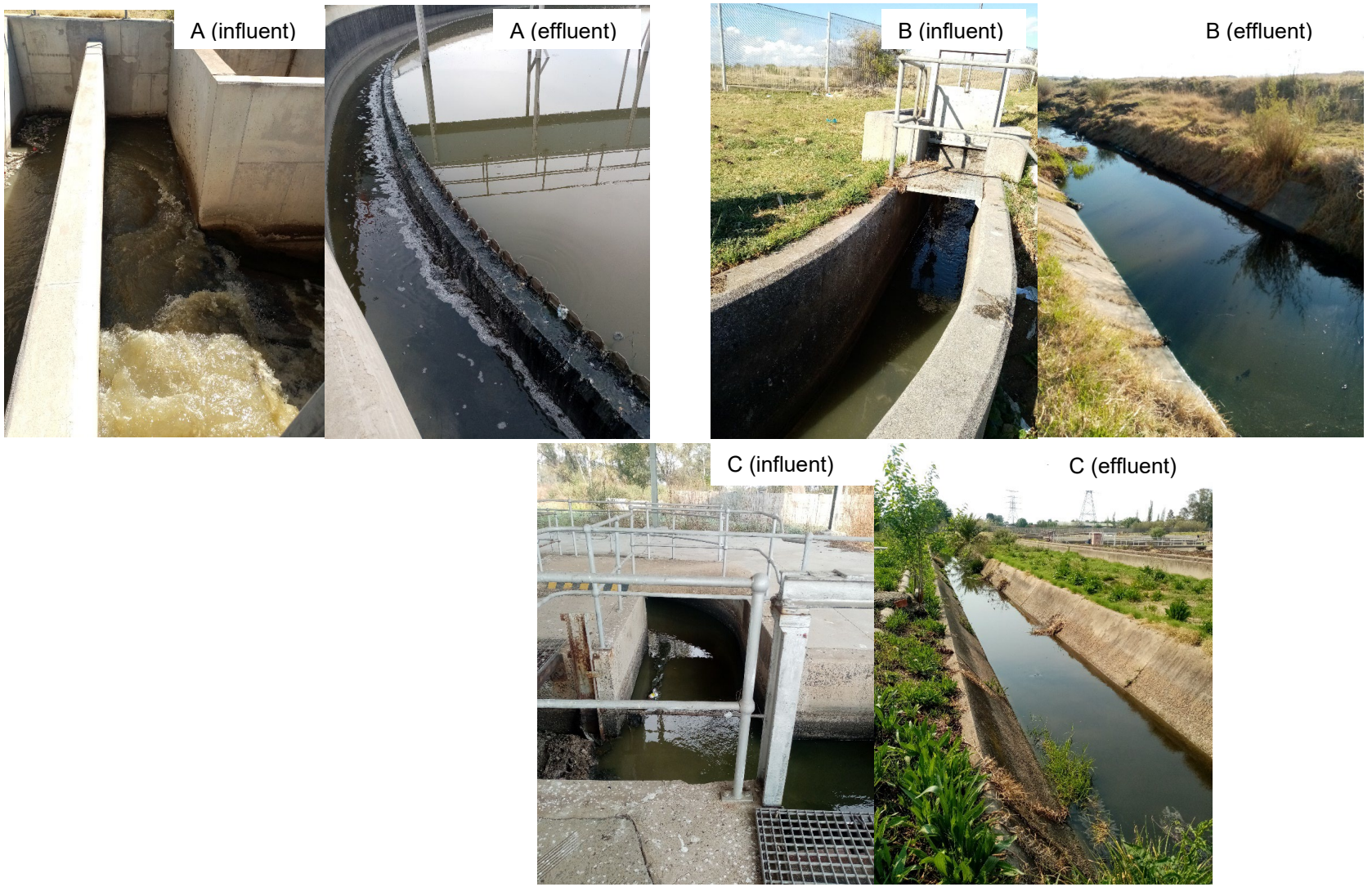
APPENDIX A: COLLECTION AND HANDLING OF WATER SAMPLES FROM VARIOUS WATER SOURCES

Sample collection material and handling procedures during field work

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



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



Collection of wastewater from influent (in) and effluent (ef) from (A) Bloemfontein NE, (B) Botshabelo, and (C) Bloemspruit wastewater treatment plants

APPENDIX B: TARGET ANALYTES MULTIPLE REACTION MONITORING TRANSITION VALUES

Positive mode			Negative mode		
Q1 (m/z)	**Q3 (m/z)**	**Analyte**	**Q1 (m/z)**	**Q3 (m/z)**	**Analyte**
152.123	109.9	Acetaminophen 1	152.123	109.9	Acetaminophen 1
152.123	64.9	Acetaminophen 2	152.123	64.9	Acetaminophen 2
205.028	161.1	Ibuprofen 1	205.028	161.1	Ibuprofen 1
205.028	159	Ibuprofen 2	205.028	159	Ibuprofen 2
202.039	132.1	Simazine 1	202.039	132.1	Simazine 1
202.039	104.1	Simazine 2	202.039	104.1	Simazine 2
230.087	174.3	Terbuthylazine 1	230.087	174.3	Terbuthylazine 1
230.087	68	Terbuthylazine 2	230.087	68	Terbuthylazine 2
216.049	174.2	Atrazine 1	216.049	174.2	Atrazine 1
216.049	68.1	Atrazine 2	216.049	68.1	Atrazine 2
284.347	252	Metolachlor 1	284.347	252	Metolachlor 1
284.347	176.2	Metolachlor 2	284.347	176.2	Metolachlor 2
237.1	194.2	Carbamazepine 1	237.1	194.2	Carbamazepine 1
237.1	192.1	Carbamazepine 2	237.1	192.1	Carbamazepine 2
315.316	109.2	Progesterone 1	315.316	109.2	Progesterone 1
315.316	97	Progesterone 2	315.316	97	Progesterone 2
289.255	97	Testosterone 1	289.255	97	Testosterone 1
289.255	109	Testosterone 2	289.255	109	Testosterone 2
295.232	144.9	17-alpha-ethinyl-estradiol 1	295.232	144.9	17-alpha-ethinyl-estradiol 1
295.232	142.9	17-alpha-ethinyl-estradiol 2	295.232	142.9	17-alpha-ethinyl-estradiol 2
286.975	35	Triclosan 1	286.975	35	Triclosan 1
286.975	33.9	Triclosan 2	286.975	33.9	Triclosan 2
271.212	145	Estradiol 1	271.212	145	Estradiol 1
271.212	182.9	Estradiol 2	271.212	182.9	Estradiol 2

APPENDIX C: TOXICITY DATA

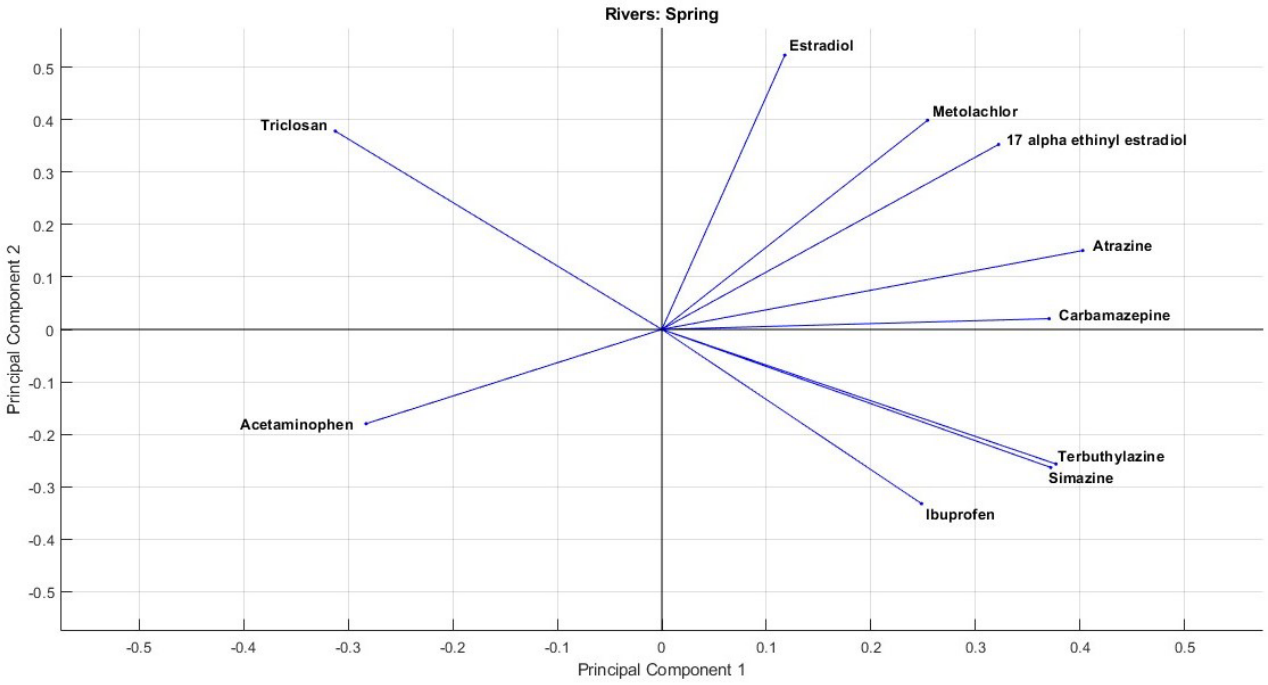
Acute and chronic toxicity data for detected emerging contaminants across the three tropic levels

