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**Evaluating the removal of emerging contaminants from the eThekweni Municipality
REMIX Water Treatment Plant**

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DECLARATION

I, Prince Manyepa, hereby declare that this dissertation, except where indicated in the text, is my work and has not been submitted in part, or in whole, at any other University or University of Technology.

The purpose of this study is to conduct a technological evaluation of the REMIX Water Treatment Plant for the removal of emerging pollutants. The analysis and quantification of the compounds was done at the Central Analytical Facility (CAF) at Stellenbosch University and at the Institute of Water and Wastewater at the Durban University of Technology where I am registered as a master's student in Civil Engineering and Geomatics under the supervision of Prof Mahommed Seyam, Prof Faizal Bux and Dr Ismail Banoo.

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ABSTRACT

The eThekweni Municipalities Department of Water and Sanitation (EWS) has initiated feasibility studies to determine whether it is financially and environmentally viable to implement direct potable water reuse (DPR) projects, and one of them is the REMIX Water Treatment Plant (RWTP) which is located within the Port of Durban and abstracts wastewater and sea water for treatment and potential future re-use. However, a review of the extant literature has highlighted that wastewater and seawater are primary sources and "sinks" for various contaminants of emerging concern (CEC). Emerging contaminants (ECs) can be endocrine-disrupting chemicals or cancer-causing agents in humans and animals if they are constantly present in drinking water.

This study evaluated the efficiency of the RWTP for the removal of different classes of pharmaceutical compounds by measuring the feed water and effluent of each treatment unit along the RWTP. The Quantitative structure-activity relationship (QSAR) model and OPBT criteria were used to screen these compounds for persistence, bioaccumulation, and toxicity (PBT) behaviour in the water matrix. This was done to produce a priority list that allowed effective monitoring of each treatment unit for observed PBT compounds that should not be present in reclaimed water intended for human consumption. The QSAR is a suitable alternative to the costly and labour-intensive *in vivo* screening experiments in the water matrix. It works in tandem with the new animal rights regulations, is safer than laboratory experiments, and also saves time. The study found that 4 out of 20 compounds were identified as potential PBT compounds by consensus agreement in both methodologies. The goal of this study was to assess the removal of ECs prioritised using the QSARINS model and OPBT criteria by carrying out a human risk analysis for reclaimed water proposed for drinking purposes within the City of Durban. This informed decision-makers, plant managers, and operators on what to constantly monitor or add to the treatment plant for the safe production of drinking water. Excellent removal rates of ECs were observed in the membrane biological reactor (MBR) and the reverse osmosis systems (ROs). The removal rates in MBR and ROs ranged from 38% to 100% and 96%, respectively. Excellent removal rates for heavy metals and nutrients across the treatment technology were also achieved in the final product water. The calculated risk/hazard quotients (RQ) for all ECs and heavy metals were also conducted in the reclaimed REMIX water. An $RQ/HQ > 1$ meant a high risk of ECs or

heavy metals, and <1 meant the risk was negligible. Except for some anomalies caused by ion suppression or matrix effects during the analysis, the majority of the ECs in the reclaimed water RQ were found to be less than 1. Identification of chemical, biological, and physical hazards using HACCP system principles led to the identification of critical control points for the technology. Five critical control points were examined, and techniques for successful RWTP monitoring were proposed based on the study findings.

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LIST OF ABBREVIATIONS

ECs	:	Emerging Contaminants
QSAR	:	Quantitative Structure Activity Relationship
PBT	:	Persistence, Bioaccumulation and Toxicity
KZN	:	kwaZulu - Natal
CSIR	:	Council for Scientific and Industrial research
EWS	:	eThekweni Water and Sanitation
RWTP	:	REMIX Water Treatment Plant
DWAF	:	Department of Water Affairs and Forestry
EC	:	Electrical Conductivity
MBR	:	Membrane Biological Reactor
AOP	:	Advanced Oxidation Process
RO	:	Reverse Osmosis
UF	:	Ultrafiltration filter
PST	:	Primary Settling Tank
HACCP	:	Hazard Analysis and Critical Control Point
CCP	:	Critical Control Point
KZN	:	KwaZulu-Natal
RQ	:	Risk Quotient
SRT	:	Solids Retention Time
NO ₃ -	:	Nitrate
PH	:	Potential of Hydrogen
EDC	:	Endocrine disrupting chemicals
DEWL	:	Drinking water equivalent Level
HIRA	:	Human Identification and Risk Assessment
As	:	Arsenic
Cd	:	Cadmium
Pb	:	Normalised Difference Vegetation Index
Co	:	Cobalt
PH	:	Potential of Hydrogen

EDC	:	Endocrine disrupting chemicals
DEWL	:	Drinking water equivalent Level
HIRA	:	Hazard Identification Risk Assessment
EPA	:	Environmental Protection Agency
DEWL	:	Drinking water equivalent Level
HIRA	:	Human Identification and Risk Assessment
TRAM	:	Tramadol
CDN	:	Codeine
SMX	:	Sulfamethoxazole
VEN	:	Venlafaxine
CBZ	:	Carbamazepine
CET	:	Cetirizine
DCN	:	Diclofenac
Npn	:	Naproxen
EFV	:	Efavirenz
Emt	:	Emtricitabine
Benz	:	Benzoyllecgonine
CAF	:	Caffeine
1.7 DMX	:	1.7 Dimethylanxine
Met	:	Methaqualone
Coc	:	Cocaine
ACET	:	Acetaminophen
MDM	:	3,4- Methylendioxyamphetamine
MET	:	Methamphetamine

LIST OF UNITS

l/s	:	Litre per Second
Mm	:	Millimetres
Mg/l	:	Milligram per litre
mS/m	:	Millisiemens per Metre
Us/cm	:	Microsiemens per Centimetre
°	:	Degree
%	:	Percent

CHAPTER 1: INTRODUCTION

1.1 Background

Due to water constraints brought on by climate change and the growing population, wastewater and seawater have been viewed as valuable water resources in more recent times. To address the demand in the city of Durban, the eThekweni municipality launched a direct potable water reuse project in response to increasing water demands. This project adopted a REMIX™ approach that extracts wastewater and seawater for treatment (*Masha, 2020*). The REMIX™ water treatment Plant technology system incorporates a hybrid approach, combining the processes of seawater desalination and the utilisation of treated effluent from a wastewater treatment facility. The effluent undergoes treatment using membrane bioreactor technology (MBR) and brackish water reverse osmosis (BWRO) for optimal purification. The reject water originating from the BRWO process unit is employed for diluting the seawater prior to its entry into the REMIX™ reverse osmosis (RRO) process, thereby resulting in a reduction in salinity levels. Moreover, the reduction in salinity results in a concomitant decrease in osmotic pressure. This results in a 40% reduction in energy consumption when compared to conventional seawater reverse osmosis desalination plants. The energy consumption of SWRO conventional desalination plants varies based on the quality of the intake water, typically averaging at 3.8 kWh/m³. In contrast, the Remix Water System exhibits a lower average energy consumption of 2.6 kWh/m³. Several studies, however, have identified wastewater, hospital effluents, and seawater as the principal sources and sinks for certain cocktails of emerging contaminants ECs (*Alygizakis et al., 2020*; *Ojemaye and Petrik, 2022*; *Urutiaga et al., 2013*). Current conventional water treatment systems are not equipped to remove such contaminants (*CD Swartz et al., 2018*). These organic micropollutants have several forms, some of which are known to have persistent, bioaccumulating, and toxic (PBT) properties. The occurrence, persistence, bioaccumulation and toxicity (OPBT) criteria and the quantitative structure activity relationship (QSAR) hazard screening tool were used in this work as an alternative approach to identify and rank potential PBT chemicals. In order to find compounds with PBT features, (QSAR) models have been effectively employed in the European region, North America, and Asia (*Gramatica et al., 2016*). These two techniques have been modified to emphasise emerging contaminants that are persistent, bioaccumulative, and potentially harmful to the environment and human health.. Furthermore, this gives a priority list of contaminants for

monitoring and effective potable water production. The use of two methodologies is a substitute for the costly and time-consuming laboratory screening tests, namely In vivo experimental testing.

With the exception of ECs, regulations or standards for water treatment plants (WTP) and water reuse projects (WRP) generally prohibit physico-chemical and biological water parameters such as turbidity, chemical oxygen demand (COD), biological oxygen demand (BOD), total suspended solids (TSS), bacteria, residual chlorine, etc. (Liu *et al.*, 2020). ECs exist in extremely low concentrations that range from n g/L to g/L; their elimination is not acceptable because of their "pseudo persistence" and inability to biodegrade. ECs comprise pharmaceutical compounds, endocrine disrupting chemicals, personal care products, illicit drugs, and pesticides.

In light of the aforementioned, the principal objectives of this investigation were to (1) screen for and determine potential PBT ECs in the reclaimed water, and (2) undertake a risk assessment on human health to make sure the recycled water produced by the (RWTP), was safe to drink. This study, however, looked at heavy metals, nitrites and nitrates, salinity, and TDS, which are common water pollutants found in wastewater and seawater. These contaminants are most likely introduced to people through drinking water. Heavy metals such as arsenic, mercury, and lead are commonly known for being toxic, bioaccumulating, and cancer-causing pollutants that have consistently been found in both surface waters and wastewater. Therefore, their total removal from reclaimed water assures the water's safety for end consumers.

In total, out of 20 compounds reviewed, 4 were identified as potential PBT compounds by a consensus agreement approach of the two methodologies among different targeted classes of emerging contaminants. For the human health assessment, risk quotient (RQ) values were estimated using measured concentrations of the emerging contaminants against their drinking water equivalent level (DWEL). The concept was derived from Riva *et al.*, (2018), where they used drinking water guidelines levels, but instead this study used DWEL for all the target emerging contaminants. An $RQ/HQ < 1$ was assumed to be of no risk, and an $RQ/HQ > 1$ showed the presence of a potential risk, implying the need for additional measures to reduce risks to acceptable levels. For emerging contaminants, the RQ was reduced below the threshold limit after the MBR.

A heavy metal risk assessment was conducted to assess the heavy metal impact of the reclaimed water. All the targeted heavy metals, such as lead, arsenic, chromium, mercury, and copper, were

all below the threshold limit of one. This highlighted that the RWTP has the potential to efficiently reduce concentrations of heavy metals to a safe level in water.

Furthermore, the use of the Hazard Analysis Critical Control Points (HACCP) methodology entailed the identification and assessment of potential hazards. The system identified critical control points. Five essential control points were identified out of six treatment stages which are the membrane biological reactor, Brackish and desalination reverse osmosis, ultrafiltration filter and advanced oxidation process. Conducting a chemical risk assessment can lead to the REMIX Water Treatment Plant being accredited by the International Organisation for Standardisation (ISO) or HACCP.

1.2 Problem statement

The Remix Water Treatment Plant (RWTP) uses seawater and wastewater as its primary sources for water treatment. These two sources are known sinks for various potential PBT emerging contaminants (ECs), both regulated and unregulated, with potential harm to public health and the environment. There are known endocrine disrupting, persistent, bioaccumulating, and toxic pesticide chemicals that have consistently been found in both surface waters and wastewater (n g-1 to g L-1) (*CD Swartz et al., 2016*). A report from the South Durban Community Environmental Alliance (SDCEA), which raised awareness among beachgoers after discovering significant sewage spills all across Durban (*Faleye et al., 2019*). This shows that there is a high likelihood that ECs mixtures will be found in RWTP abstraction sources and that these mixtures may have synergistic effects that cause cancer, birth defects, or antimicrobial gene resistance, according to studies reported in the literature (*Tran and Gin, 2017*). For the protection of humans, it is essential to do a risk assessment for PBT ECs.

1.3 Aim of the Study

This study aims to evaluate the eThekweni REMIX water treatment technology for removing emerging pollutants. This was accomplished by sampling the influent and effluent of each treatment unit along the treatment train and analysing the potential risk of PBT compounds after all the RWTP's treatment steps. There are diverse types of emerging contaminants, such as pharmaceuticals, illicit drugs, and pesticides, which were used to evaluate the efficiency of the RWTP technology.

1.4 Objectives

1. To determine the concentrations for the selected ECs in the influent and effluent from each Remix Treatment technology treatment unit.
2. To rank the most important substances in terms of persistence, bioaccumulation, and toxicity.
3. To conduct a quantitative risk assessment for potential PBT ECs.

1.5 Thesis outline

This dissertation is divided into five chapters that are organised to assist the reader to understand the goals and scope of the research as well as the methods used to achieve the research objectives. Each chapter is described briefly below. The **first chapter** is the introduction, which defines the research question and situates the study. The **second chapter** examines diverse literature to establish a foundation of knowledge for the study and provides an overview of the occurrence, transport, fate, remediation technologies, and impact of emerging contaminants on human health and the natural environment. **Chapter three** explains the research design and technique used in this study. It provides data analysis procedures as well as a human risk assessment of emerging pollutants. In **chapter four**, the study's findings are presented, discussed, and compared to existing data. The **fifth and final chapter** summarises and concludes the study, presents solutions to the research problem, and makes suggestions for future research.

1.6 Limitations of the study

The suggested sampling plan was intended to account for seasonal variations in wastewater regimes, but sampling was limited to one sampling event for the analysis of emerging contaminants, heavy metals, and other macro-determinants detected in water rather than four sampling events. This was difficult to achieve due to the shutdown of the REMIX Water treatment plant, during and post the COVID 19 pandemic period, and was beyond the control of researchers or supervisors.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

This review was prepared by searching for "emerging contaminants" or "micropollutants" in scientific databases, including Web of Science, Scopus, and Google Scholar. This chapter is broken down into four sections. The first section examines the prevalence, transit, fate, and classification of emerging pollutants found in different water matrices. It specifies the sources of these micropollutants, which include wastewater treatment plants, hospital effluents, rivers, and other such sources. The second section addresses hazard-screening models for emerging pollutants that take persistence, bioaccumulation, and toxicity into account. The three basic stages that must be followed to identify emerging contaminants in water samples are also discussed. These three important phases include sample, pre-treatment and pre-concentration, which were done to improve the method's sensitivity; the use of liquid chromatography (LC) as an analytical separation technique; and, finally, mass spectrometer detection (MS). The idea of risk assessment for human health is covered in the third section. The city of eThekweni's water demand is also discussed, along with potential treatment methods and present demand-meeting measures. In a nutshell, it is also mentioned in detail how membrane filtering works get rid of pollutants of concern like emerging toxins in wastewater and seawater.

2.2 Emerging contaminants

Emerging contaminants are chemicals, either manmade or naturally occurring, or microorganisms that are not routinely monitored in the environment. They are typically refractory, toxic, and bio-accumulative, and consequently have substantial detrimental effects on natural ecosystems and public health. However, due to their trace concentrations, which range from g/L to n g/L, most of these chemicals' environmental and human toxicity have not been studied, and they cannot be tested in municipal water systems (*Tran and Gin, 2017*).

2.3 Classes, fate and transport of emerging contaminants

Emerging pollutants include pharmaceutical chemical compounds, endocrine disrupting chemicals, illicit narcotics, personal care products, and flame retardants. Many of them have endocrine disruptive characteristics (*Santos et al., 2020*).

Emerging pollutants reach WWTPs through a variety of pathways, including residential sewage, urban storm water runoff, agricultural operations, and industrial waste, before eventually entering the water cycle. Conventional wastewater treatment plants (WWTPs) are not intended to remove these contaminants (*CD Swartz et al., 2018*). Some escape wastewater treatment facilities due to hydrophilic traits while others escape due to solubility parameters and half-life breakdown in water matrix, and they are occasionally found in drinking water treatment facilities. Continuous exposure to reclaimed water containing emerging pollutants whose fate, behaviour, and transport are unknown could threaten people's and other living creatures' short- and long-term health. However, in order to build a long-term environmental monitoring program, it is essential to have a sustainable regulatory framework. However, having a long-term regulatory framework is critical for developing long-term environmental monitoring and drinking water guidelines for ECs. As a result, this study was motivated to evaluate the removal of ECs to protect human health, informing decision makers, managers, and plant operators about the efficiency of the REMIX Water Treatment Plant treatment of the pollutants detected from two separate water abstraction sources.

2.3.1 Pharmaceutical Compounds

Pharmaceuticals are unavoidable in the lives of human beings and animals. They are carefully formulated medications or treatments intended for a specific form of illness prevention in both people and animals. They are precisely developed medications or treatments intended to prevent disease in both humans and animals. Excreta of humans, the disposal of obsolete pharmaceuticals, agricultural activities, and other factors all contribute to the release of pharmaceutical chemicals into the environment. They vary in behavior, metabolism, and chemical structure; consequently, their occurrence in aquatic environments depends on consumption patterns. (*Gomes et al., 2020*). Pharmaceuticals that have not been entirely metabolized by the body are expelled in either their original or metabolized form. *Abafe et al., (2018)*, discovered high levels of antiviral medicines in Durban wastewater influents and effluents. This has also prompted this study to look into regularly used over-the-counter prescription drugs of this nature. Impact RX in South Africa is a data base used to inform this research on prescription data. Most medications are hydrophilic in nature (water loving), meaning they ionize quickly and have a limited shelf life. Some, however, are hydrophobic and can remain and cause harm to humans and animals.

2.3.2 Personal care products

Pharmaceuticals can occasionally be found in personal care products category, however personal care products also encompass a large number of items that contain chemicals, including cosmetics, preservatives, scents, and toiletries (Ng *et al.*, 2021). The majority of these chemicals contain either parabens or polycyclic fragrance, which are used to protect against bacterial infection. For example, triclosan, a disinfectant, is commonly utilized in the production of consumer goods such as toothpaste and hand soap. Showering, bathing, dishwashing, and leisure activities such as swimming allow personal care products to infiltrate the wastewater and aquatic environment. Personal care items can accumulate in aquatic species and create a variety of negative health effects depending on their use and exposure level (CD Swartz *et al.*, 2018). Due to their physico-chemical nature most of them persist in wastewater and WWTPs into the environment and finally get discharged by the rivers into the sea.

2.3.3 Endocrine disruptors (EDCs)

Endocrine disrupting chemicals (EDCs) are chemicals which impact the endocrine system and cause adverse reproductive and developmental health effects in humans, animals, and/or their offspring. The term "EDCs" refers to a broad category of compounds, most of which are biologically active chemicals, utilized in the manufacture of a variety of industrial and consumer goods (such as pharmaceuticals, pesticides, and other consumer goods involving plastics) (CD Swartz *et al.*, 2018). However, most EDCs are synthetic organic compounds (e.g., medicines, personal care products, pesticides) transported into the environment via wastewater, storm water, and so on, but some exist naturally (e.g., estrone, 17-estradiol).

The endocrine system is an intricate interconnected system of organs, such as the thyroid, pancreas, pituitary, ovaries, testes, and adrenal glands. These organs secrete hormones into the bloodstream, which then bind to specific receptors on cells in various organs or tissues, exerting their specific effects.

2.3.4 Measurement Methods for Chemicals that Disrupt Hormones in Water

To assess whether endocrine disruptors are present in water, one of two approaches can be used:

- Individual testing for each drug thought to be capable of causing endocrine disruption as well as its potential to exist in the area being researched is one option, or.
- test the water sample using one or more of the available bioassays for endocrine disruptive activities.

Humans and aquatic animals are believed to be exposed to a diverse mixture of emerging contaminants; as a result, it is costly and time-consuming to conduct experimental or toxicity tests for all thousands emerging contaminants. However, screening methods have been developed to screen compounds that have high toxicity showing endocrine disrupting characteristics based on their chemical structure. Chemicals with similar structures have more or equal toxicity behavior in the environment (*Santos et al., 2020*). The screening tests can further help to do detailed bioassays investigations of the identified toxic compounds. Bioassays serve as valuable tools in assessing the collective estrogenic and androgenic activity induced by various endocrine-disrupting substances found within a water ecosystem, encompassing both known and unidentified agents. Endocrine disruptive substances' activity and effects are determined using both biological (in vivo and in vitro) and biochemical (in vitro) techniques. This is the case that this research also intends to investigate for monitoring chemicals that may pose adverse effects to human health.

2.3.5 Illicit drugs

Drugs that are illegal have been found all over the water, making them a new type of pollutant. The main way illegal drugs get into the water supply is when people use them. Urine and faeces carry the drugs into the sewers. Illegal drugs are used all over the world in amounts that are like therapeutic doses. Current users of illicit drugs use cocaine, heroin, methamphetamine, marijuana, MDMA and other drugs.