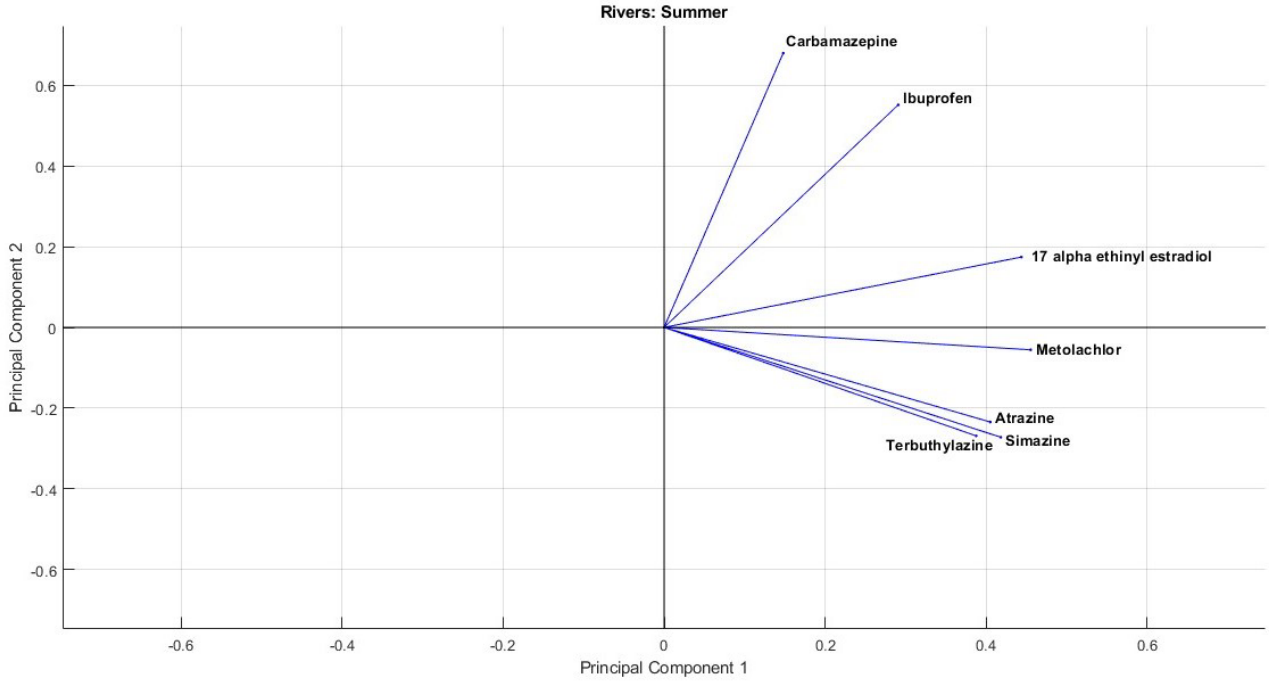
Compound	Taxon	Acute toxicity			Chronic toxicity		
		Specie	EC_{50}/LC_{50}	References	Specie	NOEC	References
Ibuprofen	Algae	*Desmodesmussubspicatus*	315 mg/ℓ	Cleuvers, 2004	*Pseudokirchneriellasubcapitata*	0.01 mg/ℓ	Brun et al., 2006
	Invertebrate	*Daphnia magna*	0.032 mg/ℓ	Brun et al., 2006	*Daphnia magma*	1.23 mg/ℓ	Ericson et al., 2010
	Fish	*Oryzias latipes*	100 mg/ℓ	Kim et al., 2009	*Danio rerio*	0.001 mg/ℓ	David and Pancharatna, 2009
Acetaminophen	Algae	*S.Subcapitata*	134 mg/ℓ	Kosma et al., 2014	*Chlorella vulgaris*	46 mg/ℓ	ECOTOX, 2018
	Invertebrate	*Daphnia magna*	9.2 mg/ℓ	Kosma et al., 2014	*Daphnia magma*	5.72 mg/ℓ	ECOTOX, 2018
	Fish	*B. Rerio*	378 mg/ℓ	Kosma et al., 2014	*Oryzias latipes*	9.5 mg/ℓ	ECOTOX, 2018
Carbamazepine	Algae	*C. maneghiniana*	31.6 mg/ℓ	Ferrari et al., 2004	*P. subcapitata*	10 mg/ℓ	Kosma et al., 2014
	Invertebrate	*Daphnia magna*	6.36 mg/ℓ	Santos et al., 2007	*C. dubia*	0.025 mg/ℓ	Kosma et al., 2014
	Fish	*Pimephales promelas*	35.4 mg/ℓ	Kuzmanovic et al., 2015	*D. rerio*	25 mg/ℓ	Kosma et al., 2014
Triclosan	Algae	*P. Subcapitata*	0.56 mg/ℓ	ECOTOX, 2018	*P. subcapitata*	0.2 mg/ℓ	Brausch and Rand, 2011
	Invertebrate	*Daphnia magna*	0.39 mg/ℓ	ECOTOX, 2018	*Daphnia magma*	200 mg/ℓ	Brausch and Rand, 2011
	Fish	*Lepomis mocrochirus*	0.26 mg/ℓ	ECOTOX, 2018	*O. mykiss*	71.3 mg/ℓ	Brausch and Rand, 2011
17-alpha-ethinylestradiol	Algae	*Fathead minnows*	0.0008 mg/ℓ	Adjei et al., 2022	-	-	-
	Invertebrate	*Daphnia magna*	0.0012 mg/ℓ	Adjei et al., 2022	-	-	-
	Fish	*T. pyriformis*	0.002 mg/ℓ	Adjei et al., 2022	*Oryzias latipes*	0.03 mg/ℓ	Liu et al., 2020
Estradiol	Algae	*Fathead minnows*	0.0016 mg/ℓ	Adjei et al., 2022	-	-	-
	Invertebrate	*Daphnia magna*	0.003 mg/ℓ	Adjei et al., 2022	-	-	-
	Fish	*T. pyriformis*	0.003 mg/ℓ	Adjei et al., 2022	*Oncorrhynchus mykiss*	0.42 mg/ℓ	Liu et al., 2020
Progesterone	Algae	*Fathead minnows*	0.001 mg/ℓ	Adjei et al., 2022	-	-	-
	Invertebrate	*Fathead minnows*	0.007 mg/ℓ	Adjei et al., 2022	-	-	-
	Fish	*T. pyriformis*	-	-	-	-	-
Testosterone	Algae	*Fathead minnows*	0.0014 mg/ℓ	Adjei et al., 2022	-	-	-
	Invertebrate	*Fathead minnows*	0.006 mg/ℓ	Adjei et al., 2022	-	-	-
	Fish	*T. pyriformis*	-	-	*Oncorhynchus kisutch*	30 mg/ℓ (Lowest Observed Effect Concentration)	Liu et al., 2020
Atrazine	Algae	*P. Subcapitata*	0.059 mg/ℓ	ECOTOX, 2018, Kock-Schulmeyer et al., 2012	*P. Subcapitata*	0.1 mg/ℓ	ECOTOX, 2018, Kock-Schulmeyer et al., 2012

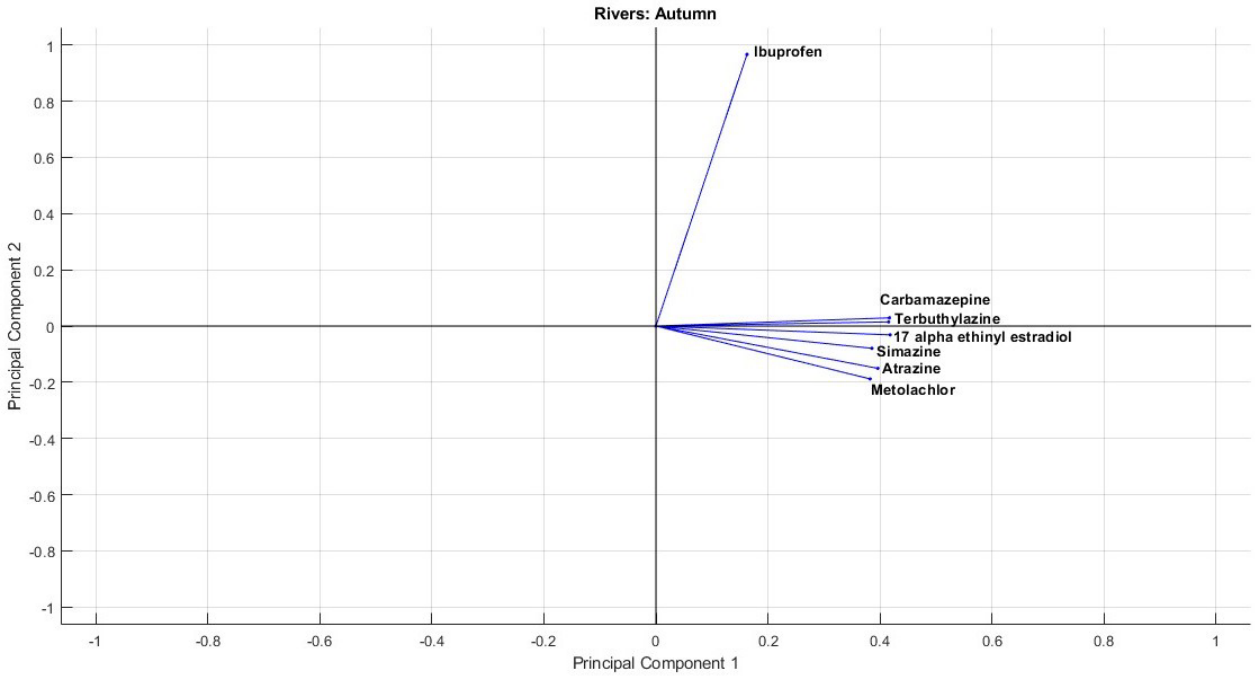
Compound	Taxon	Acute toxicity			Chronic toxicity		
		Specie	EC_{50}/LC_{50}	References	Specie	NOEC	References
Metolachlor	Invertebrate	*Daphnia magma*	6.9 mg/ℓ	ECOTOX, 2018, Kock-Schulmeyer et al., 2012	*Daphnia magma*	0.1 mg/ℓ	ECOTOX, 2018, Kock-Schulmeyer et al., 2012
	Fish	*Oncorhynchus mykiss*	4.5 mg/ℓ	ECOTOX, 2018, Kock-Schulmeyer et al., 2012	*Oncorhynchus mykiss*	2 mg/ℓ	ECOTOX, 2018, Kock-Schulmeyer et al., 2012
	Algae	*P. Subcapitata*	57.1 mg/ℓ	ECOTOX, 2018, Kock-Schulmeyer et al., 2012	*P. Subcapitata*	3.0 mg/ℓ	ECOTOX, 2018, Kock-Schulmeyer et al., 2012
	Invertebrate	*Daphnia magma*	23.5 mg/ℓ	ECOTOX, 2018, Kock-Schulmeyer et al., 2012	*Daphnia magma*	3.0 mg/ℓ	ECOTOX, 2018, Kock-Schulmeyer et al., 2012
	Fish	*Oncorhynchus mykiss*	3.9 mg/ℓ	ECOTOX, 2018, Kock-Schulmeyer et al., 2012	*Oncorhynchus mykiss*	1.0 mg/ℓ	ECOTOX, 2018, Kock-Schulmeyer et al., 2012
Simazine	Algae	*P. Subcapitata*	0.04 mg/ℓ	ECOTOX, 2018, Kock-Schulmeyer et al., 2012	*P. Subcapitata*	0.6 mg/ℓ	ECOTOX, 2018, Kock-Schulmeyer et al., 2012
	Invertebrate	*Daphnia magma*	1.1 mg/ℓ	ECOTOX, 2018, Kock-Schulmeyer et al., 2012	*Daphnia magma*	0.6 mg/ℓ	ECOTOX, 2018, Kock-Schulmeyer et al., 2012
	Fish	*Oncorhynchus mykiss*	9.0 mg/ℓ	ECOTOX, 2018, Kock-Schulmeyer et al., 2012	*Oncorhynchus mykiss*	0.7 mg/ℓ	ECOTOX, 2018, Kock-Schulmeyer et al., 2012
Terbuthylazine	Algae	*P. Subcapitata*	0.02 mg/ℓ	NRA, 2001	*P. Subcapitata*	-	-
	Invertebrate	*Daphnia magma*	39.4 mg/ℓ	NRA, 2001	*Daphnia magma*	0.21 mg/ℓ	NRA, 2001
	Fish	*Oncorrhynchus mykiss*	3.6 mg/ℓ	NRA, 2001	*Mysid shrimp*	0.13 mg/ℓ	NRA, 2001

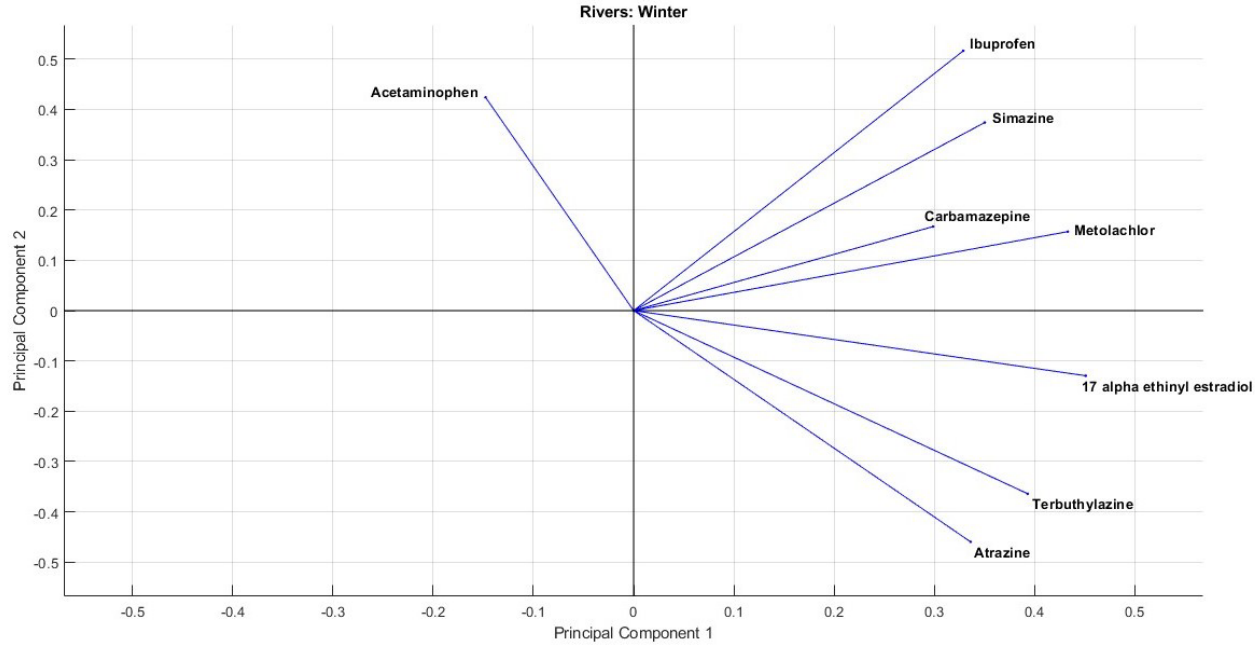
APPENDIX D: PCA RESULTS OF THE FIRST TWO FACTORS PC1 AND PC2 IN WATER SOURCES WITHIN THE MODDER RIVER CATCHMENT