Methamphetamine is known in South Africa as 'tik' but as crystal meth, ice in different parts of the world. It has been found out to be most prevalent illicit drug in Gauteng and Western Cape but much higher in Western Cape. However, cocaine use is considerably higher in Europe, particularly in cities in Belgium and the Netherlands. In Durban Hawks members from Durban and serious organised Investigation working together Explosives Unit seized 300 000 tablets of mandrax which is also known as Methaqualone. This literally shows how illicit drugs are being used in the Durban Metro and surrounding communities in South Africa. The confiscation of these drugs in Durban has also encouraged this research to investigate the presence and removal of various illicit

drugs that are commonly used around the world in the wastewater and seawater (*CD Swartz et al., 2018*).

2.4 Occurrence levels of micropollutants in South Africa

The occurrence of ECs in the water matrix exhibits regional variability, which is contingent upon factors such as lifestyle, epidemic disease outbreaks, and the presence of chemical or manufacturing industries within a given locality. The main origin of emerging contaminants in aquatic environments is commonly attributed to wastewater. In the scope of environmental monitoring, the analysis of wastewater has emerged as a valuable tool for studying the behavioural patterns of a specific population within a defined geographic area (*Archer et al., 2021*). This has aided researchers in their analysis of South African intake of numerous pharmaceutical substances, personal care items, endocrine disruptors, and illegal narcotics (*Abafe et al., 2018; Gani et al., 2021*). In the environment, the micropollutants find their ultimate destination through various processes. These processes include sorption, mineralisation, diluting it, photolysis, hydrolysis, oxidation, decomposition, and complexation. All these processes are affected by the contaminant's physicochemical properties, how they interact with various environmental matrices, and the wastewater treatment plant methods. The different steps in treating wastewater depend on the physical and chemical qualities of the toxins, how they react with different parts of the environment. (*Dolar et al., 2012*). *Gani et al., (2021)*, reviewed various emerging contaminants in various geographical zones recorded in the Southern Northern, Western parts and Eastern (KwaZulu-Natal, Free State) of South Africa.

2.4.1 Wastewater

The untreated wastewater in South Africa was found to contain a diverse range of emerging contaminants comprising of such as analgesics, anti-inflammatory drugs, and antibiotics (*Gani et al., 2021*). The North zone has reported the presence of Triclosan, Ibuprofen, Naproxen, Acetaminophen, Efavirenz (128 g/L), 112 g/L, 55 g/L, and 50 g/L. The South Zone was reported to have a significant presence of Diethyl phthalates DEP (6596.7 g/L), Dibutyl phthalates DBP (5267 g/L), and Benzyl butyl phthalates BBP (846 g/L). High amounts of Diethylhexyl phthalates DEHP (3917 g/L) and Pentachlorophenol PCP (843 g/L) were also reported. Neither of these studies investigated illicit drugs. This results in a gap in the study of illicit drugs. Illicit substances were not examined in either of these studies. Consequently, there exists a gap in the investigation

of prohibited substances. The present study examines the efficiency of RWTP in treating wastewater influent, which may contain emerging contaminants as suggested by previous research.

2.4.2 Drinking Water

The presence of emerging contaminants in sources of drinking water was observed across South African provinces, exhibiting diverse concentration levels. The eastern zone displayed a concentration range of 0 to 330 n g-1, while the northern zone exhibited a concentration range of 0.03-220 n g-1. The southern zone, on the other hand, showed a 0 to 10 n g-1 concentration range (*Gani et al., 2021*).

There has been no research undertaken in the West zone to yet. The North zone has the highest concentrations of carbamazepine (150 n g-1), atrazine (160 n g-1), and terbuthylazine (220 n g-1).

2.4.3 Surface water

Many cocktail ECs are present in wastewater treatment plants located near rivers and streams. Surface waterways are also polluted by livestock effluents. As a result, if that water is not adequately cleaned, it has the potential to pollute surrounding surface waterways or rivers. Presented below is an inventory of ECs that have been identified in surface water throughout the geographical expanse of South Africa. Several compounds have been identified in the North zone, with antiretroviral drugs (ARVs and herbicides) being detected in significant quantities. The order of prevalence for these compounds is as follows: The compounds detected based on their respective concentrations in Nano-gram per litre is as follows: Terbuthylazine, Nevirapine Atrazine, Stavudine, Zidovudine (1969 n g-1) (1480 n g-1) (1237 n g-1). (973 n g-1) (778 n g-1). According to reports, the catchment area of the Hartbeespoort Dam has the highest concentrations of Terbuthylazine and Atrazine, while the catchment area of the Roodeplaat Dam has high concentrations of Nevirapine, Zidovudine, and Stavudine. The results of these investigations underscore the inadequacy of conventional wastewater treatment facilities in effectively treating wastewater. Consequently, this has prompted the exploration of the potential of RWTPs for eliminating ECs (*Gani et al., 2021*).

Table 2.1 Prevalence and removal of the targeted emerging contaminants in different Wastewater Treatment Plants in South Africa

Compounds	KZN		western Cape		Gauteng		average	Average	Removal %	References
	Influent n g-1	Effluent n g-1	Influent n g-1	Effluent n g-1	Influent n g-1	Effluent n g-1	Influent n g-1	Effluent n g-1		
Acetaminophen	5800	4.6	0	500	136900	40	142700	544.6	99.6	(Archer <i>et al.</i> , 2017; Gani <i>et al.</i> , 2021; Madikizela and Chimuka, 2017; Verlicchi <i>et al.</i> , 2023)
Tramadol	0	0	836	83.6	0	0	836	83.6	90.0	(Archer <i>et al.</i> , 2021; Chris Swartz <i>et al.</i> , 2015)
Codeine	0	0	100600	60	0	0	100600	60	99.9	(Archer <i>et al.</i> , 2021)
Sulfamethoxazole	34500	0	0	0	26000	40000	60500	40000	33.9	(Gani <i>et al.</i> , 2021; Verlicchi <i>et al.</i> , 2023)(Rimayi <i>et al.</i> , 2019)
Trimethoprim	0	0	0		11100	1600	11100	1600	85.6	(Archer <i>et al.</i> , 2021)(Gani <i>et al.</i> , 2021)
Venlafaxine			50.5	45.9	300	180	350.5	225.9	35.5	(Archer <i>et al.</i> , 2021, 2017; Verlicchi <i>et al.</i> , 2023)

Carbamazepine	2200	900	0	0	600	400	2800	1300	53.6	(Gani <i>et al.</i> , 2021; Verlicchi <i>et al.</i> , 2023)
Cetirizine					4000	800	4000	800	80.0	(Archer <i>et al.</i> , 2021, 2017; Verlicchi <i>et al.</i> , 2023)
Naproxen	0		0	0	55000	13500	55000	13500	75.5	(Archer <i>et al.</i> , 2017; Gani <i>et al.</i> , 2021; Madikizela and Chimuka, 2017; Verlicchi <i>et al.</i> , 2023)

2.4.4 Ground water

South Africa is inadequately monitoring groundwater sources for the presence of ECs, According to *Gani et al., (2021)*, only one study has reported EC presence in ground water in the north zone. There were 11 ECs detected in groundwater samples taken near the Hartbeespoort Dam in Gauteng province, with the anti-retroviral medicine Nevirapine being the most prevalent chemical at a value of 13 ng-1. Since South Africa relies heavily upon surface water for its freshwater supply, there is a large body of literature on the monitoring of EC in surface waters (*Rimayi et al., 2019*).

2.4.5 Seawater and Emerging contaminants

In a study conducted by *Ojemaye and Petrik, (2022)*, medications and personal care items were evaluated in several environmental compartments. Among all the samples from the various sites, diclofenac was found to be the most prevalent compound, with a higher concentration than the other pharmaceutical compounds.

According to *Govender, (2022)*, popular beaches in Durban and on the kwaZulu Natal south coast were brimming with faecal matter and other contaminants.. This validates a report by *Carnie, (2022)*, indicating sewage flowing into the ocean from the city with close to four million people. Moreover, the REMIX Water Treatment Plant abstraction water for treatment from the ocean is very likely to have a cocktail of various ECs. This led to the study's need to undertake a detailed risk analysis to safeguard public health from any harmful ECs.

2.4.6 Regulations of emerging contaminants

One reason why emerging contaminants in wastewater are not controlled yet many of them are found ubiquitous in wastewater and surface waters is that their perceived risk to human health and aquatic animals is not clearly known and there is limited research towards their toxicity endpoints. Emerging contaminants data collection and monitoring is by no means easy, building systematic sampling needs a lot of money and expertise. This sometimes makes it hard to put rules in place. So, there are no limits on how much of some chemicals can be in a wastewater treatment plant's effluent before it is released into the natural environment. However, in other developed countries such as Australia other ECs threshold limit concentration of some of the ECs have been proposed especially in water reuse projects, for instance carbamazepine, sulfamethoxazole and tetracycline threshold guide line concentrations are as follows 3.5 µg L⁻¹ , 3.5 µg L⁻¹ and 1.5 µg L⁻¹ respectively (*Khan and Anderson, 2018*).

2.4.7 Human and environmental impacts of emerging contaminants

The toxicity of EPs is significant, with amounts as low Nano grams per litre (n g-1) having adverse effects on both people and creatures that live in water. These effects include hormonal interference in fishes, genotoxicity, carcinogenicity in lab animals, endocrine disruption, and immune toxicity (*Vasilachi et al., 2021*). Continuous antibiotic exposure in water led in the development of anti-resistance genes in bacteria, reducing the therapeutic potential of antibiotics. According to *CD Swartz et al., (2016)*, the presence of HIV-ARVs in water can be regarded as a concealed or dormant hazard. The consumption of HIV-ARVs at low concentrations through drinking water may give rise to the potential development of resistance by the HIV virus. These dangers were not previously recognized or have existed for some time but are only now being recognized or uncovered. The best method for reducing the emergence of resistance is maximally suppressive AR treatments, or HAART, which lower the risk of viral mutations.

HIV-ARVs may have an impact on the natural viral component of municipal wastewater treatment works as well as viruses' ecological role in receiving natural water. Aquatic viruses may perform a critical but little-understood function in the environment. The phenomenon in question exerts significant impacts on bacterial and algal populations in aquatic environments, potentially serving as a regulator of phosphorus cycling and primary productivity. The importance of ARV therapy in South Africa is indisputable, given the staggering number of 1.9 million individuals currently undergoing treatment. However, the potential ramifications of inadvertent ARV drug release into the environment and water bodies warrant scrutiny, particularly with regard to their impact on the ecosystem and human health.

2.5 Conventional wastewater treatment plants and emerging contaminants removal

Activated sludge, which utilizes a consortium of mixed microbial communities to degrade contaminants through aerobic or anaerobic biological processes, is the most prevalent form of wastewater remediation. Several ECs cannot be eradicated by conventional methods for treating wastewater (*Ghernaout and Elboughdiri, 2019*). Water reuse regulations and standards in developing countries, including South Africa, currently focus on prohibiting conventional contaminants, while neglecting emerging contaminants such as residual chlorine, BOD, turbidity, TSS ,COD and others (*Liu et al., 2020*). Typically, conventional treatment technologies comply with the established regulations that regulate the release of potable water and wastewater effluents. Due to a combination of biotic and abiotic mechanisms, certain ECs undergo partial elimination

or degradation. However, certain ECs that are more resistant in nature escape treatment facilities and infiltrate the surface water. Compounds possessing high octanol/water partition coefficient and low solubility but remain trapped in the underlying sediment contingent upon the efficacy of WWTPs. The identification of these substances within effluent and particulate matter has been established as a pathway for the entry of stated pollutants into groundwater, surface water, and potable water sources (CD Swartz *et al.*, 2018).

2.5.1 Chemical properties of emerging Contaminants

2.5.1.1 Solubility

The partition coefficient (K_{ow}) is a physical factor that characterizes a chemical. The partition coefficient can be defined as the quotient of the concentration of the chemical present in n-octanol and the concentration of the CEC present in water. This parameter holds significant importance in the determination of water solubility and bioconcentration, as well as in the estimation of water solubility.

The application of partition coefficients is imperative in assessing the behaviour of a contaminant within a given environment. The range of K_{ow} is from -3 to 4. K_{ow} exceeding 4 is classified as hydrophobic, resulting in low solubility in water. K_{ow} with skin absorption potential lie within the 2-4 range (Zabalza, 2019).

2.5.1.2 Molecular weight

The smallest unit of chemical that comprises all a substance's chemical attributes is defined as its molecular weight. Filtering pollutants successfully with membranes is mostly dependent on the contaminants' molecular weight, which guarantees that greater molecular weight contaminants are not retained in the final product. RO has been shown to be capable of removing substances with molecular weights larger than 200 g/mol. However, the molecular weight measure does not offer specific geometric information and is not a reliable indicator of the process's success (Zabalza, 2019).

2.6 Water demand in eThekweni Municipality

The average daily water consumption in eThekweni Municipality amounts to 905 mega litres, which is supplied by a network of 10 potable water treatment plants. Umgeni Water is responsible

for supplying a significant portion of the Municipality's water, while the remaining fraction is provided by the Municipality's proprietary water treatment facilities. The adverse impact of unpredictable climatic patterns has resulted in a reduction of eThekweni's water supply, leading to the implementation of water rationing measures throughout Durban City. The municipality has executed various water reuse initiatives, comprising a trial REMIX water treatment facility that is undergoing testing to assess its dependability in delivering potable water (*Masha, 2020*). According to *Masha, (2020)*, the facility employs a hybrid treatment system that combines various technologies to effectively recycle both seawater and wastewater. Conducting a chemical risk assessment of the hazardous chemical compounds present in the reclaimed water is crucial to meet the current water demand. Diverse cutting-edge technologies for wastewater treatment are employed to enhance the elimination of ECs from WWTPs, classified according to the mechanism accountable for removing these contaminants. The effective technologies currently employed encompass adsorption on activated carbon, advanced oxidation processes, membrane filtration, and ozonation.

2.6.1.1 The REMIX treatment technology

The system employs a combination of multi-barrier treatment methods, integrating seawater desalination and wastewater treatment technologies, leveraging membrane bioreactors and brackish/seawater reverse osmosis (*Masha, 2020*). The reject water from the BWRO process unit dilutes the seawater, decreasing the osmotic pressure before the seawater reverse osmosis (SWRO) process decreases the salt of the water. As a consequence, energy consumption is lowered by 40% when compared to standard SWRO desalination units used in other water reuse projects (*Oscar et al., 2017*). SWRO conventional desalination facilities spend an average of 3.8 kWh/m, based on how good the input water quality (*Masha, 2020*).

The major objective of RWTP technology, according to *Masha, (2020)*, is to produce reclaimed water that can be used for human consumption as well as discharged into the environment. According to reports, this system consumes an average of 2.6 kWh/m³. Because RWTP has never been studied, our work was driven to evaluate the system for eliminating new pollutants. Evaluating the removal of ECs from recovered water produced is critical for future planning and effective monitoring of each chemical class under investigation.

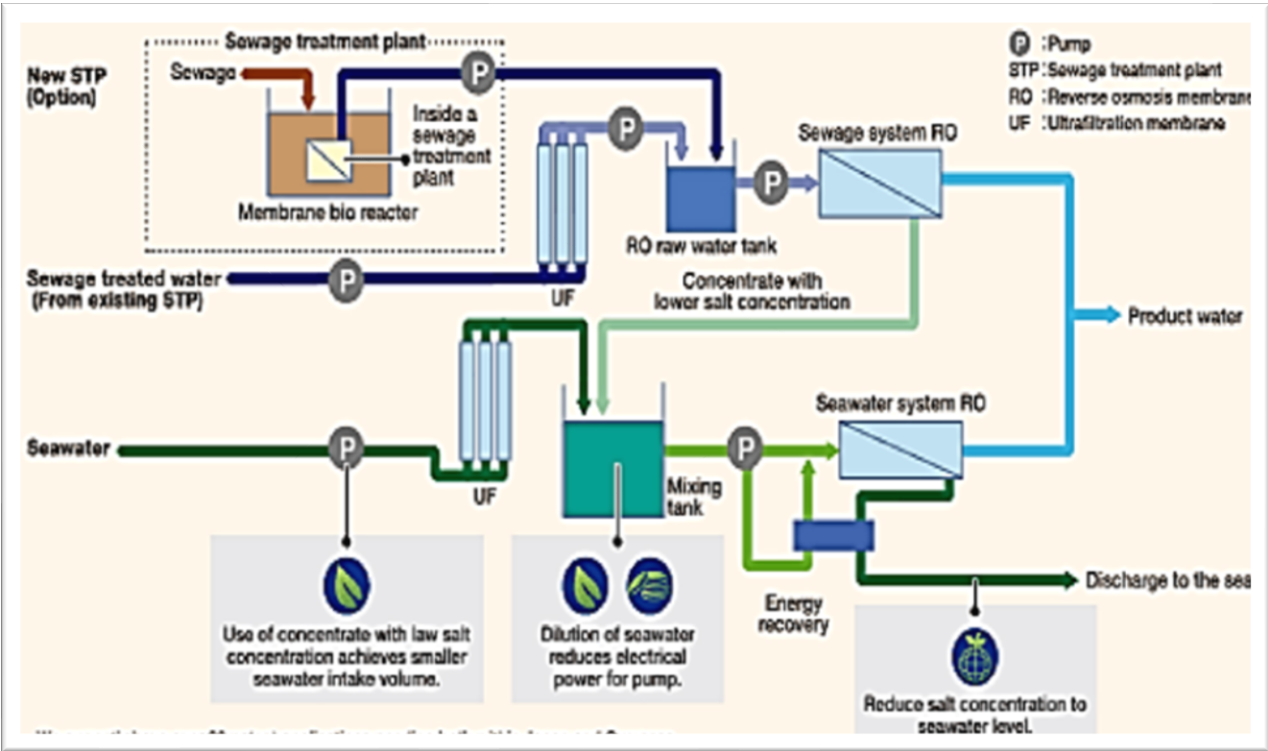


Figure 2.1 Schematic diagram of the REMIX Water Treatment Plant (Masha, 2020)

The RWTP is made up of 98% pressure driven membrane treatment processes (physical processes), and 2% biological and chemical processes, as seen in Figure 2.1. The product water in the sewage system before the mixing tank and primary treatment is diluted by ultrafiltration filter making it less concentrated with salts.

According to *Yangali-Quintanilla et al., (2010)*, a membrane-filtration separation technology has been proved to be successful in eliminating developing pollutants such as medicines, personal goods, endocrine disrupting chemicals, and so on. The membrane processes are either driven by electricity or by pressure. In the literature, pressure-driven membranes have been used to remove different pollutants from feed water. Pressure membranes are divided into the following types:

- Microfiltration
- Ultrafiltration
- Nano-filtration
- Reverse Osmosis

2.7 Membrane filtration technology

Membrane filtration has been studied as a possible method for removing harmful organic micropollutants such as pesticides and dyes, as well as a variety of other synthetic compounds. Most separation techniques include selectively filtering influent via holes of varying diameters. When extracting ECs from aqueous solution, the physicochemical properties of the target ingredient, membrane type, and operating circumstances all contribute to the performance of polymeric membrane systems (Warsinger et al., 2018).

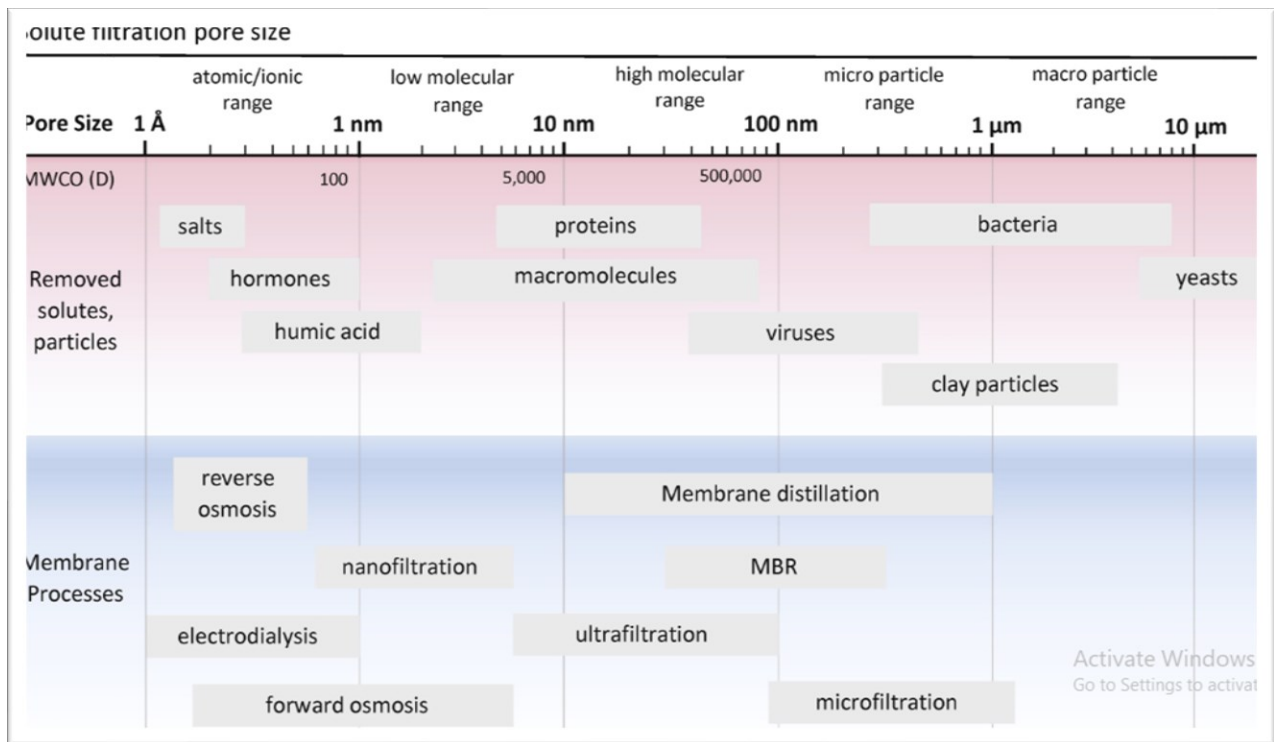


Figure 2.2 A diagram depicting membrane separation processes, apertures, and molecular weight cut-offs (MWCO) as well as various solute particles. Adapted from (Lee, S. and Kim, J., 2020)

Membrane processes are classified into different categories based on several characteristics, such as membrane configuration, membrane material type, driving force, mechanism of separation, and size range of removed elements (Warsinger et al., 2018). The classification of technologies into high-pressure (NF, RO) and low-pressure (MF, UF) is a widely accepted practice.

Notwithstanding, the utilization of high-pressure (NF, RO) methodologies is frequently correlated with increased energy requirements.

2.7.1 Microfiltration and ultrafiltration

The category in question encompasses the low-pressure techniques of microfiltration (MF) and ultrafiltration (UF). UF is used in the treatment of drinking water and wastewater to remove micro pollutants and natural organic materials (*Heo et al., 2019*).

MF separation is primarily performed using sieve methods. Because of the relatively large pore diameters, which vary from about 0.1 to 1.0 μm , this approach is mostly used for the removal of suspended solids or particles, bacteria, and, to a lesser extent, organic colloids. UF membranes exhibit a wider separation spectrum compared to MF membranes and can effectively eliminate particles, bacteria, viruses, and colloids contingent upon the pore size, typically ranging from 0.01 to 0.1 μm . The primary operational purpose of UF membranes is to perform filtration via sieving. The efficacy of UF membranes in water reuse facilities worldwide has been established, as they can reject all suspended solids, eliminating organic matter, achieving a minimum of 95% reduction in BOD₅ (biological oxygen demand over a 5-day test), and significantly decreasing turbidity. The RWTP employs ultrafiltration for pathogen removal, suspended solids removal, and as a pre-treatment for RO. Additionally, additional studies show that the UF is effective in eliminating newly emerging pollutants. The effectiveness of the NF/RO system depends on this pre-treatment.

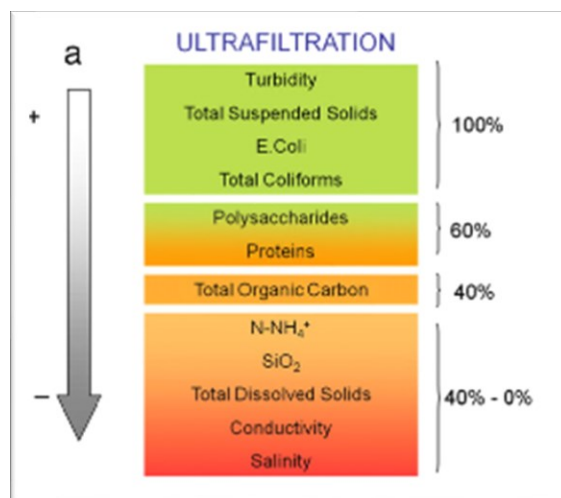


Figure 2.3 Removal of micro contaminants during the UF process (Urtiaga et al., 2013)

2.7.2 Membrane bioreactor removal of emerging contaminants

The employment of MBR technology represents a state-of-the-art approach for the treatment and recycling of municipal or industrial wastewater, presently implemented in various applications. Ghernaout and Elboughdiri, (2019), have reported that the efficacy of emerging contaminant removal in MBRs is significantly impacted by their physiochemical characteristics and operational parameters. The majority of strongly polar compounds, including various pharmaceuticals and their corresponding metabolites, undergo elimination through biological conversion or mineralization via microbial activity in MBRs. The MBRs have the option of being either submerged or arranged in a series configuration, with the latter being the more energy-efficient choice. The current MBR configuration being studied involves submerging the membrane within the bioreactor and utilizing suction to facilitate the passage of treated water while retaining solids within the bioreactor. This is a standard operating procedure (Ghernaout and Elboughdiri, 2019). MBR systems operate at significantly elevated mixed liquor suspended solids (MLSS) concentrations compared to traditional activated sludge processes (CAS), while simultaneously eliminating biodegradable and hydrophobic trace organic compounds. (Dhangar and Kumar, 2020).

2.7.3 Nano filtration and reverse osmosis

Nano filtration and reverse osmosis are two techniques employed for the separation of dissolved chemical species, with a particular focus on the elimination of salts, from aqueous solutions. Both methodologies employ analogous membrane constituents and rely on elevated hydraulic forces. NF is being considered as a viable option by treatment facilities for potable reuse operations due to its lower energy consumption compared to RO. Although it is not commonly used, NF can effectively remove many of the same solutes (*Warsinger et al., 2018*).

2.7.4 Principle of reverse osmosis

Reverse osmosis is a process that takes place when a concentrated solution is exposed to a pressure that exceeds the osmotic pressure. The Reverse Osmosis (RO) separation technique finds its application in various scenarios where the elimination of dissolved solids, such as salt, from a solution is required. Upon application of a transmembrane driving force, the concentrated aqueous phase selectively permeates the membrane, wherein the solutes are retained, and the water is rejected. A semi-permeable membrane selectively inhibits the passage of molecules that exceed the pore size of the membrane, while allowing the passage of smaller molecules (*Lee, S. and Kim, J., 2020*).

2.7.5 Reverse osmosis membranes and flow rate

The schematic in Figure 2.4.1 depicts the composition of RO membranes, comprising a uniform polymeric layer (such as polyamide) that selectively allows water permeation, overlaid on a polymer support structure with an ordered structure. The fabrication of RO membranes involves the utilisation of either polysulfone coated with aromatic polyamides or cellulose acetate. Reverse osmosis (RO) membranes are employed to eliminate dissolved solids, organic substances (including emerging contaminants), and ionic matter. Most solutes exhibit retention on the feed side of the membrane subsequent to the propulsion of the solvent (water) through it. The feed water is subjected to a pressure that surpasses the osmotic pressure to generate fresh water. The efficacy of potable reuse is contingent upon the elimination of organic solutes, including but not limited to pharmaceuticals, pesticides, and endocrine disruptors, with the degree of rejection being subject to variation based on the specific solute and membrane utilized. Henceforth, additional investigation is required to comprehend this matter (*Warsinger et al., 2018*).

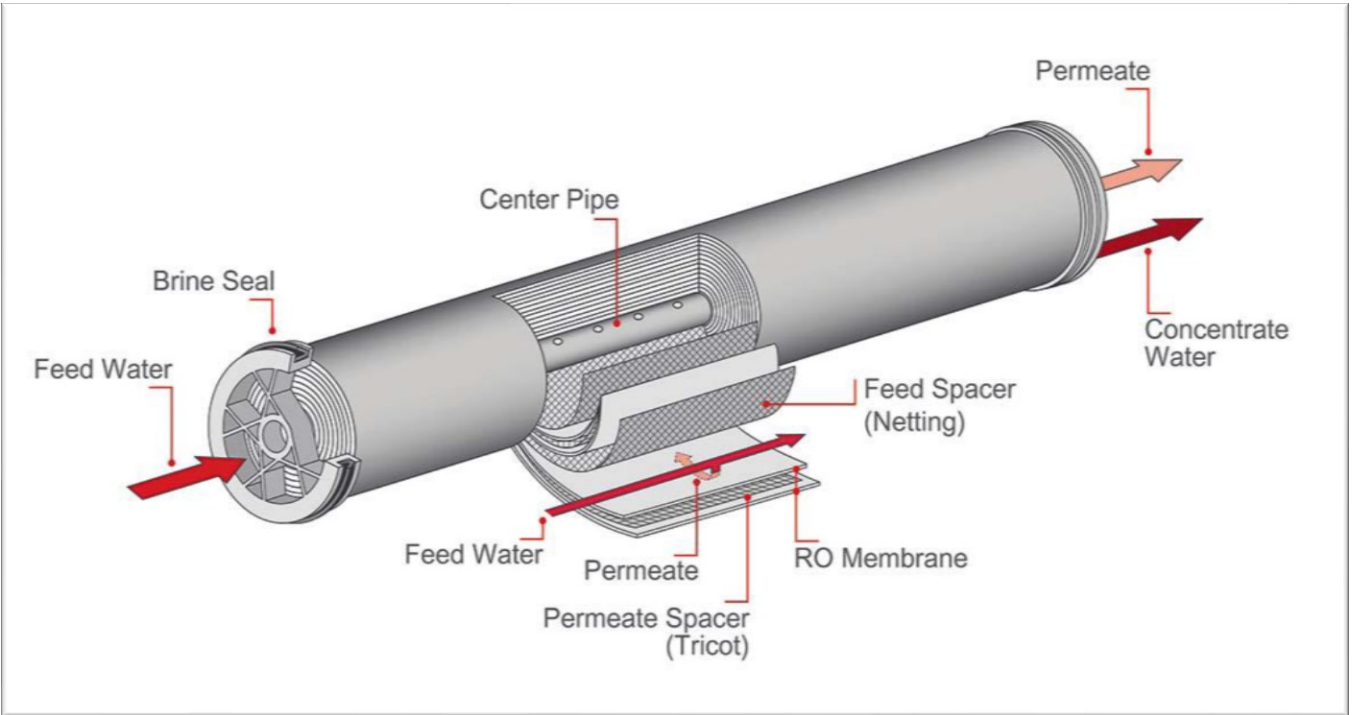


Figure 2.4 A schematic representation depicting the cross-sectional view of a customary Reverse Osmosis membrane (Hollman *et al.*, 2020).

The aqueous solvent is subjected to a transmembrane pressure gradient, effectively segregating the majority of the solutes. A force is exerted to the feed water for the purpose of generating potable water. The system must generate a pressure differential greater than the osmotic pressure of the solution to achieve desalination. In the context of potable reuse, the elimination of organic solutes, including but not limited to pharmaceuticals, pesticides, and endocrine disruptors, is of utmost importance. However, the efficacy of solute rejection is contingent upon both the specific type of solute and the particular membrane employed in the process. This finding serves as an opportunity for additional investigation within this field of study. The constraints imposed restrict the available options for the cleaning process (Warsinger *et al.*, 2018). In comparison to CA membranes, The membranes of (TFC) polyamide have shown superior physical and biological properties, according to (Heo *et al.*, 2019).

2.7.6 Reverse osmosis membranes removal efficiency

Yangali-Quintanilla et al., (2010), found that RO membranes are capable of effectively removing high molecular weight organic components such as medicines, insecticides, humic acids, and fulvic acids. It is possible to reject up to 96% of the TOC, as well as reduce the BOD, COD, and COD by up to 98% and 96%, respectively. *Urriaga et al., (2013)*, conducted pilot-scale research on the rejection of pharmaceuticals with UF and RO treatment of wastewater effluent in a pilot-scale study. A rejection value of more than 99.3% was found for all 12 substances in his inquiry study. It has been noted that high-pressure filters are incompletely removing several DBPs, such as nitrosamines, and micro pollutants with low molecular weights, such as 1,4-dioxane. Removal of Emerging Contaminants by membranes.

Most emerging pollutants can be removed by reverse osmosis with an efficiency of better than 90%. *Heo et al., (2019)*, claim that ECs' differences and physical characteristics (such as molecular weight [MW], hydrophobicity, and solubility) have a significant impact on membrane removal.

According to *Yangali-Quintanilla et al., (2010)*, the importance of membrane properties like salt rejection, hydrophobicity (contact angle), and surface charge (zeta potential) has been further confirmed. In addition to compound properties like molecular depth ($\log K_{ow}$, $\log D$), equivalent width, polarity (dipole moment), hydrophobicity, and size (molar volume, molecular length, and molecular weight), and operating conditions including flux, and pressure.

According to *Kiso et al., (2001)*, the key factor driving rejection for hydrophilic solutes such as saccharides and alcohols was steric hindrance, and molecular weight were good descriptors for steric hindrance. Because of the hydrophobic compounds deposited on the membranes in that experiment, hydrophobicity-measured by $\log P$ -had a significant impact on rejection.

2.8 Advanced oxidation process

Advanced oxidation processes (AOPs) are a class of chemical treatment methods designed to remove organic and, in some cases, inorganic contaminants. Hydroxyl radicals aid in the elimination of developing contaminants, making them an effective water treatment approach. In the context of wastewater treatment, certain advanced oxidation processes (AOPs) utilize chemical reactions involving ozone (O₃) and UV light (photocatalysis), as well as hydrogen peroxide (H₂O₂) and/or UV light, to produce potent oxidizing agents like hydroxyl. This chemical reaction is commonly referred to as the Fenton Reagent. Additionally, the procedures are utilized in water

treatment techniques. They can oxidize an extensive range of hard water contaminants. At the Durban Central Wastewater Works, it is one of the RWTP's (study site) treatment units. Pesticides, cosmetics, dyes, plasticizers, toxic metals, and other types of water contaminants are potential contaminants likely to be removed significantly by AOP processes (Taoufik *et al.*, 2020).

2.8.1 Advanced oxidation process removal efficiency

In contrast to traditional oxidation methods, AOPs performed better at removing MP because of strong oxidant doses, high free radical concentrations, and longer contact times. The AOP process consists of two processes stages, the reaction of oxidants with contaminants and the formation of reactive oxidative species in situ. The mechanism of radical formation varies from process to process. There are numerous ways to activate and generate oxidants for AOPs, and they can potentially use a variety of different mechanisms for organic destruction. By oxidizing, refractory substances are destroyed and transformed into simpler ones. As traditional oxidation methods (e.g., Cl₂, KMnO₄, ClO₂, H₂O₂, and HClO) fail to tackle MPs, advanced oxidation methods (AOPs) like O₃, UV/O₃, H₂O₂ / UV/H/O₂, O₃, and have been proposed as an alternative specific parameters and can be affected by system design and water quality (Zabalza, 2019). Other parameters (such as radical mass transfer in surface based AOPs, hydrodynamics), in addition to radical scavenging, can affect the efficiency of contaminant destruction. In municipal wastewater treatment plants, AOPs are capable of treating primary effluents, conditioning sludge, treating secondary effluent, treating reverse osmosis concentrates, and disinfecting effluent, among others (Zabalza, 2019).

The rate constants for most chemical reactions involving hydroxyl radicals in water range between 10⁶ and 10⁹ M⁻¹ S⁻¹. It has been observed that chemical oxidation processes (such as ozonation /H₂O₂, UV photolysis/ H₂O₂, and Photo-Fenton) are the most effective methods for reducing pesticides, beta-blockers, and pharmaceuticals. However, chemical oxidation processes can alter the polarity and quantity of pharmaceuticals' functional groups, which impacts how well they function in organisms (Ghernaout and Elboughdiri, 2019). The study conducted by Swartz *et al.*, (2018), exhibited remarkable elimination efficiencies exceeding 90% for the intended micropollutants, namely naproxen, carbamazepine, diclofenac, ibuprofen, caffeine, and other compounds, via the implementation of photolysis, UV, and hydrogen peroxide. Alygizakis *et al.*, (2020), conducted a study on the oxidation of emerging contaminants. The study reported that UV-based oxidation processes exhibited significantly higher removal rates for organic compounds

compared to hydroxyl and sulfate radicals. These disagreements emerge, and the outcome is dependent on rigorous monitoring of the treatment technique and the type of pollutant being treated or oxidized.

2.8.2 Limitations of a system with Advanced Oxidation Processing

Advanced oxidation process generally is expensive to run, they have high consumption of energy and maintenance costs. However, formation of potentially toxic products can be of great concern especially in drinking water. These disinfection by-products may include organic intermediates, or transformational products. In one of the water reuse investigations, *Roccaro, (2018)*, discovered that MBR/RO/UV/H₂O₂ treatment train-based operations created unexplained precursors of the extremely carcinogenic compound called N-nitrosodiethylamine (NDMA). NDMA is considered a toxic substance and a probable human carcinogen. It has been recorded that NDMA can increase the risk of cancer in liver, kidney, and gastrointestinal cancers. In actuality, the use of AOPs at the REMIX Water Treatment Plant might potentially boost the production of NDMA. More research will be required because this falls beyond the scope of the study (*Baken et al., 2018*).

2.9 Water Sample Preservation

Sample preservation refers to the techniques and methods used in chemistry and biology to maintain the integrity and stability of a sample over time. The purpose of sample preservation procedures is to retain the collected sample as close to its original state as feasible (*Kalkhajeh et al., 2019*). The primary goal of preservation strategies is to:

- Reduce biological activity.
- Prevent a chemical reaction.
- Reduce the level of volatility.

Correct sampling, processing, and preservation lowers sample error and improves accuracy. This informs this investigation, to take note and keep all water samples in integrity for examination.

2.10 Analysis and Methods of Detecting emerging contaminants

Several analytical approaches for quantifying ECs in water have been developed. The quantification of specific target analyses was conducted in Western cape, South Africa by (*Archer et al., 2021*). The analysis was performed utilizing an UPLC system (Waters Acquity) in

conjunction with a Xevo Triple Quadrupole mass spectrometer (TQ-MS, Waters Acquity) that featured an electro-spray ionisation (ESI) source. The user quantified the pharmaceutical compounds diclofenac, acetaminophen, naproxen, sulfamethoxazole, codeine, and carbamazepine. The primary techniques utilized for quantifying emerging contaminants entail an extraction protocol proceeded by instrumental assessments. In the current literature, a plethora of analytical procedures for pharmaceuticals and personal care products (PPCPs) have been recorded. Through the process of isolation and purification of ECs from water, the sensitivity of analytical equipment can be enhanced for their detection. The predominant methodology employed in this procedure is solid-phase extraction (SPE), complemented by supplementary techniques such as dispersive liquid-liquid micro-extraction (DLLME), buck paper, multi-cartridge SPE, among others.

2.10.1 Solid Phase Extraction

The utilisation of solid-phase extraction (SPE) for the extraction of ECs has been standard procedure. Upon its widespread availability in the late 1970s, this method rapidly replaced the older liquid-liquid extraction technique. The utilization of SPE is widely prevalent owing to its numerous benefits such as its uncomplicated nature, adaptability, potential for automation, and various other factors. The utilisation of SPE methodology enables the augmentation of analytical quality through heightened precision and accuracy.

The separation type is influenced by the characteristics and type of the target compound, as well as the matrix of the sample. There exist two distinct configurations of SPE, namely cartridge and disk. The utilisation of disks for analyte elution necessitates a larger quantity of solvent, thereby prolonging the procedure and rendering the concentration of the eluted sample more difficult, despite the disks' reduced likelihood of sample clogging due to their expansive surface area. This statement refers to the selection of suitable solid phase extraction materials for the evaluation of specific analytes.

According to *Marasco et al., (2019)*, SPE is a sample preparation technique that needs at least four steps: sorbent conditioning, sample loading, clean-up (remove the interferers and matrix concomitants), and analyte elution.