PCA results of the first two factors PC1 and PC2 in rivers

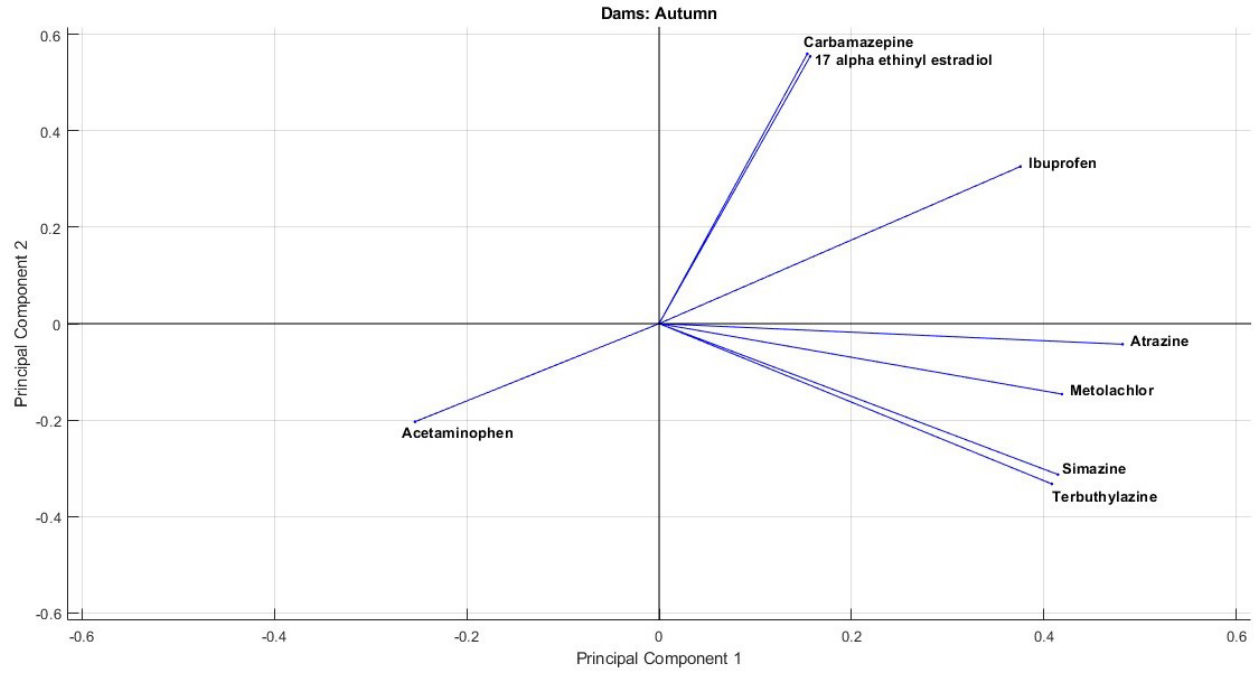


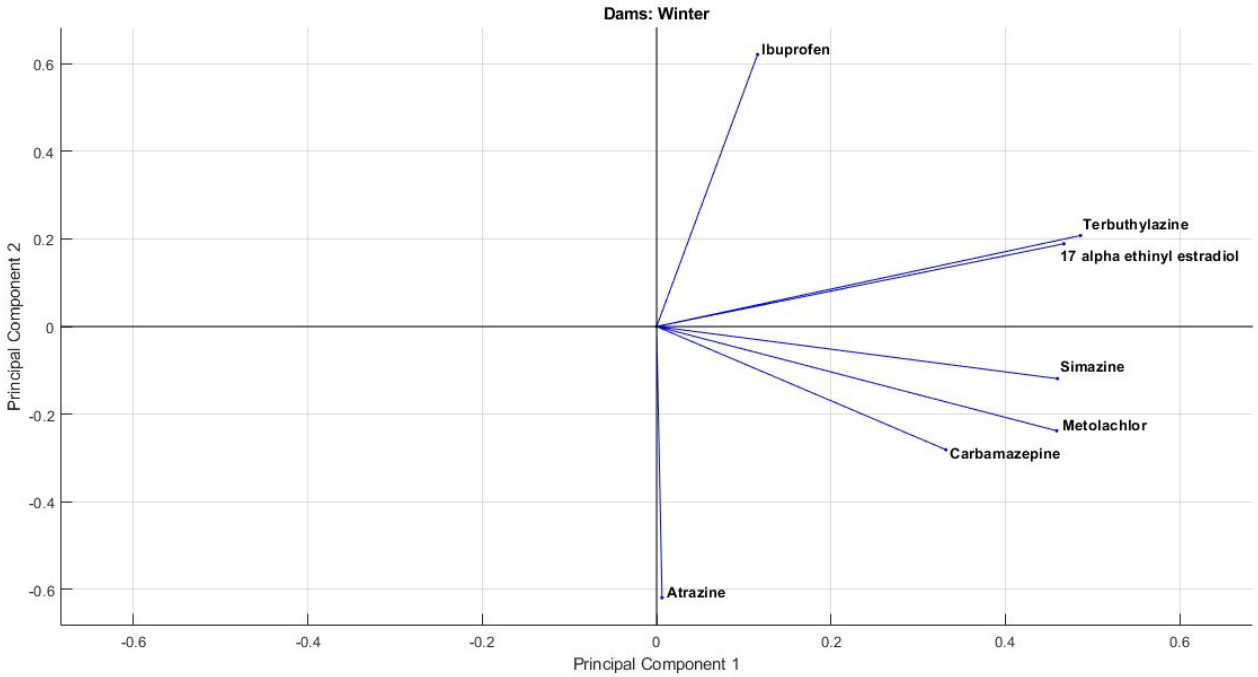


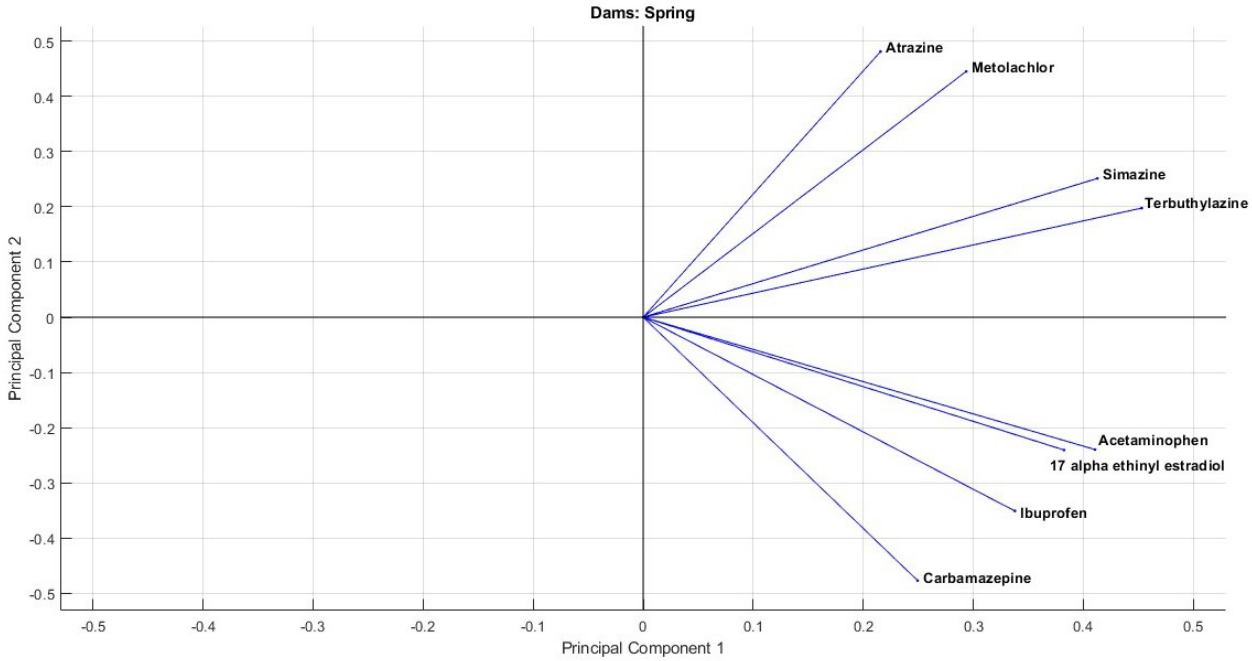

Rivers: Autumn
Ibuprofen
Carbamazepine
Terbuthylazine
17 alpha ethinyl estradiol
Simazine
Atrazine
Metolachlor
Principal Component 2
Principal Component 1

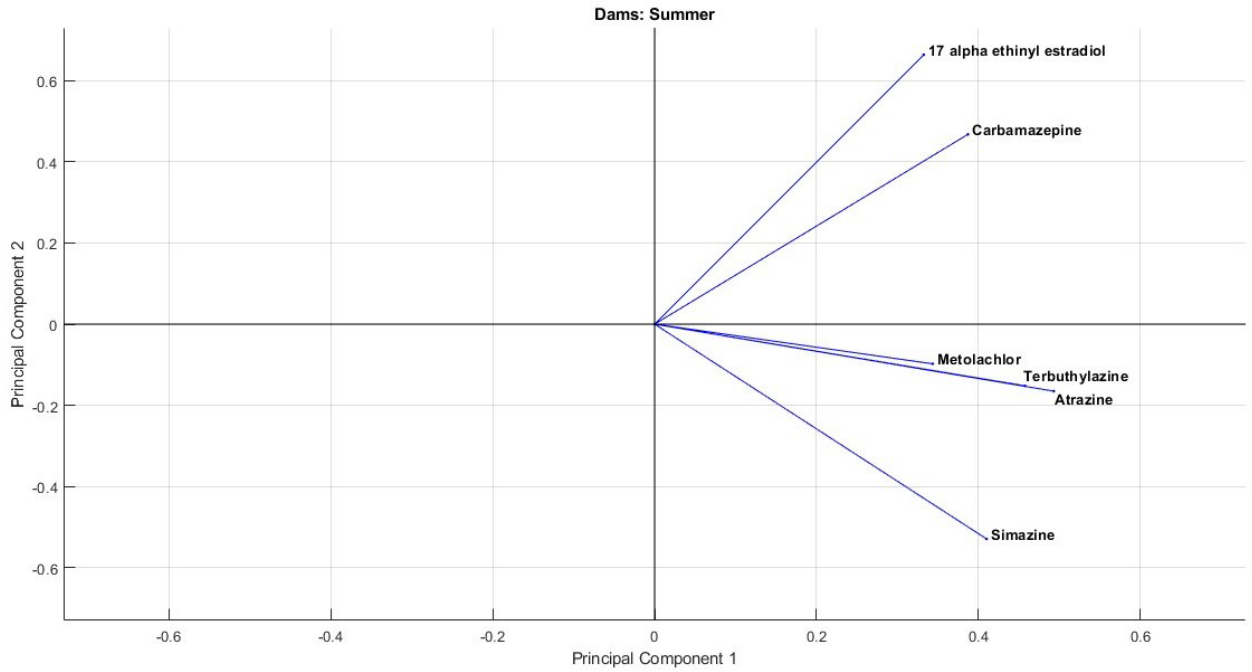

Rivers: Winter
Acetaminophen
Ibuprofen
Simazine
Carbamazepine
Metolachlor
17 alpha ethinyl estradiol
Terbuthylazine
Atrazine
Principal Component 2
Principal Component 1

PCA results of the first two factors PC1 and PC2 in dams

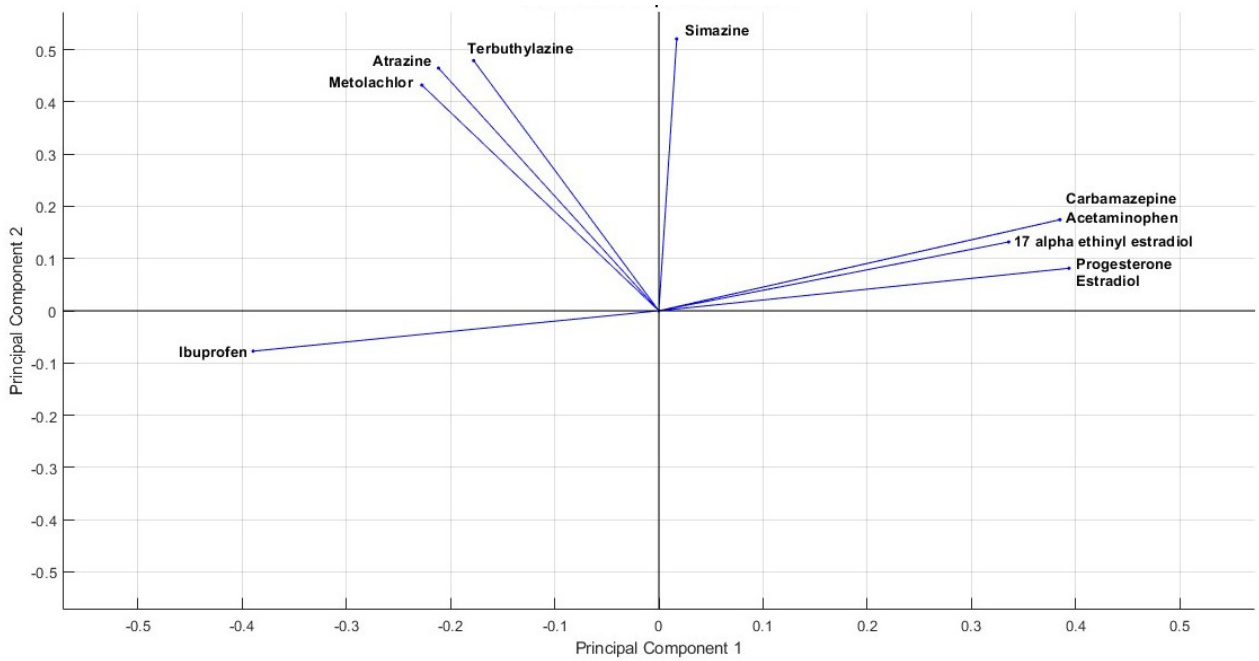




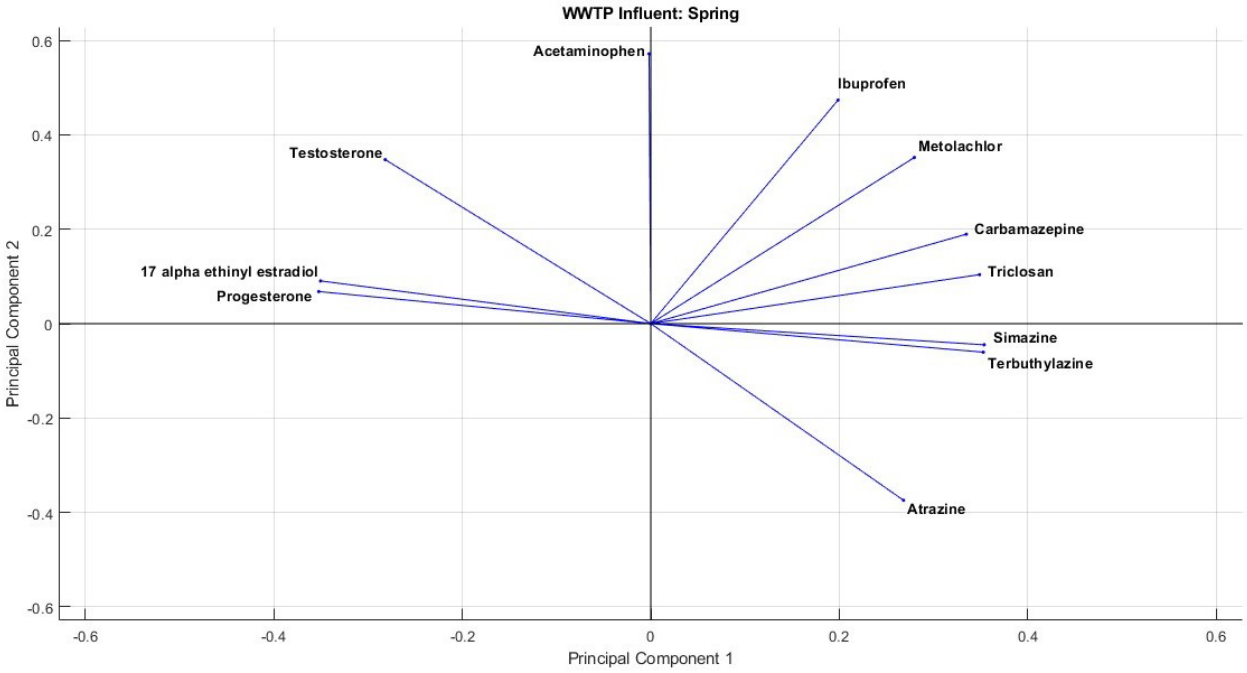

Dams: Spring
Atrazine
Metolachlor
Simazine
Terbuthylazine
Acetaminophen
17 alpha ethinyl estradiol
Ibuprofen
Carbamazepine
Principal Component 2
Principal Component 1
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
-0.5