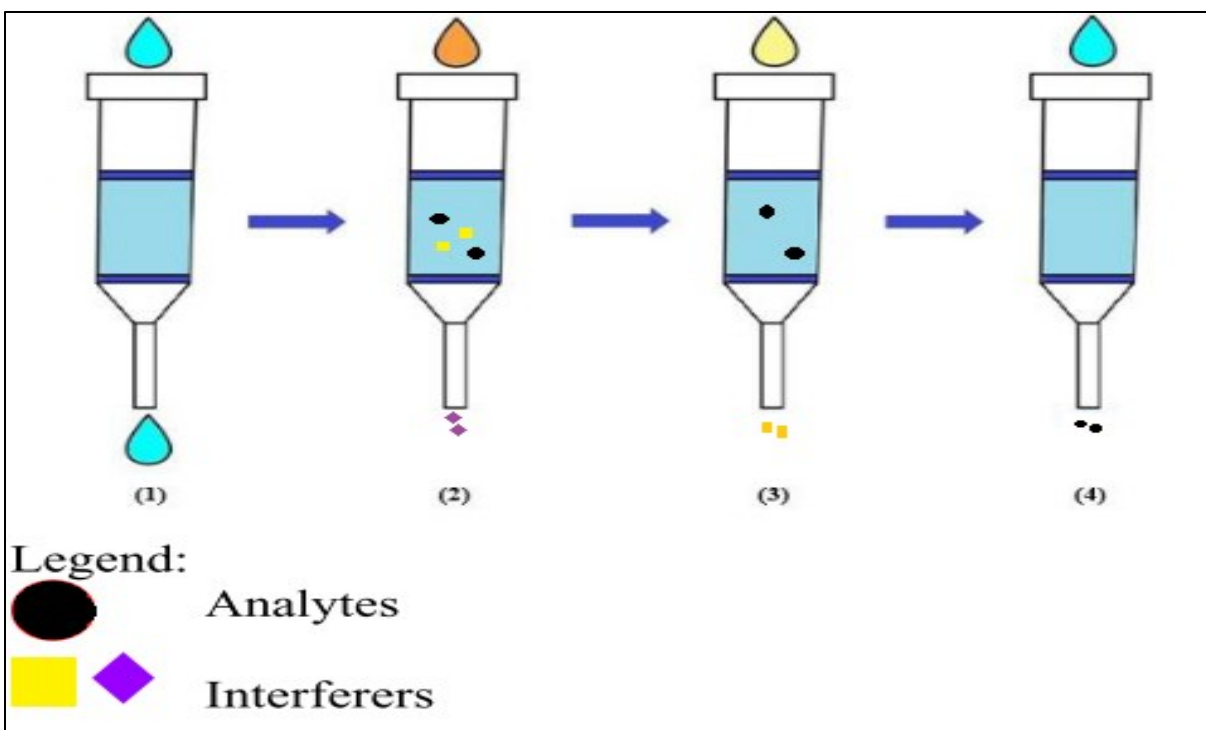


Figure 2.5 Adapted SPE analytical steps from (1) conditioning, (2) loading sample, (3) Wash, (4) elution. Adopted from (Marasco et al., 2019).

As per the findings of Marasco *et al.*, (2019), SPE has been established as the preferred sample preparation technique for organic contaminants. It is noteworthy that the development of novel SPE sorbent materials has engendered several alterations in recent times. The predominant alterations were centered around miniaturisation and automation, resulting in the emergence of innovative extraction methodologies such as micro extraction by packed sorbent (MEPS solid phase dynamic extraction (SPDE) etc. (Marasco et al., 2019).

2.10.2 Quantification of emerging contaminants

A variety of methodologies may be used to quantify ECs in the aquatic environment. Immunoassay is one of the most sensitive analytical procedures, although it is limited by a lack of specific antisera and is prone to cross-reactivity (Faleye *et al.*, 2019). After extraction, the other two procedures, liquid chromatography (LC) and gas chromatography (GC) paired with mass spectrometry (MS/MS), are typically used to quantify compounds of interest. Despite being less sensitive than biological approaches, chromatographic methods are useful because they can simultaneously screen for steroids and their conjugates.

2.10.3 Liquid Chromatography Mass Spectrometry

LCMS is a robust analytical technique that enables the identification and quantification of diverse chemical species within complex mixtures. The LCMS technique has the capability to detect and measure newly discovered contaminants that are not yet subjected to regulatory measures, but are progressively acknowledged as plausible hazards to the ecosystem and human well-being. LCMS can identify novel contaminants such as pharmaceuticals and personal care products (PPCPs), pesticides, flame retardants, perfluorinated compounds (PFCs), and micro plastics. LCMS may be used to detect emerging pollutants in a variety of environmental matrices, including water, sediment, soil and biota. Scientists may better understand the distribution, fate, and impacts of these pollutants in the environment by monitoring their concentrations. The application of LCMS is of paramount importance in the identification and quantification of nascent pollutants, enabling informed regulatory determinations, promoting scientific research, and safeguarding the well-being of both the ecosystem and the public health (*Kalkhajeh et al., 2019*).

2.10.4 The Method detection limit

The MDL, or method detection limit, refers to the lowest analyte concentration that can be determined with accuracy using LC-MS, although it may not necessarily be quantified. The limit of detection (LOD) is the minimum detectable concentration of an analyte by a given technique. It signifies the threshold below which the technique cannot reliably differentiate between the presence and absence of the analyte. The determination of MDL is based on the experimental evaluation of the signal-to-noise ratio (S/N) of the analyte. In general, the concentration is deemed acceptable when the signal-to-noise ratio reaches or exceeds 3:1, indicating that the analyte's signal is threefold more potent than the ambient noise. The Minimum Detectable Limit (MDL) denotes the minimum concentration of the analyte that can be detected with a precision of 20% or higher and an accuracy ranging from 80-120%.

The MDL is a critical parameter in LC-MS analysis as it determines the sensitivity of the method and the minimum detectable concentration of the analyte. The establishment of the lower limit of detection of an analytical method is a common practice during its development and validation. In order to ascertain the MDL, a sequence of standard solutions possessing known concentrations are subjected to analysis, and the ratio of signal-to-noise is computed for each concentration. The minimum detectable limit (MDL) is ascertained through an analysis of the standard solution,

whereby the concentration is at its lowest and generates a signal-to-noise ratio of no less than 3:1 (Archer *et al.*, 2021).

2.10.5 Limit of Quantification in LCMS

The limit of quantification in LC-MS (Liquid Chromatography-Mass Spectrometry) refers to the minimum concentration of an analyte that can be reliably and accurately measured with a high level of precision and confidence. The experimental determination of LOQ is predicated on the signal-to-noise ratio (S/N) of the analyte. The threshold is commonly defined as a signal-to-noise ratio of 10:1 or greater, indicating that the analyte signal exceeds the noise by a factor of ten. The LOQ denotes the minimum analyte concentration that can be detected and quantified with a precision of 20% or higher and an accuracy within the range of 80-120%. The LOQ is a critical parameter in LC-MS analysis as it determines both the sensitivity of the method and the minimum concentration required for analyte identification and quantification. The determination of the lower limit of quantification for the analytical method is typically carried out during the process of method development and validation. The LOQ is determined by subjecting a set of standard solutions with known concentration to analysis, followed by computation of the signal-to-noise ratio for each concentration. The examination of the standard solution demonstrating the minimal concentration that gives a signal-to-noise ratio of no less than 10:1 is used to determine the limit of quantification (LOQ) (Kalkhajeh *et al.*, 2019).

2.10.6 Gas chromatography–mass spectrometry

GC-MS, an established technique, is utilised for the analysis of emerging contaminants. The implementation of this technique necessitates the derivatisation of carboxylic acid and hydroxyl functional groups to comparatively nonpolar substituents. Various techniques have been employed to identify EDCs and PPCPs in water, with solid-phase extraction (SPE) followed by GC-MS being a commonly used methodology. Unlike LC/MS/MS, GC/MS and GC/MS/MS techniques are limited by the volatility and molecular weight characteristics of the target compound (Archer *et al.*, 2021). LC/MS has the capability to perform screening of both conjugated and unconjugated compounds without the need for derivatisation. The wastewater samples' matrix resulted in higher limit of detection for some approaches compared to the pure river or lake water or drinking water samples LC/MS is capable of screening conjugated and unaltered chemicals without the need for derivatisation. As a result of the wastewater sample matrix, certain techniques demonstrated a higher limit of detection in the wastewater samples as compared to other samples obtained from

pristine river or lake water or drinkable water. The reported limit of detection for steroids in urine ranged from 0.3 to 600 n g-1, whereas it ranged from 0.6 to 35 n g-1 for hormones and antibiotics in influent and effluent wastewater in Germany (*Mosekiemang et al., 2019*).

2.11 Prioritisation of emerging contaminants

There exist numerous chemicals employed globally, which possess the likelihood of inducing detrimental impacts on both human and ecological systems. Several prioritisation methodologies have been developed and utilised to screen hazardous and emerging contaminants. In order to prioritise chemicals for monitoring programs, each chemical of concern must undergo a detailed examination of the health and environmental concerns. Establishing from worldwide literature which substances of emerging concern have been found in drinking water or the environment.

- Determining the prevalence of compounds identified in South African drinking or environmental waters.
- The quantification of medication prescriptions serves as a metric for assessing the likelihood of exposure in South Africa.
- Determining the recalcitrant compounds that exhibit resistance to treatment methodologies and are acknowledged for their persistence.

Prioritisation of emerging contaminants (CECs) is a difficult and critical undertaking for environmental management and the scientific community. This includes identifying priority pollution prevention and control initiatives, as well as providing resources to solve present knowledge gaps. Various chemical hazard screening and risk assessment methodologies have emerged in the European legislation REACH (Registration Evaluation Authorisation and Restriction of Chemicals) to bridge the data gap of chemicals through testing and non-testing techniques. However, the cost of testing methods and compliance with new animal regulations, which prohibit the sacrifice of animals for assessing the toxicity of compounds that may potentially affect humans, pose significant challenges. Screening techniques have emerged as a substitute for animal experimentation in the prioritisation of perilous substances. This study has been prompted to develop a prioritisation scheme that is both user-friendly and efficient. The presence of hazard is an inherent attribute in all chemicals and is intimately linked with their molecular configuration.

2.11.1 Quantitative Structure Activity Relationship (QSAR) Models

The QSAR methodology is a prevalent technique utilised to establish correlations between the effects of a group of compounds and their structural characteristics. The application of molecular descriptors in scientific research is aimed at minimising the number of experimental tests required for drug discovery, while also enabling the prediction of drug toxicity and metabolism. Several models were developed to assess the PBT behavior (hazard screening) of membrane filtration, chlorination, ozonation, adsorption, and persistence. Several prioritisation schemes have been developed for screening and prioritising ECs based on their potential PBT characteristics. These include the online USEPA PBT profiler, Norman prioritisation scheme, and Insubria PBT Index (QSARINS-Chem).

2.12 Feed Water Chemistry

The chemistry of the water used as a feed to create high-quality water in a system is referred to as the feed water chemistry. In order to sustain the effectiveness and durability of any membrane biological reactor, reverse osmosis system, or advanced oxidation process, which is what this study is now examining, proper feed water chemistry is essential it intervenes with ECs removal. For Instance, high levels of Total Dissolved Solids (TDS) can lead to scale buildup in the permeable membranes of reverse osmosis systems, which can decrease efficiency and damage equipment. Therefore, the knowledge of feed chemistry informs this study to measure various water chemistry parameters such as dissolved oxygen (DO) temperature, pH, TDS, etc. to determine efficiency of the membrane technology under investigation.

ECs and heavy metals retention by membrane technologies can vary depending on feed water chemistry. *Heo et al., (2019)*, investigated four different feed waters to determine the removal of emerging contaminants. Key characteristics such as dissolved solids, pH, conductivity, dissolved carbon, and specific UV absorbance were used to compare chemical retentions.

2.12.1 QSARINS- Chem prioritisation method

The QSARINS-Chem tool employs machine learning techniques to forecast the toxicity of chemicals by analysing their molecular structures. The system employs a hybrid approach that integrates deep learning neural networks and molecular fingerprints to produce prognostications. The QSARINS-Chem software is capable of forecasting toxicity endpoints, including but not

limited to acute toxicity, carcinogenicity, mutagenicity, and developmental toxicity *Gramatica et al., (2018)* .

The tool is based on a large dataset of chemicals and their corresponding toxicity endpoints, which was compiled from various public databases. The dataset was curated and standardised to ensure accuracy and consistency. This method is adopted to predict the targeted analytes for persistency, bioaccumulation and toxicity behavior in water matrix based on their chemical intrinsic structure. QSARINS-Chem uses a multi-task deep neural network to predict toxicity endpoints based on the chemical structures. The neural network is trained on a large dataset of chemicals and their corresponding toxicity endpoints, and it learns to recognise patterns in the molecular structures that are associated with toxic endpoints.

The tool also uses molecular fingerprints to represent the chemical structures. Molecular fingerprints are a type of structural descriptor that captures the topological and physicochemical properties of a molecule. These fingerprints are used to generate input features for the neural network.

QSARINS-Chem has been used to predict the toxicity of numerous chemicals in a variety of applications, including drug development, environmental toxicology, and chemical safety assessment. It has been demonstrated to outperform other state-of-the-art methods for toxicity prediction *Gramatica et al., (2018)*.

2.12.2 Environmental Persistence

Environmental persistence refers to the ability of a substance, typically a chemical or a pollutant, to resist degradation or breakdown in the environment. Environmental persistence of a chemical is frequently regarded as an undesirable property; it increases when degradation by physical, chemical, and biological processes is slow, and the molecule can persist unaltered in the environment for an extended period of time, increasing its potential for exposure and harm to living organisms.

The ability of a substance to persist is determined by a number of factors, including its chemical composition, the environment in which it is present, and the presence of other compounds or living creatures that may interact with it. Through processes like bioaccumulation and biomagnification, persistent compounds can build up in the tissues of living things and be transferred through the air, water, and soil (*Verlicchi et al., 2023*).

The potential for environmental persistence is a key consideration in environmental risk assessment and chemical safety evaluation. To reduce the potential for environmental persistence, various measures can be taken, such as regulating the use and disposal of persistent substances, implementing pollution prevention and control measures, and using alternatives to substances that are known to persist in the environment (*Verlicchi et al., 2023*).

2.12.3 Bioaccumulation

The process through which a chemical or a metal, gradually accumulates in the tissues of living things is known as bioaccumulation. This can occur when an organism is exposed to the substance through its environment, such as through food, water, or air, and the substance cannot be broken down or eliminated by the organism's metabolic processes. Bioaccumulation can lead to a number of adverse effects on the organism, including toxicity, reproductive problems, and developmental abnormalities. It can also lead to biomagnification, which occurs when the concentration of the substance increases at higher tiers of the food chain.

The potential for bioaccumulation and biomagnification is a key consideration in environmental risk assessment and chemical safety evaluation. To assess the potential for bioaccumulation, various factors are considered, including the chemical's properties, its environmental fate and transport, and the biology of the organisms that may be exposed to it.

The bioaccumulation is proportional to the octanol-water partition coefficient (K_{ow}), which is the ratio of the CEC concentration in n-octanol to the concentration in water (*Verlicchi et al., 2023*). Lipophilic emerging contaminants culminates in high bioaccumulation up the trophic levels in the ecosystem.

2.12.4 Toxicity of Chemical

The toxicity of a chemical refers to its ability to cause detrimental impacts on organisms. In this research the toxicity is directed to human beings. Chemical toxicity to humans can result from exposure to a substance through various routes, such as inhalation, ingestion, or skin contact. The effects of chemical toxicity can vary depending on the type of chemical and the dose and duration of exposure.

Chemical toxicity can cause a diverse range of adverse effects on living organisms, including damage to organs and tissues, disruption of physiological functions, and increased risk of disease

and illness. The severity of the effects depends on a variety of factors, such as the duration of exposure, susceptibility of the organism, and the chemical's toxicity.

To assess the potential toxicity of a chemical, various tests and methods can be used, including in vitro tests, in vivo tests, and computational models. These methods can help to identify the mechanisms of toxicity and the potential risks associated with exposure to the chemical.

2.13 Environmental Impacts of emerging contaminants

As previously stated, ECs can enter the aquatic food chain via several methods, resulting in bioaccumulation and biomagnification. As a result, the food chain can be observed to have an increase in the concentration of a substance in creatures at successive trophic levels. In some circumstances, consuming contaminated water by both humans and animals could result in direct exposure. Long-term exposure has a deleterious impact on aquatic ecosystem and, in rare cases, can alter the metabolism and hormones of an animal or person. (*Parida et al., 2021*).

2.14 Human Health Impacts

The process of identifying the type and likelihood of detrimental health outcomes in humans who may be exposed to chemicals in polluted environmental media now or in the future is known as human health risk assessment (*Parida et al., 2021*). Extended exposure to ECs results in diverse abnormalities in individuals, even at lower concentrations. Antibiotics have a significant impact on both human health and the environment, and their preservation requires a comprehensive approach that considers both of these factors. The existence of antibiotics has resulted in the emergence of antibiotic resistance genes (ARGs), which reduce the effectiveness of antibiotics in combating human and animal pathogens. *CD Swartz et al., (2016)*, has identified that persistent exposure to carbamazepine and atenolol may impede the proliferation of human embryonic stem cells among expectant mothers. The consumption of caffeine has been linked to the development of anxiety and panic disorders in humans, as well as potential risks for endometrial, hepatocellular, and colorectal cancer. The majority of the aforementioned research studies have certain limitations, making it challenging to deduce the toxicological implications for human well-being (*Parida et al., 2021*). However, the implementation of a deterministic approach can aid in the assessment of potential hazards posed by these chemicals in potable water through estimations that have been proven reliable.

2.14.1 Chemical Risk Assessment

Chemical risk in drinking water arises from heavy metals, fluoride, nitrate-nitrite, pesticides, microplastics, and emerging contaminants that generate public concern. These facts prompted this study to conduct a human health risk analysis for Emerging contaminants likely to be found in seawater and wastewater.

In chemical risk assessments for human health, risk assessment encompasses hazard identification, dose-response assessment, exposure assessment, and risk estimation and characterisation. The potential implications of ECs on the environment and public health remain uncertain due to gaps in toxicity data and uncertainties in the assessment of human health risks methodologies for chemical substances (*Baken et al., 2018*). Various methodologies are available to account for variations in the toxic mechanisms exhibited by diverse chemical classes and the toxicological endpoint under consideration. In this study, the deterministic approach has been selected as a preferred alternative to experimental methodologies that are time-consuming and may not align with animal welfare principles (*Parida et al., 2021*).

2.14.2 Hazard Identification

The initial and crucial phase in the risk assessment procedure involves identifying the source and frequency of potential hazards that contribute to the degree of risk linked to a newly emerging pollutant. The absence of dependable data on emerging pollutants in distinct environmental compartments and species has led many environmental engineers and scientists to rely heavily on in vivo data. Hence, there is a requirement for further efforts to optimise the employment of in vitro assays, in silico evaluations, and computational techniques in the domains of biology, chemistry, and environmental engineering. (*CD Swartz et al., 2018*).

2.14.3 Dose response Assessment

This method involves the characterisation of the relationship between the dose of a particular agent and the probability of an adverse impact. Various dose-response relationships can be observed for a particular chemical, depending on factors such as the nature of the reaction (carcinogenic or non-carcinogenic) and the duration of the experiment (acute or chronic). To conduct a thorough risk assessment of potential hazards, it is imperative to determine the threshold dose at which toxic effects occur. The implementation of quantitative high-throughput screening (q-HTS) is recommended to gather dose-response information encompassing a wide spectrum of test doses.

Sensitive environmental assays must be capable of detecting toxicity at extremely low concentrations, even below the levels encountered by organisms in their natural surroundings. Adequate opportunities must be provided to predict potential negative reactions and evaluate crucial concentration information using statistical methodologies. (*Santos et al., 2020*).

2.14.4 Accepted daily Intake of Emerging contaminants

Regarding emerging contaminants, the acceptable daily intake (ADI) is an estimation of the quantity of a contaminant present in drinking water that can be safely consumed by an individual throughout their lifetime without posing any significant health risks.

In certain situations, it is recommended by the *World Health Organisation, (2017)*, to utilise a surrogate acceptable daily intake (ADI). This is achieved by dividing the minimum daily therapeutic dose by safety factors that range from 1000 to 10000 (*CD Swartz et al., 2018*).

This guides this research in determining the acceptable daily intake of certain compounds for which reference dose values are unavailable, using principles of TTC approach.

2.14.5 Threshold Toxicological Concerns (TTC) Approach

The categorisation of chemicals is based on the Threshold of Toxicological Concerns (TTC) methodology, which classifies them into three broad categories:

- Category I comprises uncomplicated compounds that can be easily metabolised and have low oral toxicity.
- Class II substances are more environmentally hazardous compared to Class I materials because of the existence of reactive functional groups.
- Class III compounds are characterized by structural features that hinder the establishment of a reliable initial safety assumption or indicate a high likelihood of toxicity.

Based on the findings of *CD Swartz et al., (2018)*, it has been established that the exposure thresholds for three chemical classes in humans are 1800, 540, and 90 g/person/day. The thresholds are equivalent to daily doses of 30, 9, and 1.5 g/kg body weight, respectively, assuming a human body weight of 60 kg and a safety/uncertainty factor of 100.

The admissible values for the three categories of impurities in the reclaimed water were determined utilising the TTC approach:

- The maximum allowable concentration for Class I compounds is 180 grams per liter.
- The concentration limit for Class II chemicals is 54 grams per liter,
- while for Class III chemicals, it is 9 grams per liter.

It is crucial to consider that the TTC approach was developed with the sole purpose of producing a relatively rapid and prudent risk appraisal for substances that lack extensive risk assessment or have restricted datasets (*CD Swartz et al., 2018*).

2.14.6 Deterministic Approach and Calculation of Risk Quotients

The deterministic risk quotient methodology is a frequently used chemical analysis technique for assessing the possible dangers of chemical pollutants in the environment or drinking water. The process entails comparing the chemical's exposure levels to a specified threshold or reference dose, which indicates the level of exposure that is expected to have no detrimental effects. The Environmental Protection Agency (EPA) evaluates the toxicological impact of environmental exposure using either deterministic methodology or the risk quotient (RQ) technique. The process entails dividing a single approximation of exposure by a single approximation of effect, as determined by the Environmental Protection Agency (EPA). The RQ calculation procedure includes an examination of ecological impact data, information on drug distribution and mobility, and an estimate of the likelihood of exposure to environmental dangers. An analysis is performed in the field of environmental engineering to compare the estimated environmental concentration (EEC) with an effect level, specifically the LC50, which defines the concentration at which 50% of the organisms perish. The current analysis takes a methodical approach to assessing and scrutinising the hazard trajectory throughout the RWTP (*CD Swartz et al., 2018*).

2.15 Emerging Contaminants Statutory Guidelines

In South Africa the regulations or standards for water treatment plants (WTP) and water reuse projects (WRP) generally prohibit physico-chemical and biological water parameters such as turbidity, chemical oxygen demand (COD), biological oxygen demand (BOD), total suspended solids (TSS), bacteria, residual chlorine, etc.(Liu et al., 2020). Emerging contaminants threshold limit values have not been published in SANS241 -2015 for drinking water. However other development countries such as Australia, Canada, Singapore and United States of America have some of the emerging contaminants drinking water guidelines.

Table 2.2.1 Legislative drinking recommendations in developing countries for certain water reuse facilities for emerging pollutants, as well as their drinking water equivalent level values.

Contaminants	Statutory guidelines				PNEC n g-l	DWEL Europe	References
	EU	USEPA	ADWG	WHO			
Paracetamol		175 000			1 400	11 788.3	(NRMMC et al., 2008; Parida et al., 2021; U.S. Environmental Protection Agency, 2018)
Trimethoprim	120 000		70 000				(NRMMC et al., 2008; Parida et al., 2021; U.S. Environmental Protection Agency, 2018)
Tetracycline			105 000			10 040.1	(NRMMC et al., 2008; Parida et al., 2021; U.S. Environmental Protection Agency, 2018)
carbamazepine			100 000		10	11	(NRMMC et al., 2008; Parida et al., 2021; U.S. Environmental Protection Agency, 2018)

17 β -estradiol	175	175	1	1.6	1.6	(NRMMC <i>et al.</i> , 2008; Parida <i>et al.</i> , 2021; U.S. Environmental Protection Agency, 2018)
Codeine		50 000		976	64.9	(NRMMC <i>et al.</i> , 2008; Parida <i>et al.</i> , 2021; U.S. Environmental Protection Agency, 2018)
Amphetamine				3800	9735.4	(NRMMC <i>et al.</i> , 2008; Parida <i>et al.</i> , 2021; U.S. Environmental Protection Agency, 2018)
Caffeine	87 000	350		320	18 4973.3	(NRMMC <i>et al.</i> , 2008; Parida <i>et al.</i> , 2021; U.S. Environmental Protection Agency, 2018)

2.16 Hazard identification and critical control points system

The HACCP methodology is employed in the field of environmental engineering to detect and manage potential hazards throughout the critical phases of water manufacturing. This is a preventive measure that ensures the suitability of each product for consumption. The potential outcome entails the detection, elucidation, and mitigation of hazards within the water sector. The fundamental concept proposed by the WHO's drinking water quality standards serves as the cornerstone for water safety strategies (CD Swartz *et al.*, 2016). The HACCP system comprises seven principles that are meticulously followed during implementation. The accurate determination of crucial control points, along with the Codex Alimentarius, offers a decision-making framework to aid in the systematic process of the systems (Zhang *et al.*, 2021).

2.17 Motivation of study research gaps

Emerging contaminants have become a pressing issue of concern in the water matrix around the world due to the adverse environmental and human health impacts posed by them. Identification of toxic, bioaccumulating, and persisting chemicals through laboratory screening tests takes time and is against new animal regulations. Therefore, smart screening of chemical compounds that are toxic, bioaccumulating, and persisting can be done using models. Little is known about the efficiency of the REMIX Water Treatment in terms of emerging contaminants removal. This then forms the basis of this investigation, evaluating the RWTP for the removal of screened ECs in the influent waters that are abstracted for treatment, that is, seawater and wastewater. One of the Quantitative structure-activity relationship models called the Insurbria PBT Index is known to screen the compounds for potential persistence, bioaccumulating, and toxicity characteristics; it is a hazard screening tool that has not been used in South Africa to screen potential PBT compounds. A risk evaluation of the product's potential impact on human health was conducted to assist decision makers in improving and planning effective monitoring practises safeguarding human health from adverse effects of PBT ECs.

CHAPTER 3: METHODOLOGY

3.1 Introduction

This study follows a pragmatic approach in the evaluation of the REMIX Water Treatment Plant (RWTP) for the removal of emerging contaminants, heavy metals, and nutrients. Transformational products or metabolites of emerging contaminants are not considered in this study; rather, parent compounds are discussed. This work is carried out for the validation of the REMIX Water Treatment Plant to determine whether it works to provide safe drinking water free of emerging contaminants for people in the city of Durban. Performing studies used in water quality testing as well as assessing and analysing the available scientific and technical information are all part of the validation process. Sections 3.2 to 3.3 describe the study site, the procedures involved in the collection of water samples, and the technology process. The methods for ranking emerging pollutants based on their potential for persistence, bioaccumulation, and toxicity (PBT) behaviour in the water matrix are described in the second part. The human health risk assessment procedure is discussed in the third section, and lastly, the hazard analysis and identification of critical control points of the RWTP technology are discussed in the fourth section.

3.2 Description of the Study site



Figure 3.1 REMIX Water Treatment Plant (a)Site location (b) and intake location of the REMIX Water Treatment Plant (Masha, 2020)

The research site is centred on RWTP, which is located at eThekweni's current Central WWTW along the KwaZulu-Natal coastline near Durban, as shown in figure: 3.1. The Central WWTW is designed to treat up to 133 ML of primarily household wastewater per day. Water samples were obtained prior to the BWRO process's input water, which is removed from one of the existing primary settling tanks (PSTs) and others along different treatment units, as indicated in Fig. 3.1.1. The treated wastewater effluent is released over a 3.2km-long existing outfall conduit. According to *Masha, (2020)*, it was a good location since the demonstration plant will use part of the existing infrastructure, lowering the project cost. The ideal intake location for seawater desalination technology was determined by the required water quality and quantity to be abstracted, the expenses connected with the building of the intake works, and environmental laws.

The harbor intake point, as illustrated in Figure in fig 3.1 (b) was preferred for the

Based on the following reasons.

- Significantly less construction risk.
- Ease of maintenance as it is less weather dependent compared to an offshore intake.
- Water quantity is guaranteed.

The RWTP technique uses an advanced oxidation treatment method and a modern membrane, as shown in Fig. 3.3.1. The system receives primary treated wastewater from a primary settling tank with optional settling of solids before biological nutrient removal by the activated sludge process. The water from the primary tank enters the REMIX treatment plant and is treated by MBR, RO, and AOP. The saltwater extracted is first filtered by the UF system and then diluted with the rejected water from the brackish RO. The permeate water from UF then mixes with the reject water from brackish RO in a tank, and the mix is filtered by the desalination RO. The brine from the desalination RO is discharged via the existing outfall pipeline at Central WWTW. The brackish and desalination permeates are combined and then treated by AOP. AOP is the polishing stage along the treatment train (*Masha, 2020*).

3.2.1 Sampling Points

Samples were obtained at various points along the treatment process, in the following manner:
Raw wastewater from the primary settling tank.

- After the Membrane biological reactor.
- Before the Reverse Osmosis.
- Reject water from the brackish RO.
- After the ultrafiltration system.
- After desalination RO.
- After AOP thus reclaimed water.

All the sampling points are denoted by the green dots on the schematic diagram of the RWTP in fig:3.2.

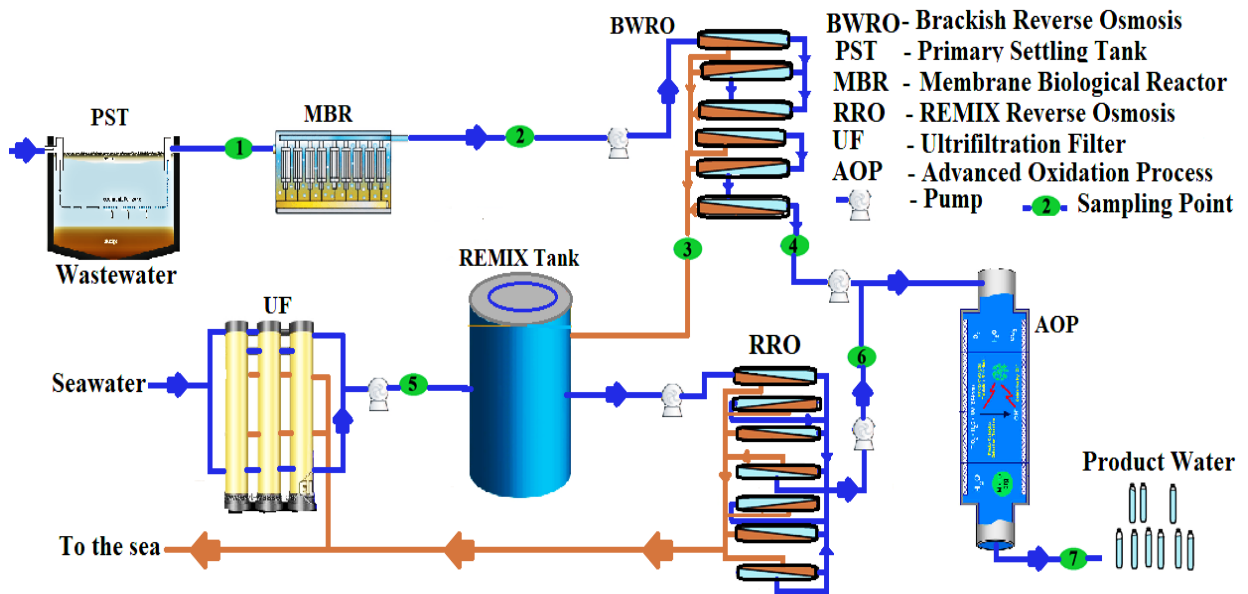


Figure 3.2 A diagram illustrating the locations of the sampling points within the REMIX Water Treatment Plant.

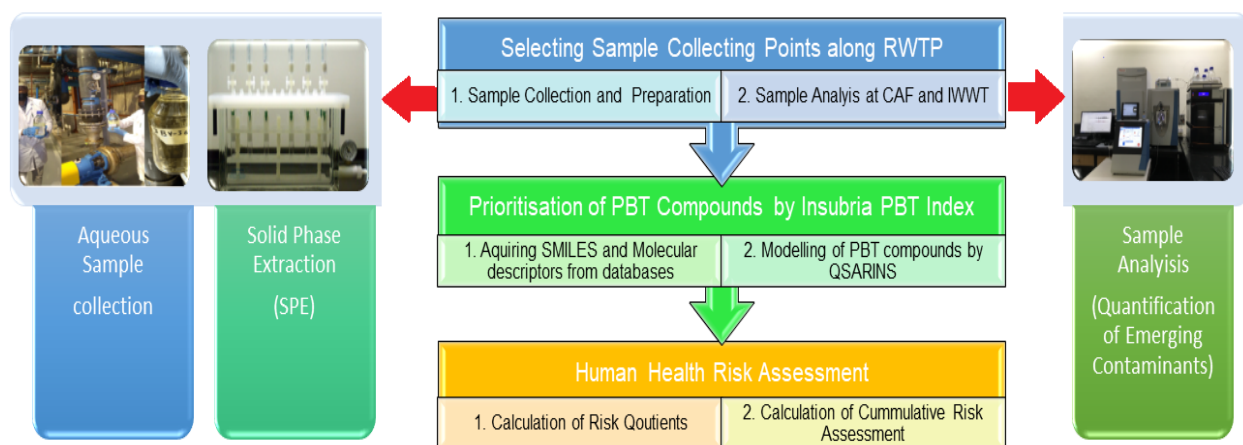


Figure 3.3 Schematic diagram summarising sample collection, preparation, and analysis.

3.2.2 Water Sample Collection

Samples were prepared using amber glass bottles that were pre-washed with methanol and distilled water. This action was executed to obtain the sample that is most representative. The implementation of a prewashing step for amber glass is essential to mitigate the undesirable effects of analyte adsorption on container walls and photooxidation. A total of seven samples were collected from the points shown in Fig. 3.3.1. Fig. 3.4.1 below shows a picture summarising the collection of the water samples from different points and their analysis along the RWTP. The samples were kept on ice to reduce degradation of the targeted analytes within the water matrix. However, the study site's closure for reasons beyond the researcher's control prevented the scheduled work from proceeding as intended. To account for the seasonal change in the wastewater regime over the year, just one sample event was carried out as opposed to the four that were originally planned.



Figure 3.4 Depiction of water samples collection at the REMIX Water Treatment Plant.

3.2.3 Water Chemical Analysis

Chemical and physical parameters of all samples were done. The following water parameters were analysed in all water samples collected namely:

- pH
- Temperature
- Conductivity
- Dissolved Oxygen
- Total dissolved solids TDS
- Salinity

Following sample collection, the YSI 50 probe was used to quantify each of these macro determinants on the spot. Ammonia, nitrates, nitrites, TON, and phosphorus are among the nutrients that were measured at the Institute of Water and Wastewater Technology at Durban University of Technology's Gallery filtered and examined the samples.

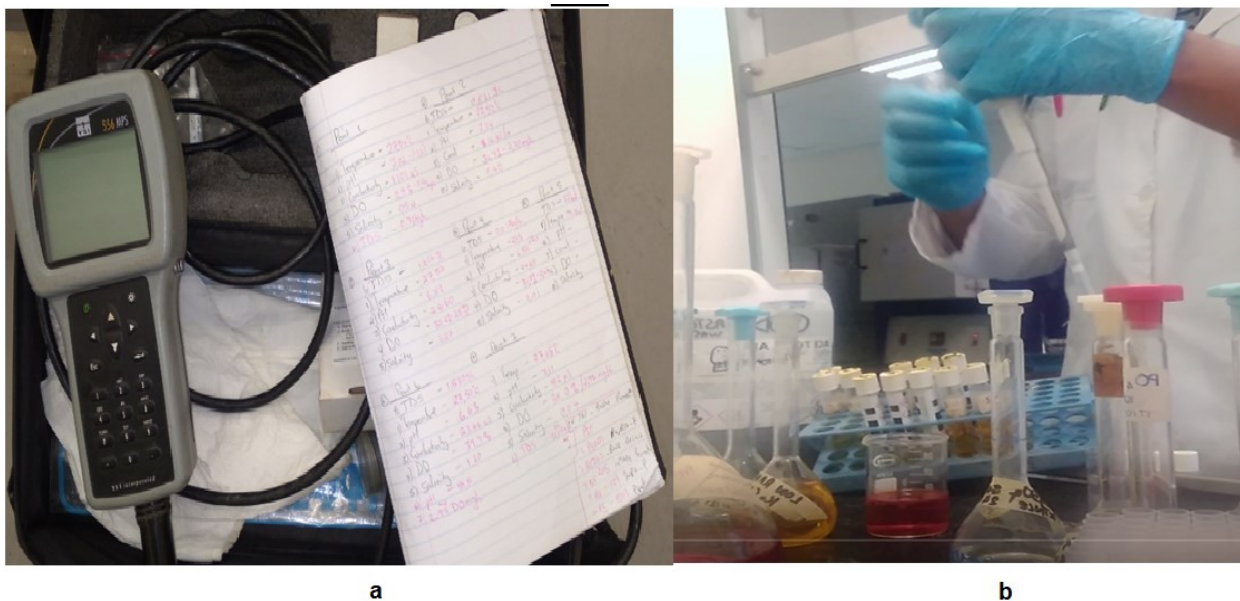


Figure 3.5 (a) Shows the YSI probe used to analyse samples and (b) COD analysis of water samples.

3.3 Quantification of Analytes

As per CAF laboratory sample preservation requirements, one-litre water samples were taken to the Central Analytical Facility (CAF) at Stellenbosch University for measurement by the Liquid Chromatography Mass Spectrometer (LC-MS). The samples were centrifuged (5000 rpm for 15 min, 4 °C) and pre-filtered using 0.7 m glass fibre filters (Whatman, GF/F) using a vacuum filtering system before proceeding to a standard solid-phase extraction (SPE) process following Archer et al.'s (2017a) method. In brief, 50 mL of each treatment's feed water influent and final effluent wastewater were extracted in duplicate using Oasis® HLB cartridges (3 cc, 60 mg; Waters). To account for matrix effects between sample types, internal standards that were deuterated and labels were introduced. Solid phase extraction (Oasis HLB) Divinylbenzene is a pre-treatment method for enrichment of the compounds of interest prior to quantification by LC-MS. It was suggested especially for eluting the analytes of interest in this investigation because it is polar and can hold the intended analytes based on their different physiochemical properties.

3.3.1 Removal Efficiency Equation

The following equation was used to evaluate the effectiveness of removal (% R) for all emerging contaminants entering the MBR and RO (CD Swartz et al., 2018).

$$\text{Removal Efficiency (\%R)} = \left[1 - \frac{\text{permeate concentrations } \frac{\text{ng}}{\text{L}}}{\text{Feed concentrations } \frac{\text{ng}}{\text{L}}} \right] \times 100 \dots \dots \dots (3.1)$$

The efficiency removal for other treatment units along the plant for all species was then calculated using the equation shown below:

$$\text{Removal Efficiency (\%R)} = \left[1 - \frac{\text{effluent concentration in treatment unit } \frac{\text{mg}}{\text{L}}}{\text{Influent concentration in treatment unit } \frac{\text{mg}}{\text{L}}} \right] \times 100 \dots \dots \dots (3.2)$$

3.4 Prioritization by quantitative structure activity relationship

In the initial stage of this risk prioritisation process, the Simplified Molecular Input Line Entry System (SMILES) was assigned to all identified emerging contaminants (ECs). The SMILES notation may be used to represent a bidimensional chemical structure in linear text. The SMILES for each targeted compound were downloaded from a database at www.zincdocking.org as a csv file. This step makes the process of molecular descriptor calculation easier and more compatible with the PDeL-Descriptor. The PaDel-Descriptor calculates the molecular descriptors.