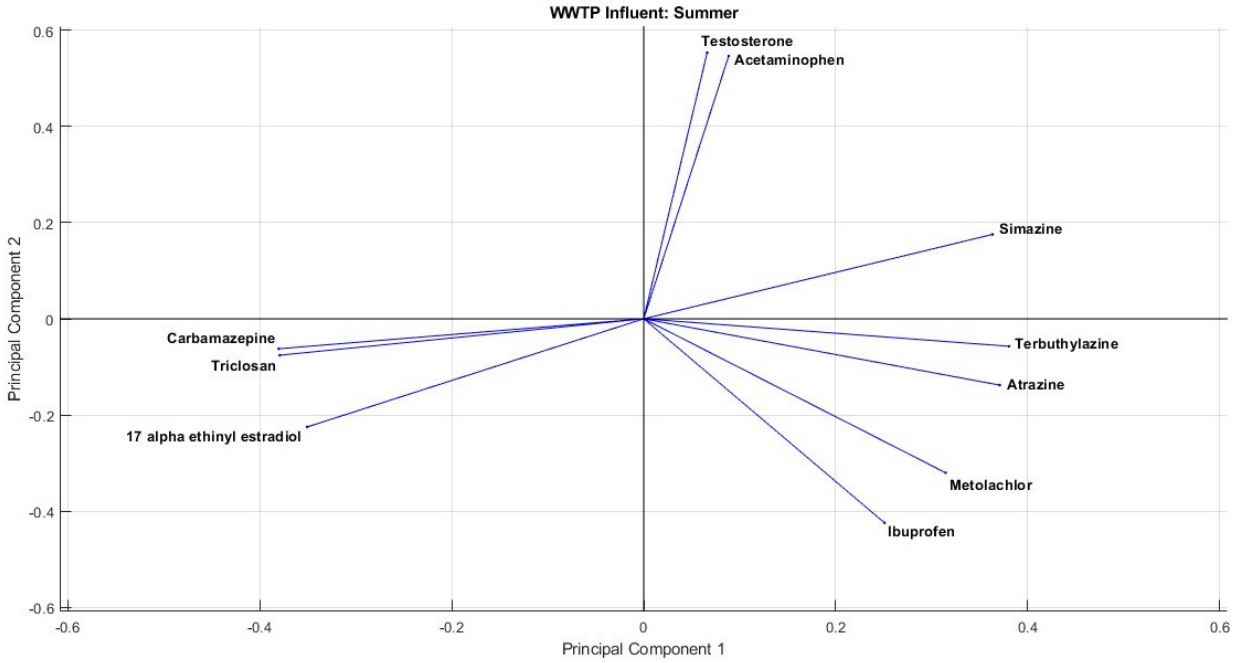

Dams: Summer
17 alpha ethinyl estradiol
Carbamazepine
Metolachlor
Terbuthylazine
Atrazine
Simazine
Principal Component 2
Principal Component 1
0.6
0.4
0.2
0
-0.2
-0.4
-0.6

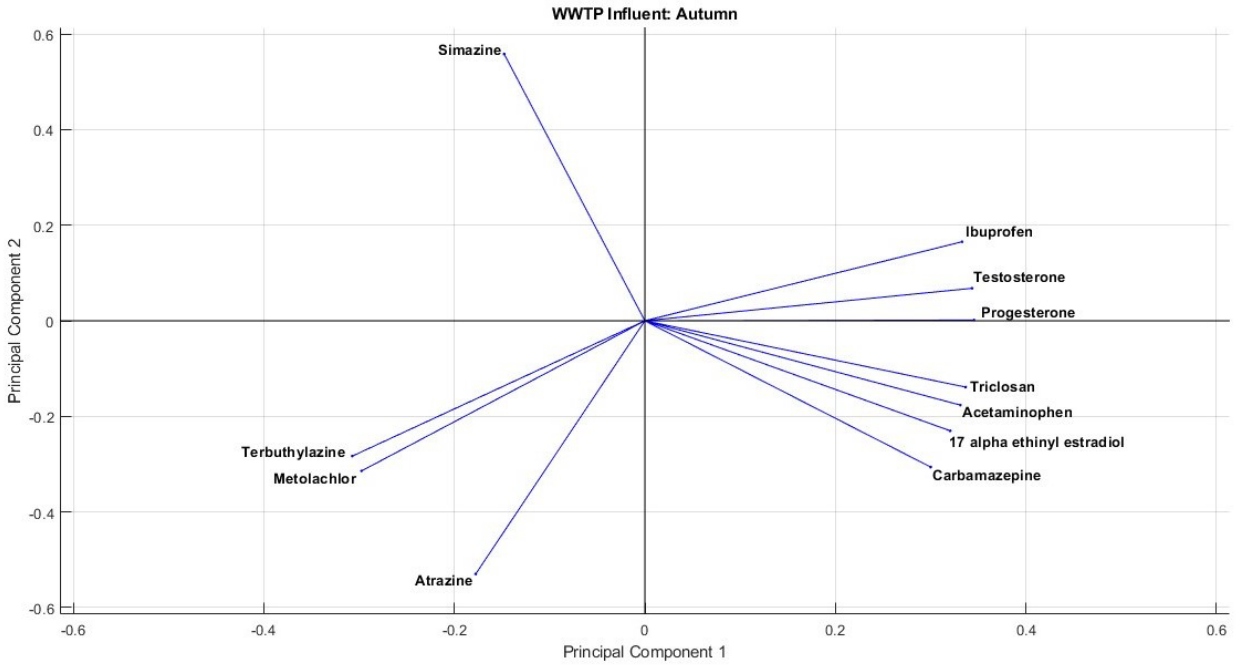
PCA results of the first two factors PC1 and PC2 in treated drinking water