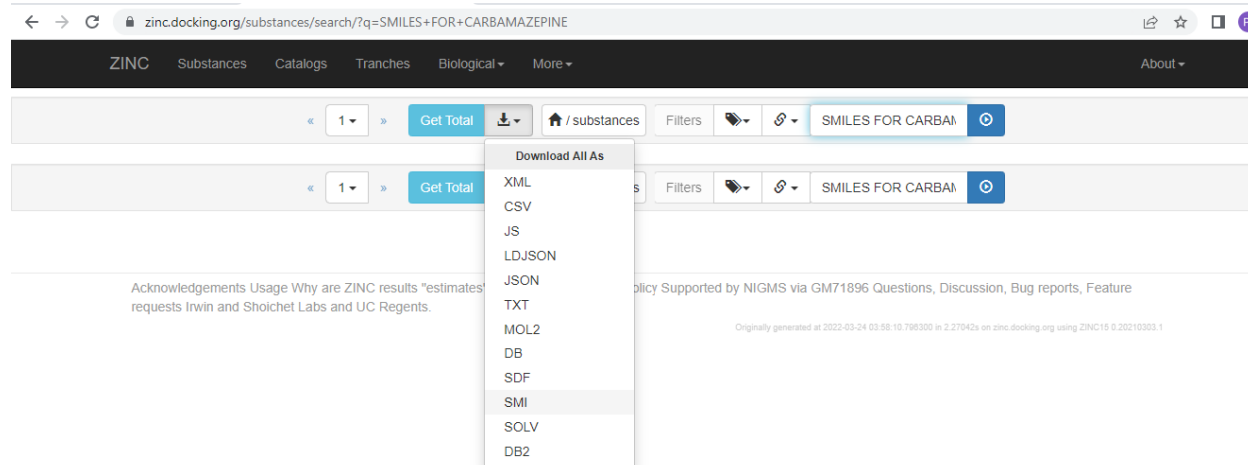


Figure 3.6 Shows a picture of how SMILES of targeted analytes were downloaded

3.4.1 Molecular Descriptors for the targeted analytes

The molecular descriptors were computed using the PaDEL-Descriptor programme, which is open-source software. The interphase of the software is shown in figure 3.5. The PaDEL-

Descriptor programme was utilised to load the SMILES csv file for the molecular descriptor calculation. The PaDEL-Descriptor software was utilised to calculate numerous molecular descriptors, out of which four were extracted. In order to link the chemical structure-property relationship of the selected compounds for the prediction of PBT chemical characteristics, these molecular descriptors were then input into the QSARINS-Chem programme. *Gramatica et al., (2018)*, invented the Insubria PBT Index using the equation below for hazard screening of chemical compounds. This study adopts the model equation (see equation 3.3) to rank and identify the compounds of concern for potential PBT.

$$\text{PBT Index} = -1.46 + 0.64nX + 0.22n\text{BondsM} - 0.39n\text{HBDonLipinski} - 0.06\text{MAXDP2} \dots (3.3)$$

Where:

The Significance of Molecular descriptors of the model are described below:

- $n(X)$ denotes the number of halogen atoms (chlorine, fluorine, iodine etc.) indicates that halogens are being substituted, and it is known that this improves the PBT behaviour of the compound.

Dimensionless **nBondsM** is for bond orders, bond orders greater than one are found in the vast majority of bonds (aromatic bonds have a bond order of 1.5) encoding unsaturation and enhancing the PBT behaviour of compounds.

- Based on Lipinski's definition, the dimensionless **nHBDon_Lipinski** variable represents the number of OH or NH donors. One hydrogen bond donor is designated to each accessible hydrogen atom. It is inversely proportional to the PBT Index and represents a compound's ability to form hydrogen bonds with the ambient medium.
- Non-dimensional **MAXDP2** Using the formula $\Delta V = Z_V - \max \text{Bonded Hydrogens}$, the maximal positive intrinsic state difference of the molecule can be calculated. It pertains to molecule electrophilicity and takes the topological graph's electronic distribution into

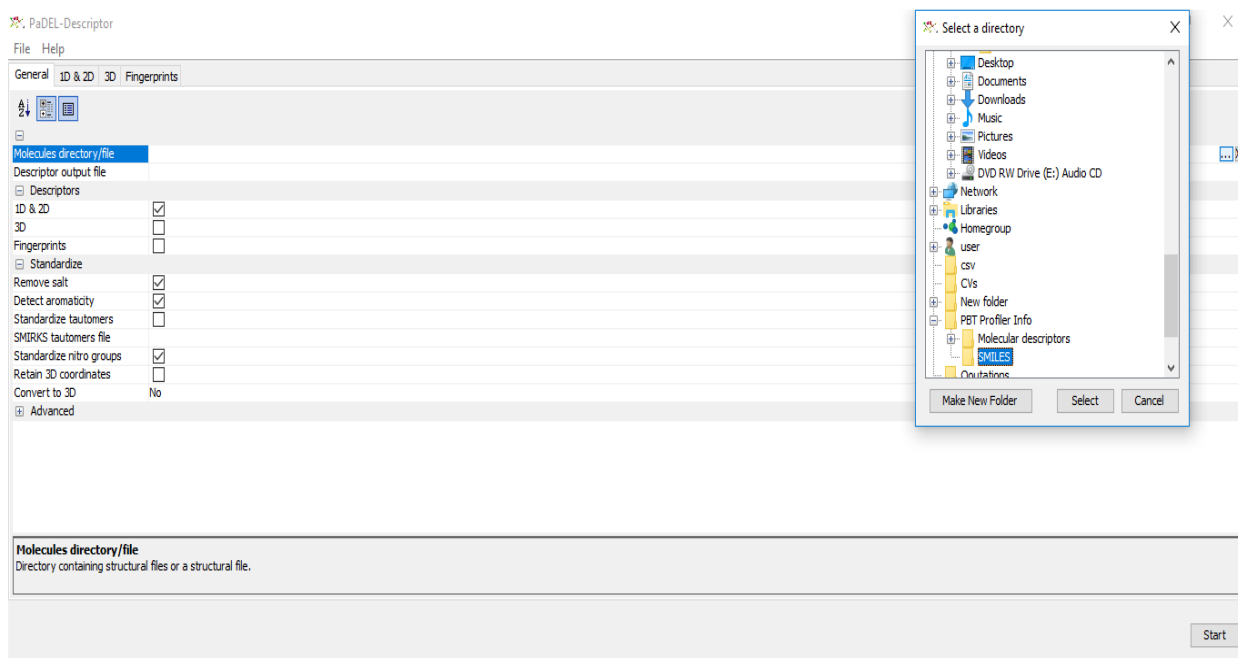


Figure 3.7 Molecular descriptors calculated by PaDEL software.

Table 3.8 Calculated molecular descriptors of the targeted analytes found in water matrix.

ID	Chemical compound	nX	nBonds	MAXDP2	nHBDOn	Lipinski
1	MDMA	0	6	1.757630385	2	
2	Tramadol	0	6	5.188993764	1	
3	Caffeine	0	12	4.672037037	0	
4	Diclofenac	2	13	3.8273384	2	
5	Carbamazepine	0	14	4.752970522	2	
6	Venlafaxine	0	6	5.101926886	1	
7	Sulfamethoxazole	0	13	4.888543084	3	
8	Naproxen	0	12	3.916244734	1	
9	1.7 Dimethyl xanthine	0	12	4.513148148	1	
10	Benzotriazole		10	0.813148148	1	
11	Atrazine	1	6	1.440241875	3	
12	Efavirenz	4	8	5.600453515	1	
13	Methaqualone	0	19	5.624911187	0	
14	Emtricitabine	1	7	5.163945657	4	
15	Codeine	0	7	4.554213435	1	
16	Cocaine	0	8	5.296709184	0	
17	Benzoylcegonine	0	8	5.167563776	1	
18	Methamphetamine	0	6	0.713398526	1	
19	Trimethoprim	0	12	1.848108466	4	
20	Acetaminophen	0	7	2.879824263	2	

3.4.2 Insubria PBT Index (QSARINS)

QSARINS-Chem software runs on Java 8 and Java FX to run properly. The QSARINS-chem algorithm predicts a dimensionless index that ranks compound according to increasing PBT behaviour potential. There are several QSAR models; however, based on PBT screening criteria, the most commonly used one is the online US-EPA Profiler, which has been proven to be slightly less conservative than the QSARINS (*Sangion and Gramatica, 2016*). Both models were right in their predictions of potential PBT compounds, with an 86% prediction agreement. This proved that the model being used in this study to predict the amount of potential PBT compounds in reclaimed water is correct. According to *Sangion and Gramatica (2016)*, QSARINS is more precautionary in detecting PBT compounds, which is why this study adopted it. The QSARINS is a macro-variable algorithm known to condense the chemical cumulative tendency to be a PBT. A set of 180 diverse organic chemicals were analysed using environmental half-lives, bioconcentration factors, and acute toxicity in fish to derive principal component analysis (PCA) results. To assess the predictive capabilities of the algorithm, this study incorporated atrazine, a well-established persistent compound, along with the targeted ECs under investigation. The model underwent validation using OPBT criteria, which involved assessing the occurrence, removal efficiency by wastewater treatment plants, bioaccumulation of compounds based on their octanol partition water coefficient, and predicted no-effect concentration in freshwater.

3.5 OPBT criteria

The research's focus on prioritising ECs is restricted solely to the parent compounds from an environmental engineering perspective. The designated parameters in this proposed methodology (OPBT) are articulated in the form of the subsequent proxies: The parameters of interest include the occurrence and concentration of the solute, the removal efficiencies (R), the Log K_{ow} partition coefficient between octanol and water at near-infinite dilution, and the predicted no impact on concentration (PNEC). These factors are crucial in prioritizing emerging contaminants. In alternative investigations, they were represented using different parameters such as frequency of incidence, yearly excreted quantity, and anticipated environmental levels (*Verlicchi et al., 2023*). After scoring the four criteria in columns 1, 2, 3, and 4 for each compound under investigation, a

threshold of 15 is established to rank the compounds based on their potential PBT. A comprehensive investigation was conducted on the presence of ECs in the influent and effluent of wastewater treatment facilities in three provinces of South Africa, namely Gauteng, KwaZulu Natal, and the Western Cape. Compounds that score above 10 are regarded as potential PBT compounds. The threshold value of 10 states that compounds above 10 are potential PBT. The assignment of the scores is shown in Table 3.1 below.

Table 3.1 Assigning of Scores ranking emerging contaminants.

Occurrence (n g/L)	Persistence RE%	Bioaccumulat ion (Log K_{ow})	Toxicity PNEC_{water} (µg L⁻¹)	Assign ed Score	References
$c < 50$	$R > 80$	$(\text{Log } K_{ow} < 1)$	$\text{PNEC}_{\text{water}} > 100$	1	(Verlicchi <i>et al.</i> , 2023)
$50 \leq c < 100$	$60 < R \leq 80$	$(1 \leq \text{Log } K_{ow} < 2)$	$10 < \text{PNEC}_{\text{water}} \leq 100$	2	(Verlicchi <i>et al.</i> , 2023)
$100 \leq c < 500$	$40 < R \leq 60$	$(2 \leq \text{Log } K_{ow} < 3)$	$1 < \text{PNEC}_{\text{water}} \leq 10$	3	(Verlicchi <i>et al.</i> , 2023)
$500 \leq c < 1000$	$20 < R \leq 40$	$(3 \leq \text{Log } K_{ow} < 4.5)$	$0.1 < \text{PNEC}_{\text{water}} \leq 1$	4	(Verlicchi <i>et al.</i> , 2023)
$c \geq 1000$	$R \leq 20$	$\text{Log } K_{ow} \geq 4.5$	$\text{PNEC}_{\text{water}} \leq 0.1$	5	(Verlicchi <i>et al.</i> , 2023)

3.6 Human health risk assessment

This section focuses on how early warning signs for human health risk analysis are conducted for ECs based on the state of known and unknowns using data-driven inputs for ease of calculation for risk analysis. The QSAR approach was utilised as a modelling technique for conducting hazard identification. The objective of this hazard identification is to recognise the possible crucial endpoints of emerging contaminants that could affect human health and the environment. The Insubria PBT Index is a chemical approach that was used as a substitute for the traditional dose-response relationship analysis employed in animal toxicity experiments for identifying toxicity

endpoints. In Europe, there is a current promotion of *in silico* models (algorithms) as an alternative to *in vivo* animal testing experiments, in compliance with animal rights and regulations. The methodology entails evaluating the inherent composition of substances to establish their precedence in terms of ecological impact. In addition, chemicals possessing similar chemical configurations are prone to induce identical unfavourable impacts on the environment and human well-being.

3.6.1 Calculations of risk assessments

The human health risk assessment of the target ECs found in reclaimed water from the RWTP was based on the risk quotient (RQ) for infants, adolescents and adults weighing on average 5.6kg, 57kg and 65 kg respectively (CD Swartz *et al.*, 2018). RQ was determined as ratio of the measured concentration (MC) of each EC found in the reclaimed water and the respective drinking water equivalent level (DWEL) of that EC (Eq. 1) (Wu *et al.*, 2022)

$$RQ = \frac{MC}{DWEL} \dots\dots\dots(3.4)$$

The DWEL for the targeted ECs were calculated using the equation 2 below according to Parida *et al.* (2021)

$$DWEL = \frac{ADI \times BW}{DWI \times AB \times FE} \dots\dots\dots (2)$$

Where:

ADI ($\mu\text{g}/\text{kg}/\text{day}$) represents the acceptable daily intake for target ECs. DWI (L/day) represents the drinking water intake for people weighing an average of 65 kg and drinking 2 L of water per day. The gastrointestinal absorption rate for all study compounds is assumed to be 1 (abbreviated as AB). FE relates to exposure frequency, which was assumed to be 1. A RQ value of $0.01 \leq RQ <$

0.1 represents a low human health risk, while $0.1 \leq RQ < 1$ and $RQ > 1$ indicate a medium and a high human health risk, respectively (Wu *et al.*, 2022).

3.6.2 Accepted daily water intake.

The acceptable daily intake (ADI) is an estimate of the amount of an emerging contaminant in drinking water that may be taken daily over a lifetime without posing a significant health risk to the consumer (CD Swartz *et al.*, 2018). Some of the ECs ADIs are found on databases such as the Integrated Risk Information System (USEPA), while others are calculated as shown by the equation below.

$$ADI \text{ (surrogate)} = \frac{\text{Therapeutic dose}}{\text{Uncertainty Factor}} \text{ (CD Swartz } et al., 2018)\dots\dots\dots (3.5)$$

NB: Applying an uncertainty factor of 1000 and the maximum Therapeutic dosage estimate for each emerging pollutant.

3.6.3 Surrogate Average daily Intakes of emerging contaminants

Surrogate ADI (Acceptable Daily Intake) refers to a concept used in toxicology and risk assessment when there is insufficient toxicological data available for a specific substance. In such cases, a chemically or toxicologically related compound with known toxicity data may be used as a substitute or "surrogate" to estimate the potential health risks associated with the target substance. In this study therapeutic doses of some of the pharmaceuticals were used as ADIs. These ADIs are shown in table 3.2 below.

Table 3.2 Calculated ADI surrogates for the targeted emerging contaminants compounds.

Emerging Contaminant	Therapeutic dose (mg)	ADI surrogate (µg/kg/day)
Sulfamethoxazole	800	0.8
Trimethoprim	160	0.16
Efavirenz	600	0.6
Emtricitabine	200	0.2
Cocaine	300	0.3
Methaqualone	300	0.3

3.6.4 Drinking water equivalent level

It is well known that the directive law rules for drinking water do not apply to the majority of ECs. In this regard, the current work has used equation 2 to compute the DWEL for the chosen ECs and successfully calculate the risk quotient shown in equation 1. For each PBT chemical, the associated age-dependent value (DWEL) is determined. According to the following equation (3.6).

$$DWEL = \frac{ADI \times BW}{DWI \times AB \times FOE} \text{ (Parida et al., 2021).} \dots\dots\dots (3.6)$$

Where:

- The acceptable daily intake (ADI) or risk-specific dosage (RSD) refers to the effects' relative carcinogenic and noncarcinogenic effects.
- BW is the age-specific groups' median body weight (kg) from table 1–1.
- The gastrointestinal absorption rate for all study compounds is assumed to be 1 (abbreviated as AB).
- FOE relates to exposure frequency (350 days or 365 days).

According to *CD Swartz et al. (2018)*, the typical body weight for a South African individual is 65kg, and the daily water consumption is estimated to be 2 litres. These variables will be utilised in equation 3.6 as per environmental engineering principles.

3.6.5 HACCP System

The HACCP system is used as a framework for RWTP in this investigation. It is a preventative method that results in the identification, explanation, and management of dangers associated with the production of water in this research. To effectively monitor and eliminate harmful emerging contaminants along the RWTP system, critical control point identification is absolutely essential. Prioritising particular risk assessments in the monitoring programme is the emphasis of the HACCP system (*Tsoukalas and Tsitsifli, 2018*).

It frequently finds treatment flaws early, minimising downtime and resource consumption (such as energy, chemicals, and labour). As a result, it is a suitable instrument for checking on the RWTP's effectiveness in producing reclaimed water. The analysis is based on the identification

and evaluation of significant health hazards present in the water obtained from the abstraction sources. The seven principles of the HACCP system are as follows:

3.6.6 Hazard analysis

In this study, the first stage of risk assessment involves the detection of potential PBT emerging contaminants from a priority list that could pose hazards. Chemical hazards are chosen from the priority list compiled after screening the chemicals for potential PBT chemical compounds by the Insubria PBT Index and OPBT criteria. In identifying the critical control points, Codex Alimentarius principles (see Fig. 3.9) are applied using the hazards chosen from the priority list compiled. Seawater and wastewater serve as sinks for a diverse range of developing pollutants, including medicines, pesticides, endocrine disrupting chemicals, and illegal narcotics, all of which have the potential to impair human health (Parida *et al.*, 2021). The objective of this investigation is to assess the efficiency of the RWTP in removing potential PBT substances and probable hazardous heavy metals that could be present in two potential water sources. However, other hazards such as pathogens, dissolved solids, etc. are also hazards that can have a synergistic effect on the removal of emerging contaminants on the water surface, and the surface membranes of MBR, UF, and RO are covered for effective production and removal of emerging contaminants. Moreover, these hazards can lead to the inefficiency of other treatment units along with the treatment technology.

3.6.7 Determination of the Critical Control Points (CCPs)

Accurate identification of critical control points (CCPs) is a crucial aspect of the Hazard Analysis and Critical Control Points (HACCP) approach. Substantial focus will be placed on effectively managing these designated process steps through process control measures. Ensuring the health and safety of both consumers and workers is a critical aspect of water treatment technologies. The treatment of wastewater requires careful consideration of emerging pollutants to ensure effective removal of identified chemical hazards. Optimisation and control of treatment unit processes are necessary to achieve this goal (Tsoukalas and Tsitsifli, 2018).

3.7 Limitation of the study

The study was planned to sample three times along the RWTP to cater for the seasonal wastewater variation of pollutant contamination. The RWTP was then closed and never opened to this date, this was beyond the researchers and supervisors control. **One** sampling event was done to evaluate the performance of the RWTP for the removal of emerging contaminants and heavy metals.

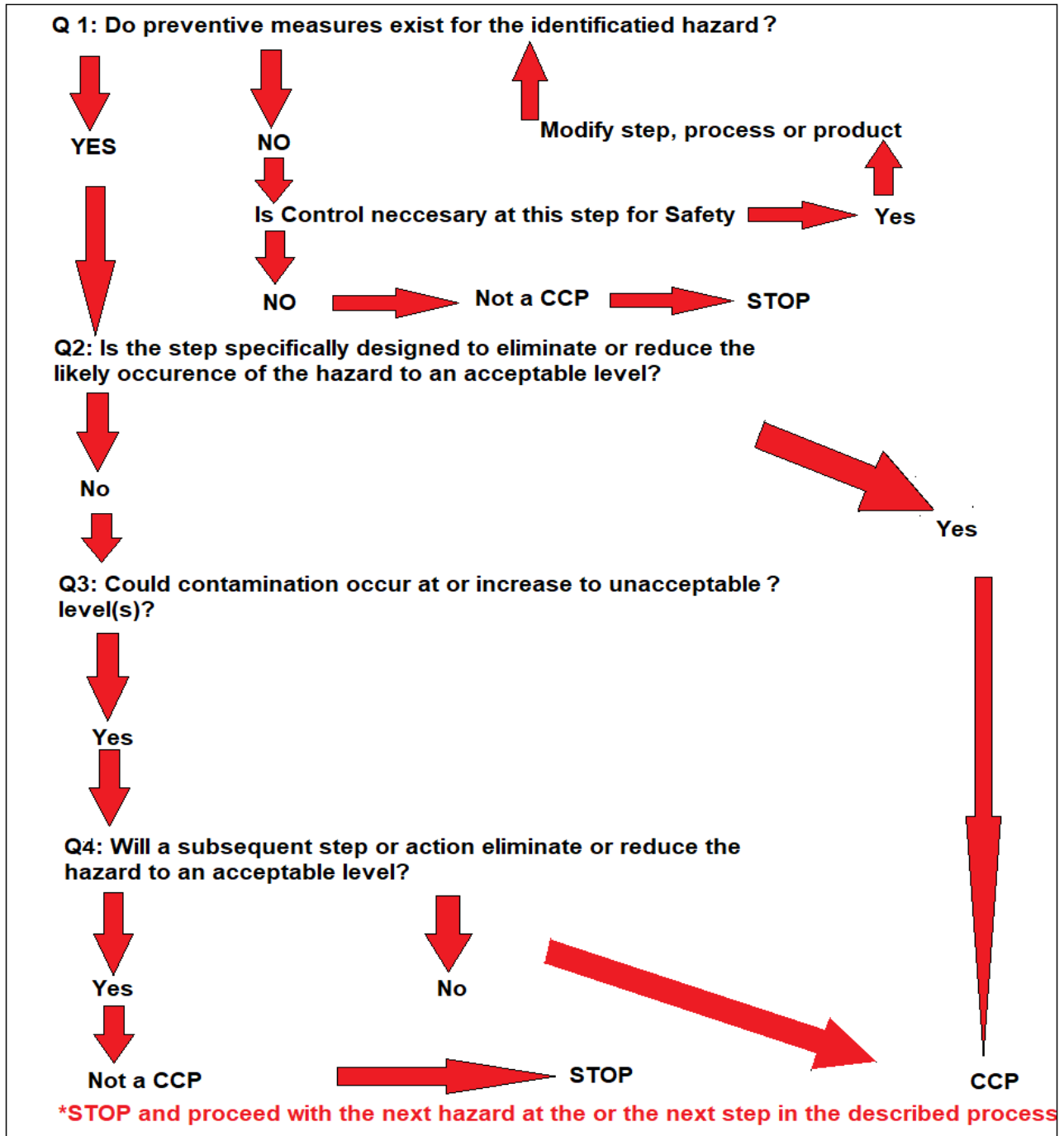


Figure 3.9 Codex Alimentarius principles for identifying critical control points

CHAPTER 4: RESULTS AND ANALYSIS

4.1 Introduction

The present chapter presents the results of our investigation of REMIX™ water treatment plant for the removal of emerging contaminants and heavy metals focusing on their presence and distribution in water samples collected. The study use SANS 241-1:2015 and other international standards for evaluating the levels of contaminants in water reuse. These benchmarks serve as a basis for comparing the study's findings. The results of the prioritised emerging contaminants' chemical risk analysis are also presented.

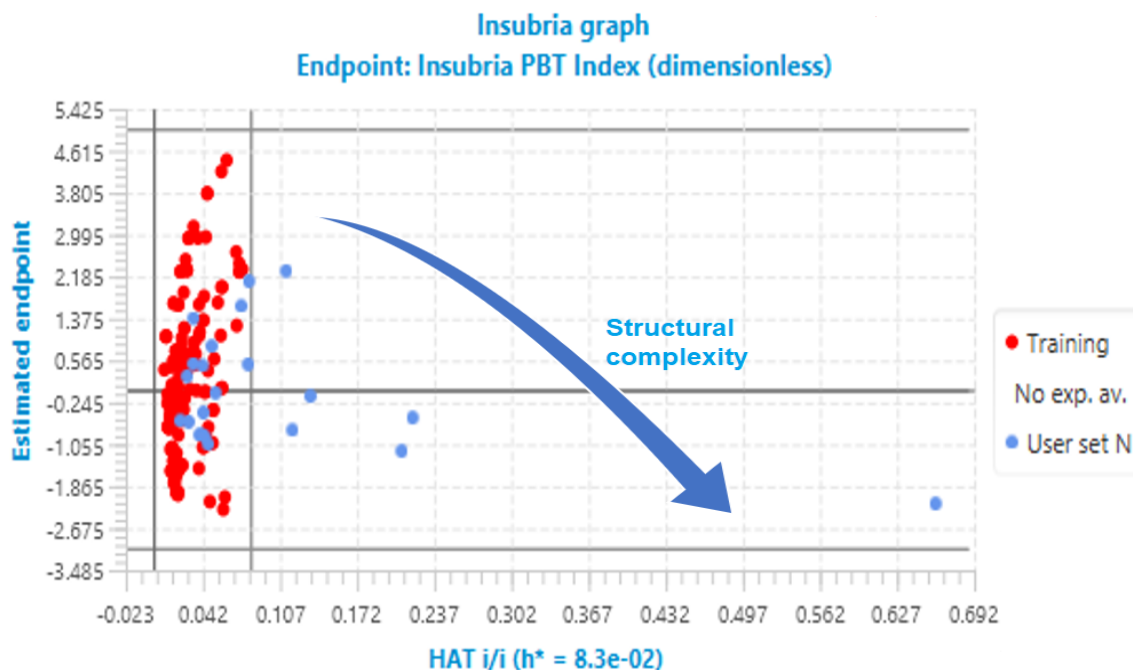


Figure 4.1 Insubria graph showing overlapping of some the targeted and trained compounds in the applicability domain of the model.

The prioritisation of the targeted emerging contaminants was performed by the QSAR. A predictive modelling approach based on molecular structure. The prediction set consisted of 20 compounds compared to 92 in the training set, thus representing less than half of the whole initial set of 180 chemicals. Quantitative measures of a model applicability domain (AD) are needed to evaluate the degree of extrapolation and identify problematic compounds (Gramatica *et al.*, 2018).

Figure 4.1 shows an Insubria graph highlighting 16 out of 20 targeted compounds inside the applicability domain of the Insubria PBT Index. The 14 compounds showed good overlap with the model training set. QSAR models are developed on a defined domain of compounds with known properties and structures (the training set) (Gramatica *et al.*, 2018). Thus, the analysis of the AD is an essential step in the application of every model, to verify if new chemicals have an acceptable structural similarity to the chemicals in the training set.

In the extrapolation zone to the right, 4 compounds out of 20 departed from the threshold (h^* value) of 0.083. According to Sangion and Gramatica, (2016), chemical compounds outside the applicability domain have extrapolated predictions and are less reliable. Sulfamethoxazole (0.132336), methaqualone (0.111949), trimethoprim (0.218445), and emtricitabine (0.209248) are chemical compounds with structural complexity characterised by high molecular weight and a high number of functional groups, very different from the chemicals used in the training set of the model.

Table 4.1 Insubria PBT Index and Applicability Domain for the targeted emerging contaminants

No.	Name	Experimental endpoint	Estimated endpoint	HAT i/i ($h^* = (8.3e-02)$)	PBT Index
1	MDMA	Not provided	-1.05187	0.046179	-0.96548
2	Tramadol	Not provided	-0.87523	0.04062	-2.23371
3	Caffeine	Not provided	0.842846	0.049143	-0.64209
4	Diclofenac	Not provided	1.616446	0.074035	1.047338
5	Carbamazepine	Not provided	0.491197	0.079884	-0.37366
6	Venlafaxine	Not provided	-0.86983	0.038849	-2.19975
7	Sulfamethoxazole	Not provided	-0.12273	0.132336	-0.71653
8	Naproxen	Not provided	0.500296	0.033598	-0.41734
9	1.7 Dimethylxanthine	Not provided	0.463283	0.041443	-0.65013
10	Benzotriazole	Not provided	0.260516	0.028425	0.352872
11	Efavirenz	Not provided	2.099362	0.080427	0.605823

12	Methaqualone	Not provided	2.296463	0.111949	0.526285
13	Emtricitabine	Not provided	-1.18385	0.209248	-1.57394
14	Codeine	Not provided	-0.61977	0.029692	-1.76614
15	Cocaine	Not provided	-0.06029	0.052306	-1.76572
16	Benzoyllecgonine	Not provided	-0.4417	0.0421	-1.78535
17	Methamphetamine	Not provided	-0.5977	0.022621	-0.48823
18	Trimethoprim	Not provided	-0.53971	0.218445	0.179238
19	Acetaminophen	Not provided	-0.90535	0.043173	-1.18313
20	Cetirizine	Not provided	1.383855	0.033749	0.602932

The identification of PBT-like compounds is based on threshold values. The PBT threshold was set at PBT Index > 1.5 and PBT Index < -1.5 to highlight non-persistent chemical compounds. Chemical compounds outside this range are considered potential PBT, persistent, and bioaccumulative. From Table 1, 6 out of 20 compounds were considered potential PBT compounds according to the threshold limits of the Insubria PBT Index. For monitoring purposes and the production of drinking water, tramadol, venlafaxine, emtricitabine, codeine, cocaine, and benzoyllecgonine were identified as potential PBT compounds by the Insubria PBT Index. Analgesic tramadol and antidepressant venlafaxine have been detected in high concentrations in the wastewater influent; hence, close monitoring is needed for their removal.

Table 4.2 Targeted emerging contaminants and their corresponding final OPBT score.

Chemical compound	(O) Score	(P) score	(B) score	(T) score	Final OPBT score
Carbamazepine	3	3	3	1	10
Codeine	5	4	2	1	12
Venlafaxine	2	3	3	1	9
Efavirenz	5	3	4	1	13
cocaine	3	3	2	1	9
Emtricitabine	3	1	1	1	6
methamphetamine	3	3		1	7

Trimethoprim	4	1	2	1	8
Sulfamethoxazole	5	1	1	1	8
Diclofenac	5	1	5	2	13
Caffeine	5	1	1	1	8
Acetaminophen	5	1	1	1	8
Naproxen	5	1	4	1	11
Cetirizine	5	2	4	1	12
benzoylecgonine	5	1	2	1	9
MDMA	3	1	2	1	7
Benzotriazole	5	4	1	1	11
1.7 Dimethylanxithine	n/a	n/a	1	1	2
Methaqualone	5	3	4	1	13

Table 4.1 shows the scoring of emerging contaminants after an in-depth literature review in relation to their occurrence and removal efficiencies from the wastewater treatment plants in the three provinces of South Africa (Gauteng, KwaZulu Natal, and Western Cape), as highlighted in Table 2. 1. Occurrence (O) was based on the average concentration of emerging contaminants measured from the influents of different wastewater treatment plants in each province. It is recorded that acetaminophen, codeine, sulfamethoxazole, trimethoprim, carbamazepine, cetirizine, diclofenac, etc. have average concentrations ≥ 1000 ng/L; this made them attain a maximum score of 5 based on assigning scores for compounds (see table 3.1). (Verlicchi *et al.*, 2023). Persistence (P) is the resistance of an emerging contaminant to being removed from the wastewater secondary treatment process (activated sludge process). In this case, persistence is identified by the removal efficiencies of compounds from the wastewater treatment plants. Emtricitabine, efavirenz, benzotriazole, and cocaine attained a maximum score of 5, which implies that the chemical compounds are hardly removed from the wastewater treatment plants. Bioaccumulation is related to the octanol water partition coefficient; these values were obtained from a database (ZINC, 2023). For toxicity, analgesic drugs, illicit drugs, and antiretroviral drugs attained a maximum score of five, showing the toxicity of long-term exposure to aquatic organisms in fresh water.

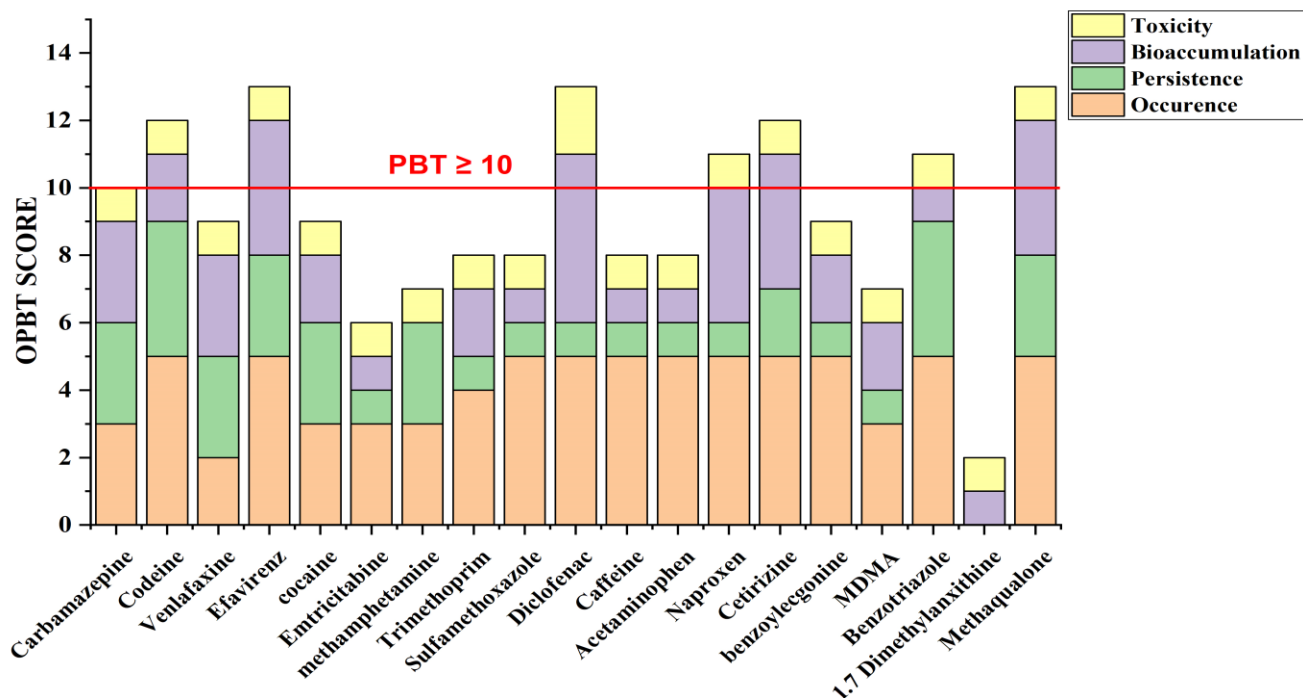
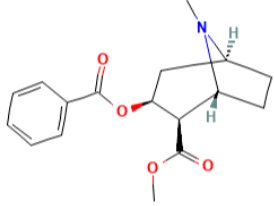
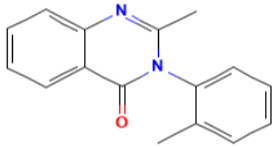
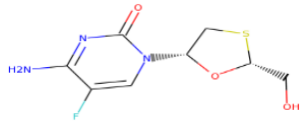


Figure 4.2 Final OPBT scores for the targeted emerging contaminants scored above the set threshold.

Fig. 4.2 shows the OPBT criteria for screening the targeted emerging contaminants for persistence, bioaccumulation, and persistence after water treatment technologies. The criteria identified seven out of twenty emerging contaminants as potential PBT chemical compounds. A threshold of 15 was proposed; compounds scoring 15 and above were considered potential PBT compounds. The following were the scores for the identified potential PBT compounds: carbamazepine (16), naproxen (16), diclofenac (15), emtricitabine (16), efavirenz (20), methaqualone (15), and cocaine (15).

Table 4.3 Consensus agreement on prioritising emerging contaminants between the two methodologies, the Insubria PBT Index and OPBT criteria, forms a priority list.

Class	CAS	Chemical	Structure
Illicit drug	50-36-2	Cocaine	

Illicit drug	60124-85-8	Methaqualone	
Antiretroviral	143491-57-0	Emtricitabine	

The level of agreement between the two predictions of the methodologies in prioritising emerging contaminants was 43%. Both methodologies leverage pre-existing knowledge to acquire insights from the established behaviour of extensively researched chemicals. They also aim to recognise and circumvent the hazardous properties of compounds in the absence of experimental evidence. Based on our research findings, we recommend that predictions obtained through the agreement of both methods be considered for effective monitoring of reclaimed water. According to the consensus of two different methods, three compounds have been predicted as potential PBTs. These are listed in Table 4.3 under the priority list. These chemicals have been identified as environmental concerns by various agencies and reports, including *Archer et al., (2021)*; and *(Swartz et al., 2018)*.

Therefore, it is imperative to monitor these contaminants in wastewater, water, and water reuse treatment plants. This is due to the observed elevated concentrations of these contaminants in our environmental waters, which can subsequently be abstracted for potable water treatment. Continuous exposure to antiretroviral drugs may pose potential dangers, such as the development of viral mutations and resistance to the HIV virus. This is similar to the case of antibiotics, where continuous exposure can trigger resistance (*Horn et al., 2021*). The toxicity experimental endpoints for illicit drugs have not been published for humans, which poses a potential danger and unknown risk to human health. Long-term exposure to such drugs may impact the endocrine system. Therefore, it is imperative to implement robust treatment measures for the effective removal of prioritised emerging contaminants.

4.2 Emerging contaminant occurrence at the REMIX™ Water Treatment Plant

The sample collected after preliminary treatment stage of the wastewater treatment plant was analyzed for the presence of various classes of emerging contaminants. The sample was the influent to the RWTP technology. The results of the analysis are given by figure below.

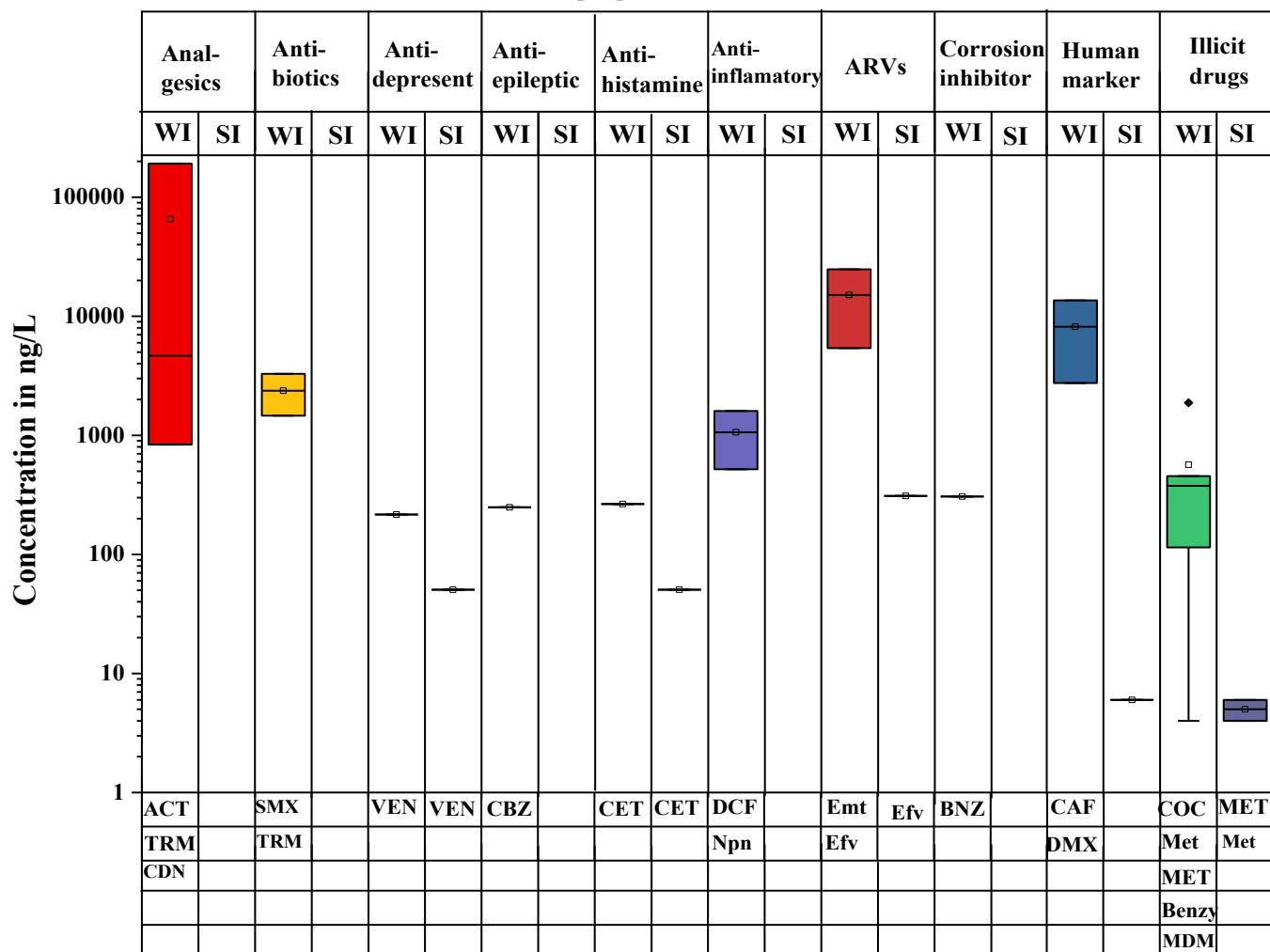


Figure 4.3 Box and whisker plots showing occurrence of emerging contaminants in the Influent to the plant.