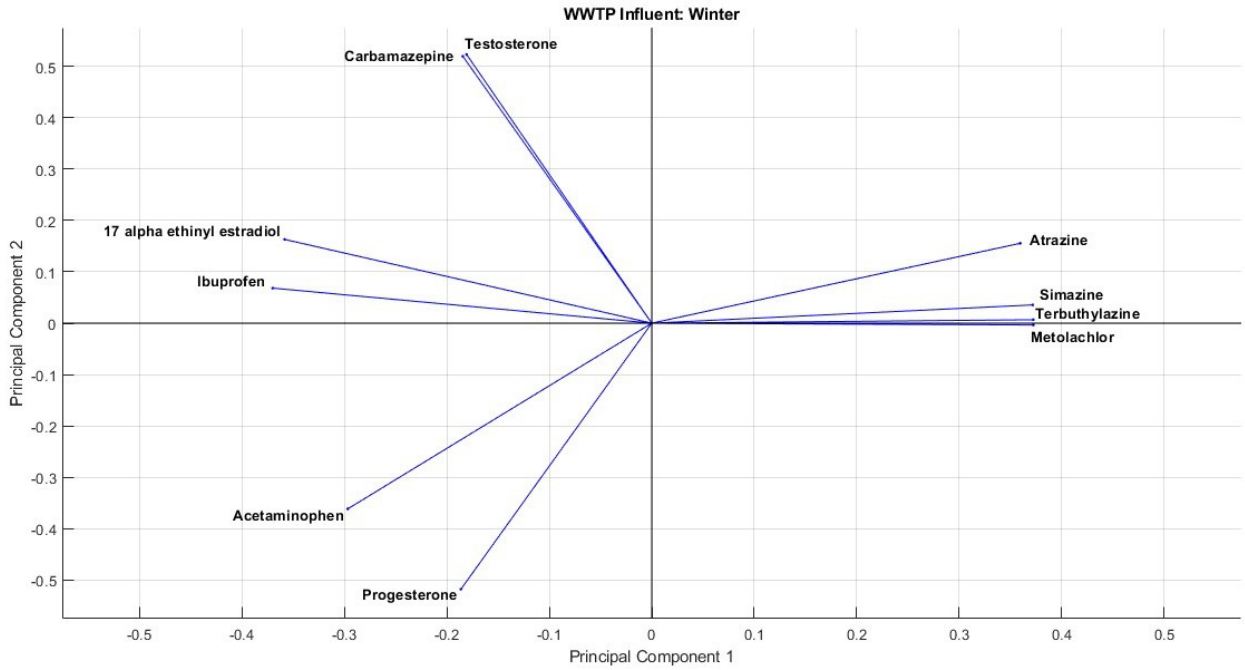


PCA results of the first two factors PC1 and PC2 in influent

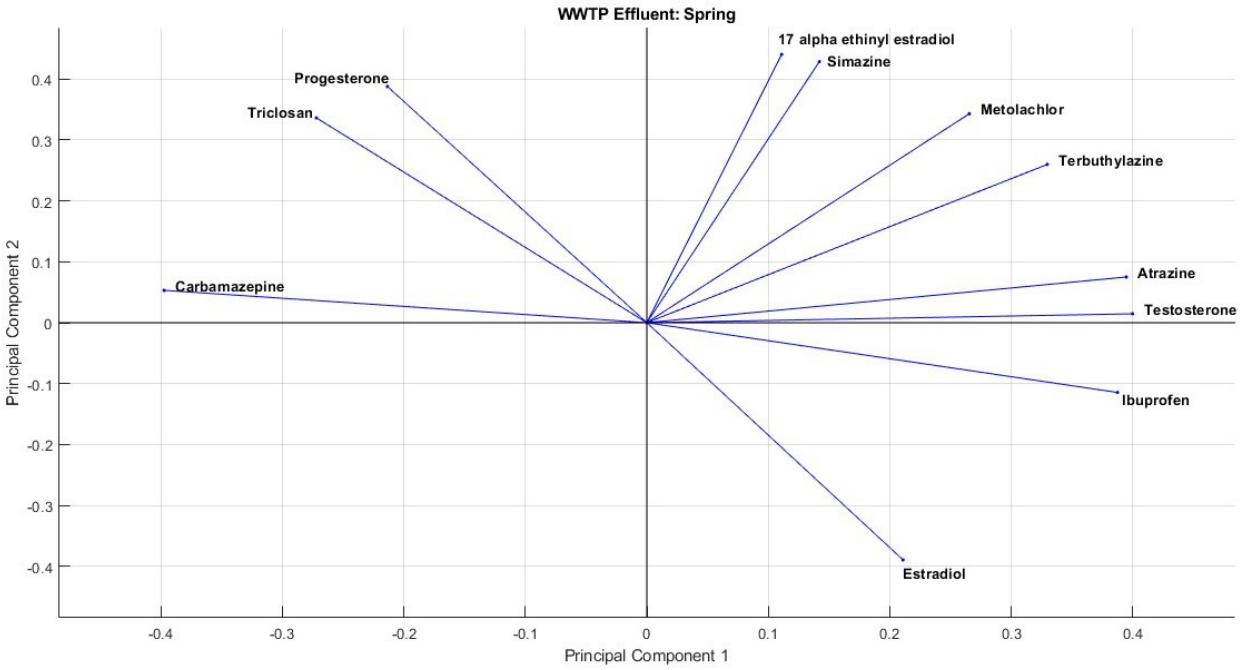


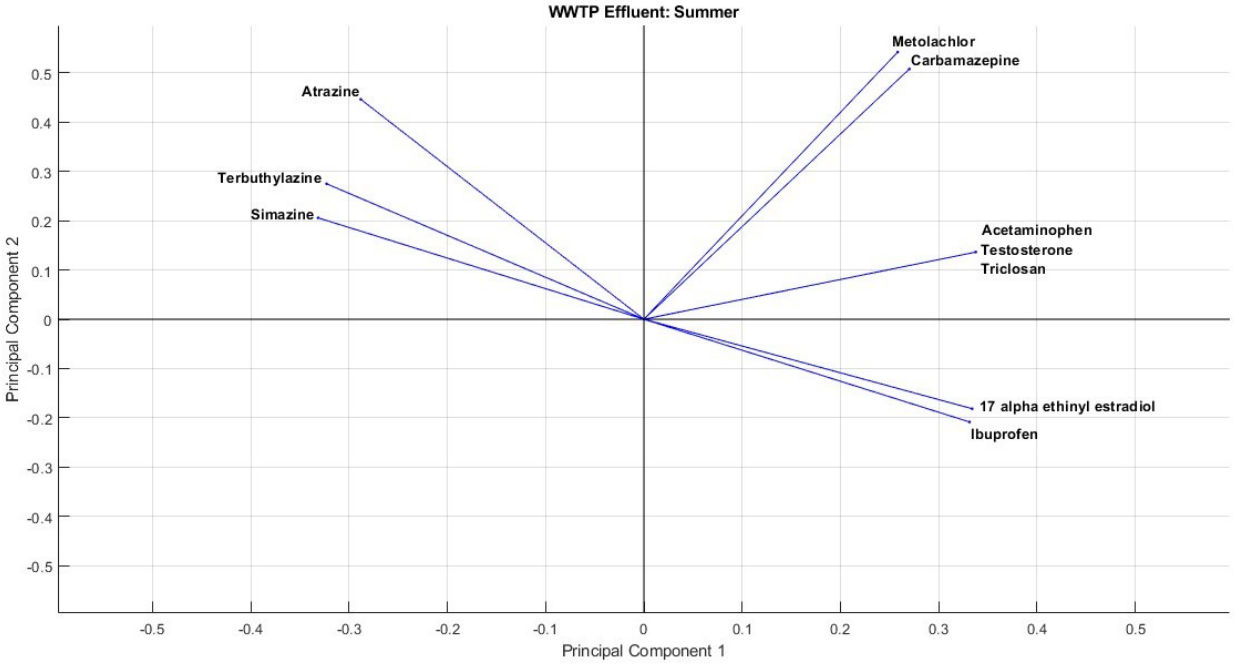


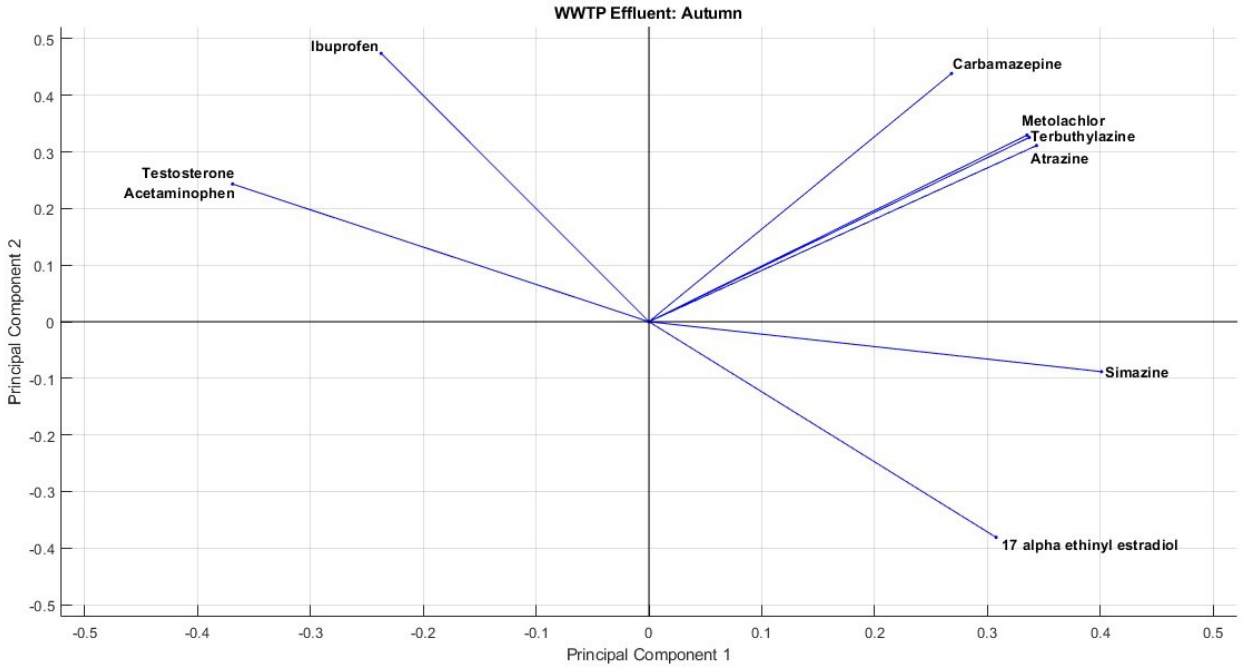

WWTP Influent: Autumn
Simazine
Ibuprofen
Testosterone
Progesterone
Triclosan
Acetaminophen
17 alpha ethinyl estradiol
Carbamazepine
Terbuthylazine
Metolachlor
Atrazine
Principal Component 2
Principal Component 1
0.6
0.4
0.2
0
-0.2
-0.4
-0.6

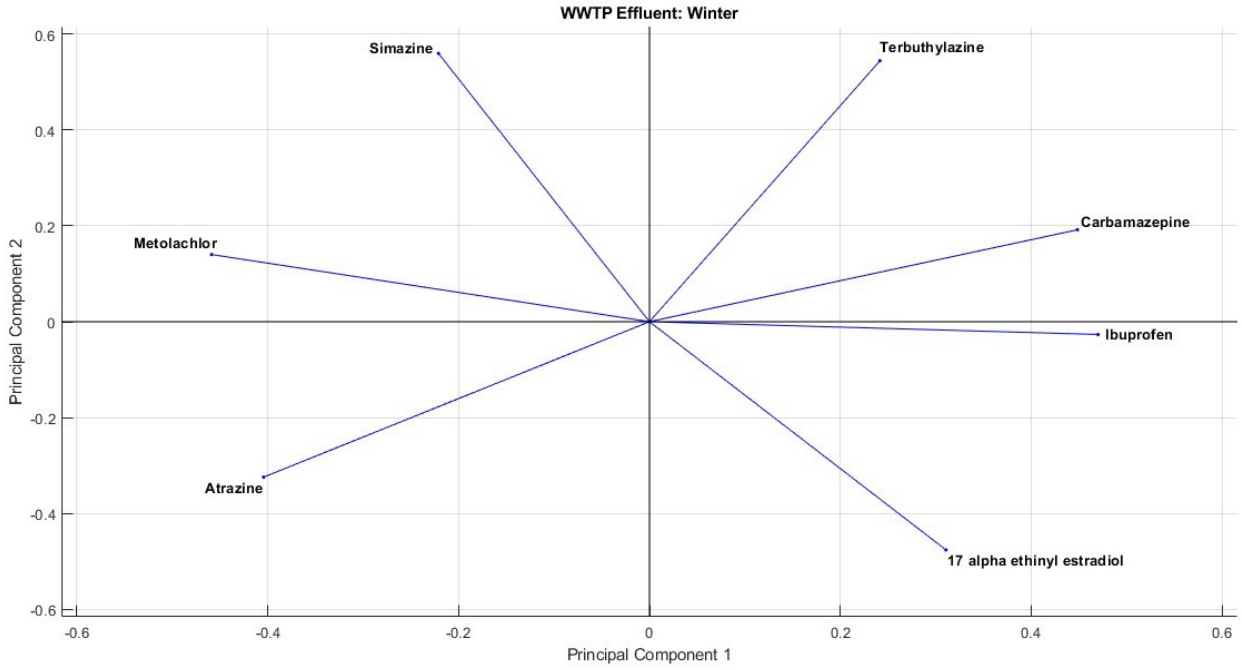

WWTP Influent: Winter
Carbamazepine
Testosterone
17 alpha ethinyl estradiol
Ibuprofen
Atrazine
Simazine
Terbuthylazine
Metolachlor
Acetaminophen
Progesterone
Principal Component 2
Principal Component 1
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
-0.5

PCA results of the first two factors PC1 and PC2 in effluent






WWTP Effluent: Autumn
Ibuprofen
Carbamazepine
Metolachlor
Terbuthylazine
Atrazine
Testosterone
Acetaminophen
Simazine
17 alpha ethinyl estradiol
Principal Component 2
Principal Component 1


WWTP Effluent: Winter
Simazine
Terbuthylazine
Carbamazepine
Metolachlor
Ibuprofen
Atrazine
17 alpha ethinyl estradiol
Principal Component 2
Principal Component 1

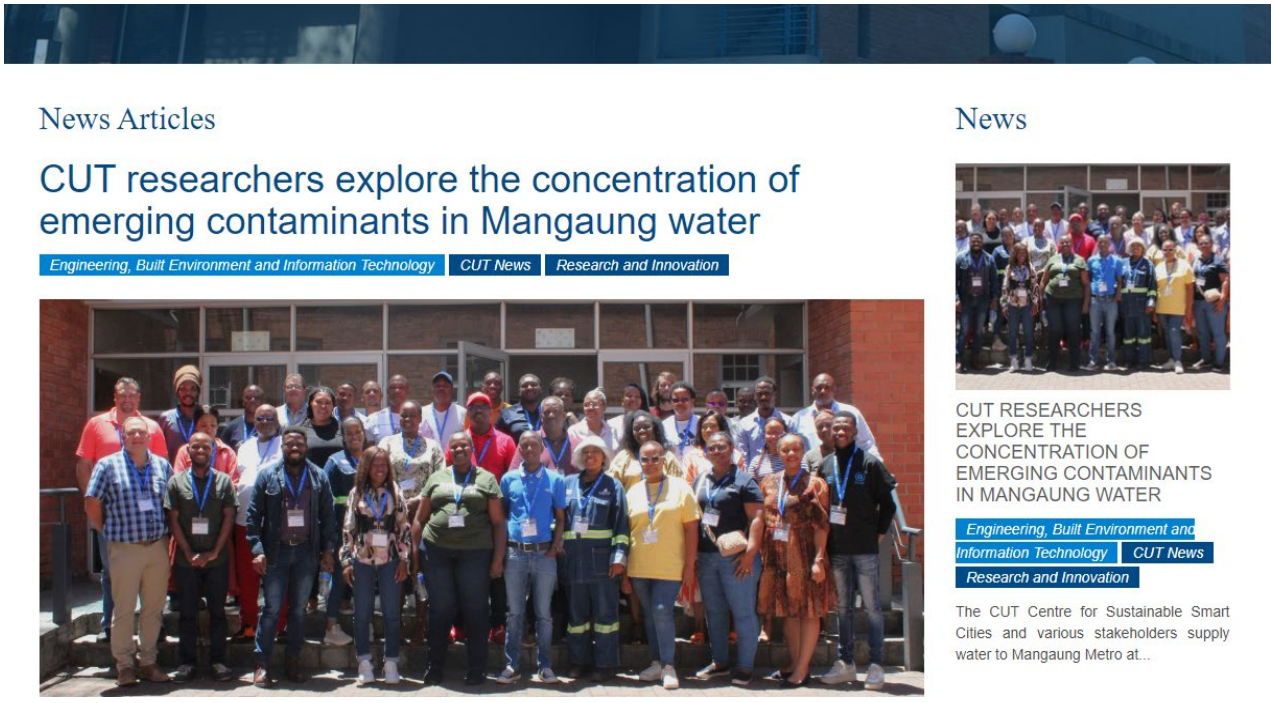
APPENDIX E: KNOWLEDGE DISSEMINATION ACTIVITIES

Technical workshop


WATER RESEARCH COMMISSION
CENTRE FOR SUSTAINABLE SMART CITIES
PROGRAMME
Chief Host
Prof SA Oke,
Civil Engineering Department, CUT)
09:00 - 10:00 Arrival and Registration
10:00 - 10:10 Welcoming speech and workshop objective (Dr Gumede & Prof Oke)
10:10 - 10:25 What is Emerging Contaminants (EC) (Dr Senbore)
10:25 - 10:35 Study Area (Dr Senbore)
10:35 - 11:05 Methods of sampling emerging contaminants (EC) (Dr Senbore)
11:05 - 11:50 Concentration of EC in Mangaung Water Sources (Prof Oke)
11:50 - 12:00 Tea Break
12:00 - 12:10 Questions, Answers, and Discussion
12:10 - 12:45 Sources of EC in Mangaung Water Sources (Prof Oke)
12:45 - 13:00 Discussion on Removal of EC in Water Sources of Mangaung (Prof Oke)
13:00 - 14:00 Lunch Time
14:00 - 14:30 Ecological risks of emerging contaminants (Mr Mugudamani)
14:30 - 14:40 Contributions from Water Research Commission (Dr Ubomba Jaswa)
14:40 Vote of Thanks (Dr Gumede)
Central University of Technology, Free State

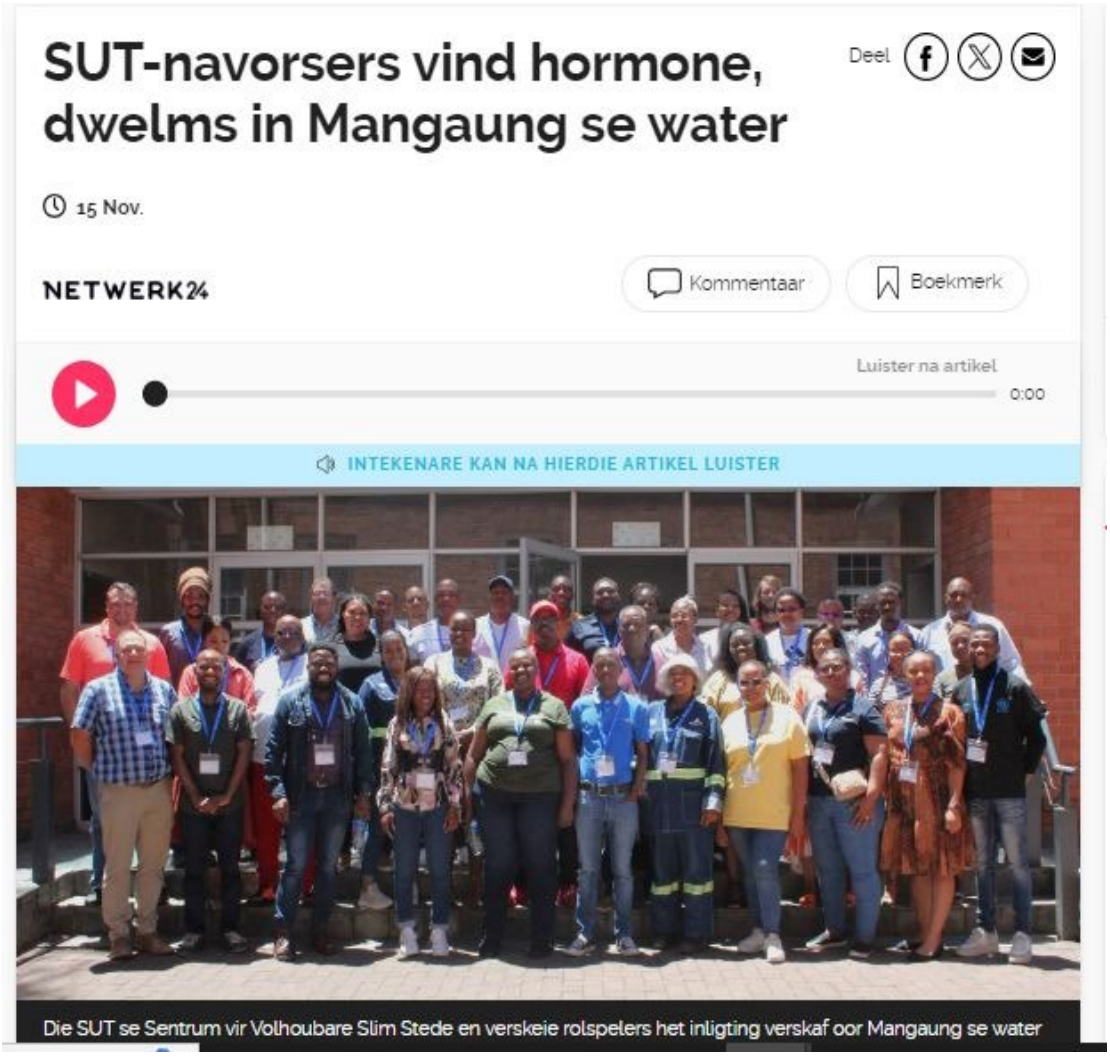
Presentation and interviews to Central University of Technology news outlet

https://www.cut.ac.za/news/cut-researchers-explore-concentration-emerging-contaminants-mangaung-water



Interviews to netwerk24 news outlet

https://www.netwerk24.com/netwerk24/nuus/wetenskap/sut-navorsers-vind-hormone-dwelms-in-mangaung-se-water-20231115



APPENDIX F: LABORATORY RESULTS

Rivers

Sample ID	Acetaminophen	Simazine	Atrazine	Terbuthylazine	Carbamazepine	Metolachlor	Testosterone	Progesterone	Ibuprofen	Estradiol	Triclosan	17-alpha-ethinyl-estradiol	Comments
Spring													
SWRS03	< LOQ	1.510	0.063	0.065	0.580	0.027	< LOQ	< LOQ	1.000	0.080	< LOQ	25.000	Renosterspruit
SWBS04	< LOQ	5.670	0.053	0.210	0.680	0.009	< LOQ	< LOQ	3.440	< LOQ	0.089	13.100	Bloemspruit
SWKOR05	0.081	< LOQ	0.002	0.007	< LOQ	0.003	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.090	Koringspruit
SWMOR06	< LOQ	0.055	0.012	0.014	0.496	0.004	< LOQ	< LOQ	1.580	0.062	< LOQ	12.200	Modder River/ Lekatlong
SWKLM07	0.149	0.047	0.015	0.012	0.512	0.006	< LOQ	< LOQ	2.870	< LOQ	< LOQ	10.500	Kleinmodder
Summer													
SWRS03	< LOQ	0.743	0.0356	0.118	0.488	0.0716	< LOQ	< LOQ	0.753	< LOQ	< LOQ	9.2	Renosterspruit
SWBS04	< LOQ	3.22	0.105	0.137	0.505	0.117	< LOQ	< LOQ	1.4	< LOQ	< LOQ	14.5	Bloemspruit
SWKOR05	< LOQ	< LOQ	0.0321	0.0349	< LOQ	0.0159	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	1.08	Koringspruit
SWMOR06	< LOQ	0.119	0.0311	0.0611	0.396	0.0248	< LOQ	< LOQ	0.383	< LOQ	< LOQ	3.85	Modder River/ Lekatlong
SWKLM07	< LOQ	0.0958	0.0347	0.0477	1.43	0.0537	< LOQ	< LOQ	2.11	< LOQ	< LOQ	10.3	Kleinmodder
Autumn													
SWRS03	< LOQ	0.9060	0.0247	0.0309	0.3200	0.0294	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	53.8000	Renosterspruit
SWBS04	< LOQ	0.4810	0.0184	0.0219	0.2850	0.0228	< LOQ	< LOQ	2.2600	< LOQ	< LOQ	38.0000	Bloemspruit
SWKOR05	< LOQ	< LOQ	0.0014	0.0016	< LOQ	0.0007	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	Koringspruit
SWMOR06	< LOQ	< LOQ	0.0099	0.0064	0.2230	0.0210	< LOQ	< LOQ	0.2220	< LOQ	< LOQ	24.6000	Modder river/ Lekatlong
SWKLM07	< LOQ	< LOQ	0.0188	0.0063	0.1680	0.0233	< LOQ	< LOQ	0.2680	< LOQ	< LOQ	9.7800	Kleinmodder
Winter													
SWRS03	< LOQ	0.12	0.316	0.156	0.304	0.0629	< LOQ	< LOQ	1.71	< LOQ	< LOQ	23.5	Renosterspruit
SWBS04	< LOQ	0.613	0.0728	0.0667	0.324	0.119	< LOQ	< LOQ	3.91	< LOQ	< LOQ	18.9	Bloemspruit
SWKOR05	< LOQ	< LOQ	0.00163	0.000701	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.281	Koringspruit
SWMOR06	< LOQ	< LOQ	0.0165	0.00917	0.358	0.00731	< LOQ	< LOQ	0.597	< LOQ	< LOQ	11.7	Modder River/ Lekatlong
SWKLM07	0.0333	0.0452	0.0088	0.00547	0.272	0.00371	< LOQ	< LOQ	2.57	< LOQ	< LOQ	7.33	Kleinmodder

Dams

Sample ID	Acetaminophen	Simazine	Atrazine	Terbuthylazine	Carbamazepine	Metolachlor	Testosterone	Progesterone	Ibuprofen	Estradiol	Triclosan	17 alpha ethinyl	Comment
Spring													
SWMS01	< LOQ	0.036	0.010	0.012	0.327	0.002	< LOQ	< LOQ	0.038	< LOQ	< LOQ	3.370	Maselspoort
SWMD02	< LOQ	0.028	0.008	0.011	0.342	0.002	< LOQ	< LOQ	0.061	< LOQ	< LOQ	4.060	Mockes
SWKD08	0.026	0.203	0.030	0.057	0.133	0.029	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	4.490	Krugerdrift
SWSD09	0.123	0.113	0.016	0.048	0.632	0.009	< LOQ	< LOQ	0.812	< LOQ	< LOQ	6.130	Seroalo
SWRUSD10	< LOQ	< LOQ	0.022	0.018	0.010	0.009	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.277	Rusfontein
Summer													
SWMS01	< LOQ	0.0529	0.031	0.0416	0.0876	0.0375	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	1.5	Maselspoort
SWMD02	< LOQ	0.0144	0.0308	0.0419	0.154	0.0273	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	3.4	Mockes
SWKD08	< LOQ	0.235	0.0392	0.0618	0.0778	0.0392	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	1.99	Krugerdrift
SWSD09	< LOQ	0.203	0.0355	0.0846	0.208	0.0238	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	2.01	Seroalo
SWRUSD10	< LOQ	< LOQ	0.0215	0.0246	0.0107	0.0101	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.251	Rusfontein
Autumn													
SWMS01	< LOQ	0.0422	0.0034	0.0070	0.0410	0.0115	< LOQ	< LOQ	0.0108	< LOQ	< LOQ	1.3000	Maselspoort
SWMD02	0.0936	0.0439	0.0047	0.0049	0.0335	0.0118	< LOQ	< LOQ	0.0297	< LOQ	< LOQ	4.3000	Mockes
SWKD08	< LOQ	0.2920	0.0191	0.0296	0.0704	0.0241	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	5.8600	Krugerdrift
SWSD09	< LOQ	0.0864	0.0099	0.0068	0.0855	0.0089	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	8.2300	Seroalo
SWRUSD10	< LOQ	< LOQ	0.0091	0.0026	0.1860	0.0153	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	14.8000	Rusfontein
Winter													
SWMS01	< LOQ	< LOQ	0.08	0.00734	0.0437	0.00385	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	1.04	Maselspoort
SWMD02	< LOQ	< LOQ	0.0515	0.00953	0.0774	0.00548	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	3.34	Mockes
SWKD08	< LOQ	0.233	0.0474	0.0301	0.0644	0.0161	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	4.53	Krugerdrift
SWSD09	< LOQ	0.0493	0.0052	0.0249	0.0455	0.00446	< LOQ	< LOQ	0.103	< LOQ	< LOQ	4.62	Seroalo
SWRUSD10	< LOQ	< LOQ	0.00911	0.00626	< LOQ	0.00287	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.387	Rusfontein

Treated drinking water

Sample ID	Acetaminophen	Simazine	Atrazine	Terbuthylazine	Carbamazepine	Metolachlor	Testosterone	Progesterone	Ibuprofen	Estradiol	Triclosan	17-alpha ethinyl-estradiol	Comment
						Spring							
TWWRUS01	< LOQ	< LOQ	0.019	0.020	0.010	0.009	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.145	Rusfontein
TWWMSPO2	0.102	0.027	0.015	0.019	0.253	0.010	< LOQ	< LOQ	0.014	< LOQ	< LOQ	2.780	Maselspoort
						Summer							
TWWRUS01	< LOQ	< LOQ	0.0175	0.0155	< LOQ	0.00652	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.144	Rusfontein
TWWMSPO2	< LOQ	0.039	0.119	0.161	< LOQ	0.0939	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.259	Maselspoort
						Autumn							
TWWRUS01	< LOQ	< LOQ	0.0083	0.0039	< LOQ	0.0038	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.4220	Rusfontein
TWWMSPO2	< LOQ	< LOQ	0.0297	0.0172	< LOQ	0.0390	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	1.0400	Maselspoort
						Winter							
TWWRUS01	0.28	< LOQ	0.0092	0.00597	< LOQ	0.00232	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.155	Rusfontein
TWWMSPO2	< LOQ	< LOQ	0.0283	0.0102	< LOQ	0.023	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.727	Maselspoort

Wastewater influent

Sample ID	Acetaminophen	Simazine	Atrazine	Terbuthylazine	Carbamazepine	Metolachlor	Testosterone	Progesterone	Ibuprofen	Estradiol	Triclosan	17-alpha-ethinyl-estradiol	Comment
						Spring							
WWTP01I	2.730	0.576	0.067	0.051	0.742	0.008	0.006	0.008	4.610	< LOQ	0.291	19.900	BNE
WWTP02I	5.350	0.040	0.018	0.006	0.164	0.003	0.009	< LOQ	3.320	< LOQ	< LOQ	47.000	Botshabelo
WWTP03I	8.810	0.483	0.030	0.042	0.945	0.014	0.008	0.028	11.100	< LOQ	0.314	26.700	Bloemspruit
						Summer							
WWTP01I	14	0.394	0.0657	0.114	0.54	0.0872	< LOQ	< LOQ	14.2	< LOQ	0.131	29.1	BNE
WWTP02I	14.3	0.107	0.0179	0.0226	0.826	0.017	0.00138	< LOQ	8.16	< LOQ	0.365	46.1	Botshabelo
WWTP03I	16.1	0.453	0.0467	0.0897	0.555	0.04	0.00288	< LOQ	8.39	< LOQ	0.137	23.1	Bloemspruit
						Autumn							
WWTP01I	< LOQ	0.1180	0.0657	0.0806	0.2540	0.0651	< LOQ	< LOQ	5.1000	< LOQ	0.4870	17.3000	BNE
WWTP02I	39.2000	< LOQ	0.0499	0.0311	0.4760	0.0220	0.0358	0.0491	9.4600	< LOQ	0.7600	62.1000	Botshabelo
WWTP03I	17.1000	0.1850	0.0170	0.0203	0.3050	0.0088	0.0286	0.0343	9.2800	< LOQ	0.6210	33.2000	Bloemspruit
						Winter							
WWTP01I	5.28	0.536	0.148	0.279	0.0819	0.211	< LOQ	0.00142	5.74	< LOQ	< LOQ	6.43	BNE
WWTP02I	18.1	0.0509	0.00975	0.00857	0.198	0.00243	< LOQ	0.023	7.58	< LOQ	< LOQ	25.8	Botshabelo
WWTP03I	10.1	0.0919	0.0491	0.0172	8.89	0.00507	0.0131	< LOQ	7.8	< LOQ	< LOQ	32.8	Bloemspruit

Wastewater effluent

Sample ID	Acetaminophen	Simazine	Atrazine	Terbuthylazine	Carbamazepine	Metolachlor	Testosterone	Progesterone	Ibuprofen	Estradiol	Triclosan	17-alpha-ethinyl-estradiol	Comment
						Spring							
WWTP01E	< LOQ	0.281	0.131	0.098	0.506	0.027	0.003	0.005	6.220	< LOQ	0.083	18.300	BNE
WWTP02E	< LOQ	0.028	0.018	0.013	1.090	0.003	< LOQ	0.006	3.830	< LOQ	< LOQ	11.200	Botshabelo
WWTP03E	< LOQ	0.322	0.034	0.059	1.200	0.022	< LOQ	< LOQ	2.860	0.034	0.166	20.300	Bloemspruit
						Summer							
WWTP01E	< LOQ	0.722	0.0719	0.106	1.64	0.0747	< LOQ	< LOQ	0.22	< LOQ	< LOQ	2.64	BNE
WWTP02E	8.7	0.131	0.0217	0.0285	2.82	0.119	0.00224	< LOQ	7.67	< LOQ	0.142	26.4	Botshabelo
WWTP03E	< LOQ	0.481	0.0374	0.0685	0.567	0.0261	< LOQ	< LOQ	3.28	< LOQ	< LOQ	11.7	Bloemspruit
						Autumn							
WWTP01E	< LOQ	0.3780	0.1110	0.0524	0.8050	0.1430	< LOQ	< LOQ	2.0500	< LOQ	< LOQ	45.2000	BNE
WWTP02E	11.8000	0.0488	0.0111	0.0102	0.5790	0.0119	0.0039	< LOQ	4.0800	< LOQ	< LOQ	26.2000	Botshabelo
WWTP03E	< LOQ	0.2850	0.0174	0.0115	0.5080	0.0147	< LOQ	< LOQ	0.0664	< LOQ	< LOQ	52.8000	Bloemspruit
						Winter							
WWTP01E	< LOQ	8.45	0.0327	0.0185	0.305	0.0279	< LOQ	< LOQ	0.421	< LOQ	< LOQ	14.7	BNE
WWTP02E	< LOQ	0.192	0.0212	0.0185	0.604	0.00343	< LOQ	< LOQ	5.58	< LOQ	< LOQ	20.1	Botshabelo
WWTP03E	< LOQ	< LOQ	0.0454	0.0148	0.162	0.0226	< LOQ	< LOQ	0.577	< LOQ	< LOQ	18.9	Bloemspruit