The Analgesics are commonly used non-prescribed medications in South Africa, and they are commonly used to relieve pain, swelling, fever, cold, flu symptoms, and headaches. For most of these pharmaceuticals, the possible entrance to the wastewater is via human excretion and the disposal of expired or unused medication (CD Swartz *et al.*, 2018). As a result, this may result in high usage patterns of these drugs. In the same sample denoted in green in Fig. 3.1, pharmaceutical

compounds such as tramadol, codeine, sulfamethoxazole, trimethoprim naproxen, emtricitabine, efavirenz, cetirizine, and carbamazepine were detected at concentration levels of 837 ng/L, 4666.5 ng/L, 3283.5 ng/L, 1462.5 ng/L, 1604 ng/L, 24,836.5 ng/L, 5,407.5 ng/L, 265 ng/L, and 248.5 ng/L, respectively. Caffeine and its metabolite were detected at concentrations ranging from 1400 to 1200 ng/L. Caffeine is a well-known central nervous system stimulant mainly found in domestic wastes of caffeinated drinks, beverages, and chocolates. It is highly soluble in water (Sutherland, et.al, 2015). It is important to highlight that drug abuse is prominent in the city of Durban. Benzoyllecgonine, which is a metabolite of cocaine, was detected in the influent among the illicit drugs with a high concentration of 1880 ng/L. Caffeine is a well-known central nervous system stimulant mainly found in domestic wastes of caffeinated drinks, beverages, and chocolates. It is highly soluble in water (Sutherland, et.al, 2015). It is important to highlight that drug abuse is prominent in the city of Durban. Benzoyllecgonine, which is a metabolite of cocaine, was detected in the influent among the illicit drugs with a high concentration of 1880 ng/L.

The concentrations of antiretroviral compounds were much higher in Durban, and the findings coincide with findings from different provinces done by (Abafe *et al.*, 2018; Archer *et al.*, 2021; Gani *et al.*, 2021; CD Swartz *et al.*, 2018). This confirms that South Africa has the highest number of people in the world on antiretroviral therapy (Abafe *et al.*, 2018).

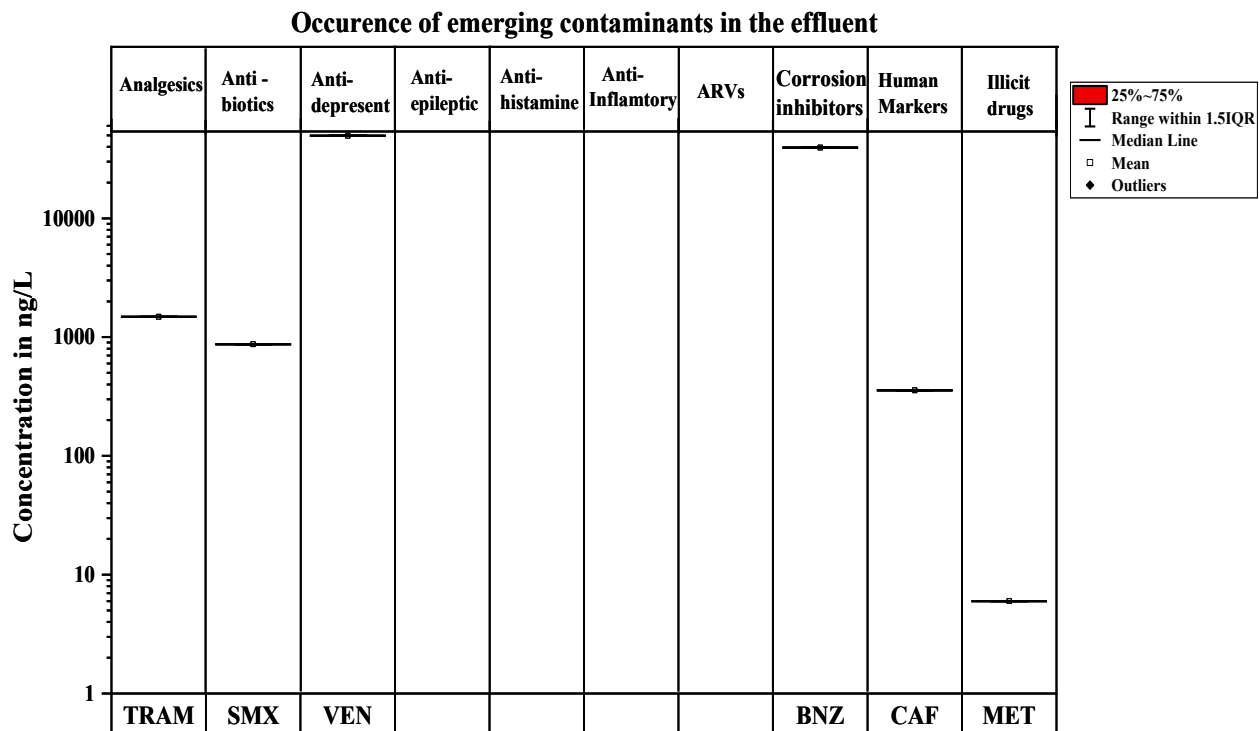


Figure 4.4 Boxer and whisker plots showing the occurrence of emerging contaminants in the effluent after REMIX treatment technology.

For most of the emerging contaminants in the effluent of the RWTP collected in sample 7 (see fig. 3.2), most of the emerging contaminants concentrations were all below the limit of quantification, indicating good removal efficacy by the RWTP, except for recorded anomalies for caffeine, venlafaxine, benzotriazole, and sulfamethoxazole. This problem only occurred in this sample. The anomalies in the four compounds could have been attributed to analytical artefacts, which are inaccuracies in sample collection, preparation, or analysis (Mosekiemang *et al.*, 2019). Contaminant interactions can also be considered a factor that led to these misleading results. This error could not be rectified due to one sampling event in this study. The RWTP operations were closed beyond researcher's control.

4.3 Removal efficiency for Membrane biological reactor

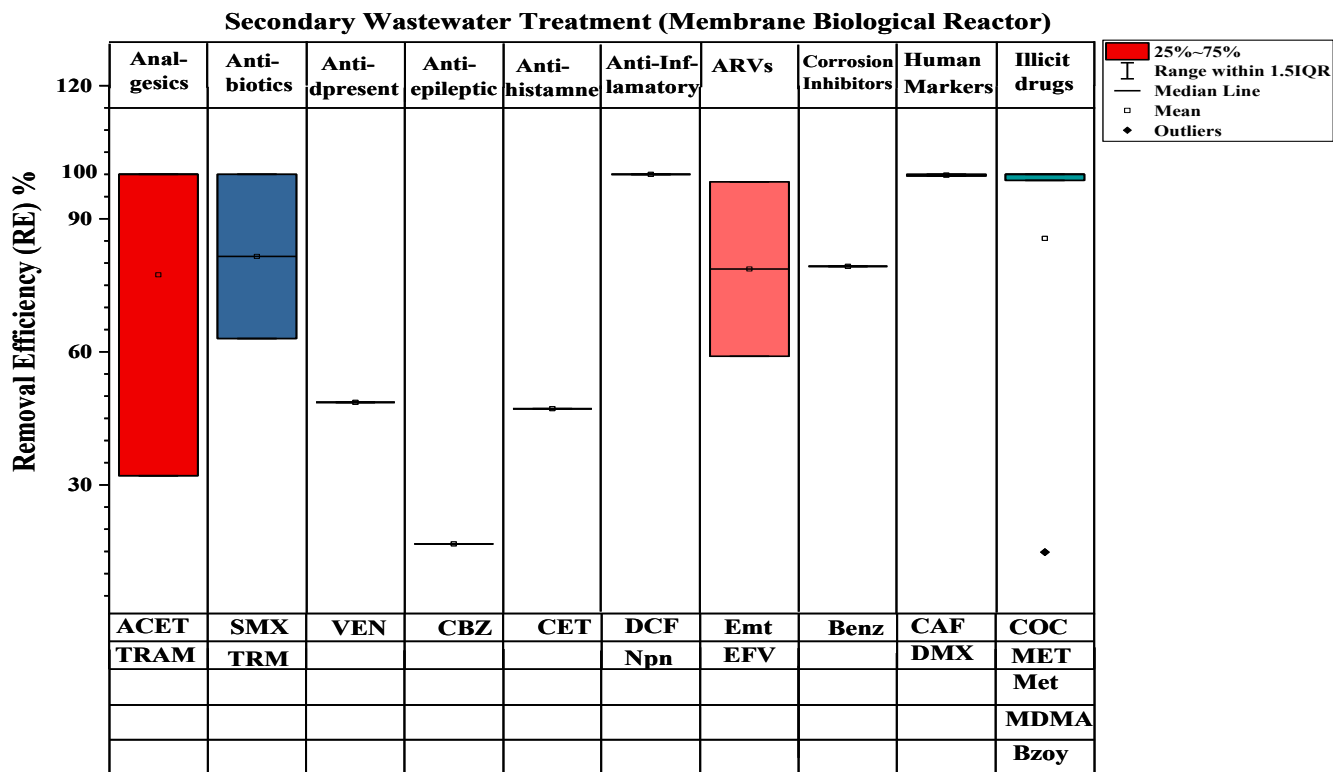


Figure 4.5 Membrane biological reactor showing removal of emerging contaminants from the feed waters.

The removal efficiency of MBR treatment technology system varied between (19-100%) for different types of emerging contaminants. It can be observed that from fig:3 the technology system could not completely remove some of the emerging contaminants in the feed water. Removal efficiencies for different classes of pharmaceuticals such as acetaminophen, trimethoprim, diclofenac, and naproxen and emtricitabine were above 95%. The removal efficiency of the MBR treatment technology system varied between 19 and 100% for different types of emerging contaminants. It can be observed from. This removal can be attributed to a combination of physico-chemical and biological processes of chemical compounds and the MBR technology. According to *Dolar et al., (2012)*, compounds with high water partition coefficient $LO (K_{ow})$, such as diclofenac (4.26) and naproxen (3.18), can be assumed to adsorb onto sludge and get removed due to their high $\log K_{ow} > 2.5$, representing high sorption.

For acetaminophen and trimethoprim, high removal rates can be attributed to biological degradation constants greater than 0.1 ($k_{\text{bio}} > 0.1 \text{ Lgss}^{-1}\text{d}^{-1}$). This confirms that compounds with $k_{\text{bio}} > 0.1 \text{ Lgss}^{-1}\text{d}^{-1}$ have high removal rates above 95% in the MBRs (*Melin et al., 2006*). The microbes in MBRs can break down many organic compounds, including some emerging contaminants, through processes such as biodegradation and biotransformation (*Melin et al., 2006; Roccaro, 2018*). In a related study on membrane biological treatment conducted by *Gulamhussein et al., (2022)*, a 100% removal rate of acetaminophen was achieved, followed by 64% removal of sulfamethoxazole. In this study, sulfamethoxazole was moderately removed (63%) in accordance with the findings of *Gulamhussein et al., 2022*. The moderate removals can be attributed to the hydraulic retention time (HRT) of the MBRs (*Leiviskä and Risteelä, 2022*). Longer HRTs provide more time for microbiological degradation to occur, leading to higher contaminant removal. For carbamazepine, poor removal rates are consistent with previous studies (*Hai et al., 2018; Leiviskä and Risteelä, 2022; Ng et al., 2021*).

The poor removal rates can be attributed to a low biological degradation constant ($k_{\text{bio}} < 0.10 \text{ Lgss}^{-1}\text{d}^{-1}$), making them not removed by biological processes (*Dolar et al., 2012*). Carbamazepine and its metabolites are poorly degraded in the biological process, and carbamazepine concentrations can even increase due to the transformation of the metabolite back into its parent compound (*Leiviskä and Risteelä, 2022*).

4.4 Removal of emerging contaminants by brackish reverse osmosis

The water sample was collected in the filtered water of brackish reverse osmosis. The analysis of different classes of emerging contaminants are shown in fig 4.6 below.

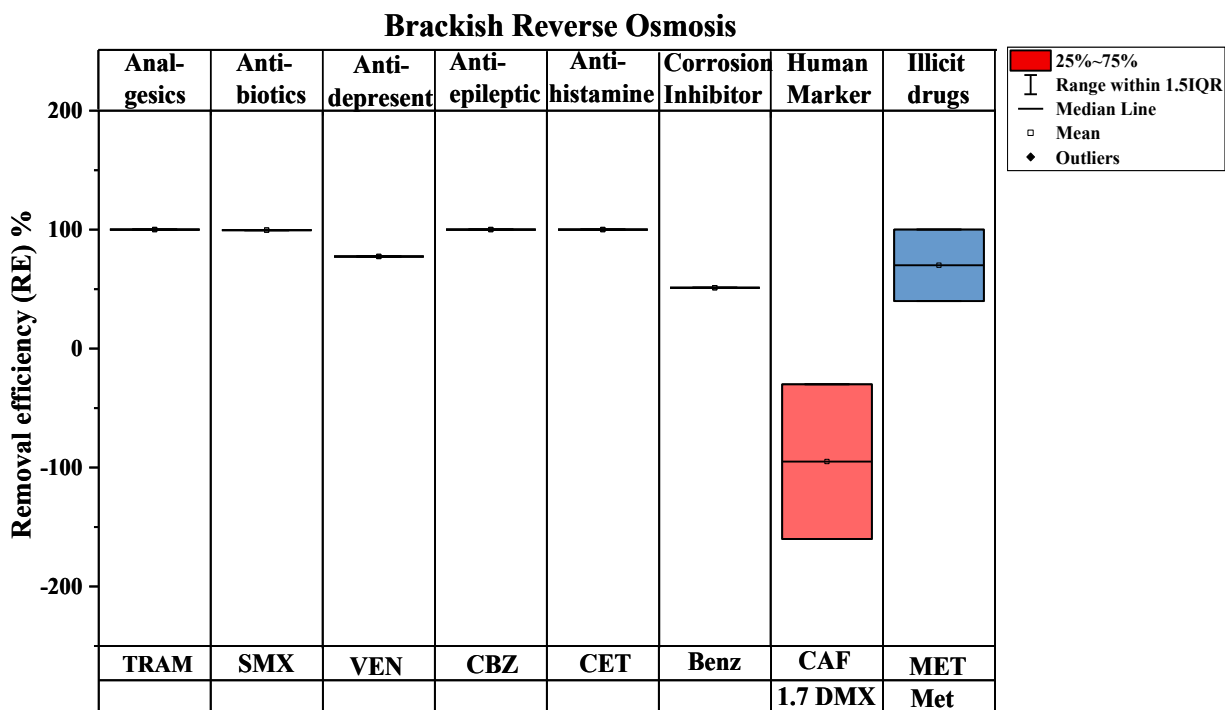


Figure 4.6 Brackish reverse osmosis shows the removal of emerging contaminants from the feed water.

The high removal efficiencies of ECs in the brackish RO system indicate that it is a highly effective treatment method for emerging contaminants considered in this study, except for the noted anomalies for caffeine and 1.7 dimethyl xanthine. The reduction in concentration between the inlet and outlet was determined to be 99.5%, 75.5%, and 51.2% for sulfamethoxazole, venlafaxine, and benzotriazole, respectively. The charge of sulfamethoxazole in the water matrix might result in electrostatic interactions with the membrane, giving rise to high removal. For venlafaxine and benzotriazole, the low removal can be a combination of factors, including size exclusion and potentially interaction with the surface membrane. The BWRO could not remove nearly half of the benzotriazole contaminant, as shown in Fig. 4.7. In this case, various conditions such as feed water chemistry parameters, and transmembrane pressure, could have affected the complete removal of this contaminant. Overall, brackish reverse osmosis showed potential for removing

recalcitrant chemicals from the wastewater. The retained emerging contaminants were then introduced to seawater in the REMIX™ Tank before the REMIX™ reverse osmosis (RRO).

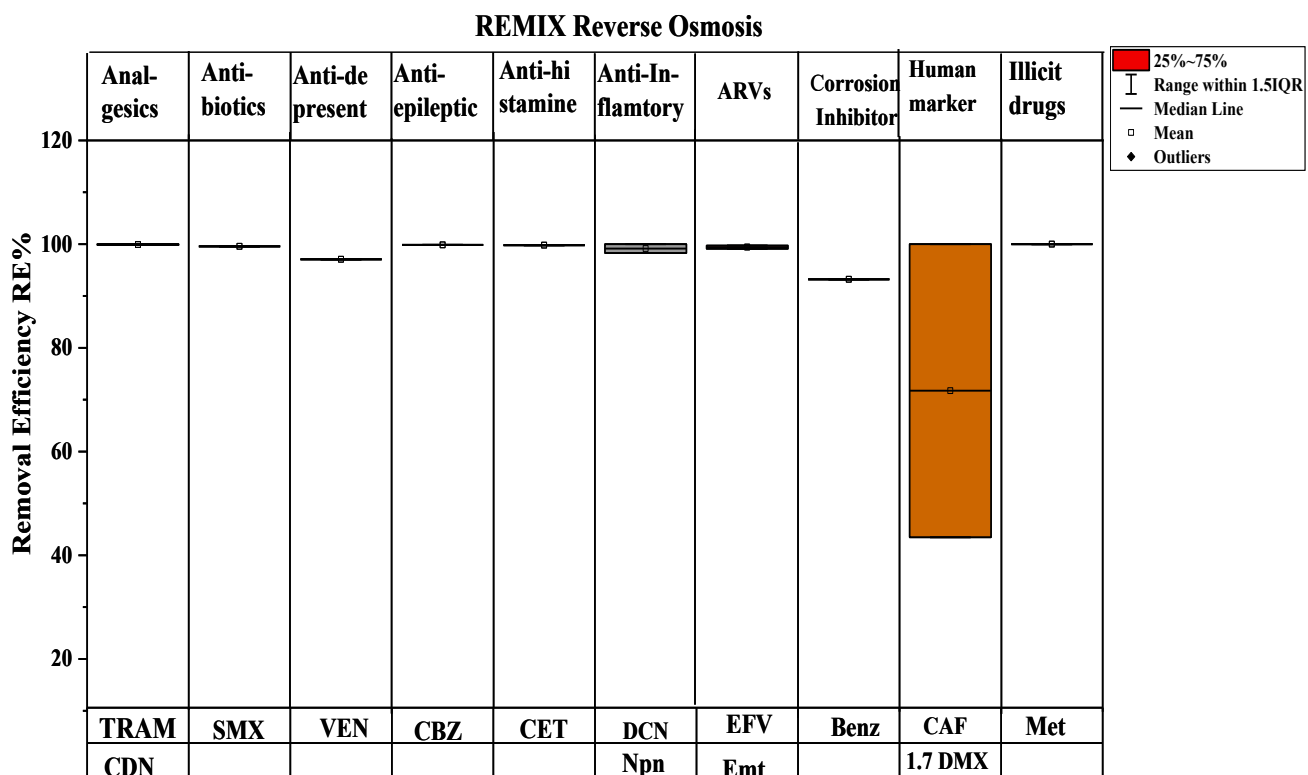


Figure 4.7 REMIX™ reverse osmosis shows the removal of emerging contaminants from the feed water

In the RRO, the reduction between the inlet and outlet was determined to be 99.7%, 100%, 99.1%, 94.5%, 99.6%, 96.65, 98.2%, 99.5%, and 86.5% for tramadol, sulfamethoxazole, venlafaxine, carbamazepine, cetirizine, diclofenac, emtricitabine, efavirenz, and benzotriazole, respectively, except for 1.7 dimethylxanthine. The high removals shown in Fig. 5 indicate that the RRO is very effective in removing emerging contaminants from two streams, seawater and wastewater, based on their occurrence concentrations. Tramadol, sulfamethoxazole, venlafaxine, diclofenac, and ARVs the high removals are attributed to size exclusion and interaction with the surface membrane through electrostatic repulsion (Hollman et al., 2020). The negative removal of caffeine and 1.7 dimethylanxine can be attributed to various factors, such as matrix effects, membrane interaction, and sample mixing. Matrix effects result when the dissolved substances in the water tend to affect the compounds during the reverse osmosis process. Membrane interaction is a phenomenon where

compounds interact with the surface membrane, leading to their accumulation and desorption from the membrane surface, resulting in a higher concentration in the treated water.

However, the high removal rates demonstrated in this study coincide with those in other large-scale and pilot-scale studies that have investigated the removal of pharmaceutical compounds (PhACs) from secondary municipal effluent. A comparable study conducted by *Rodriguez-Mozaz et al., (2015)*, for PhACs in a RO pilot plant produced comparable removal results of 97% for trimethoprim, 97% for sulfamethoxazole, and 99% for carbamazepine.

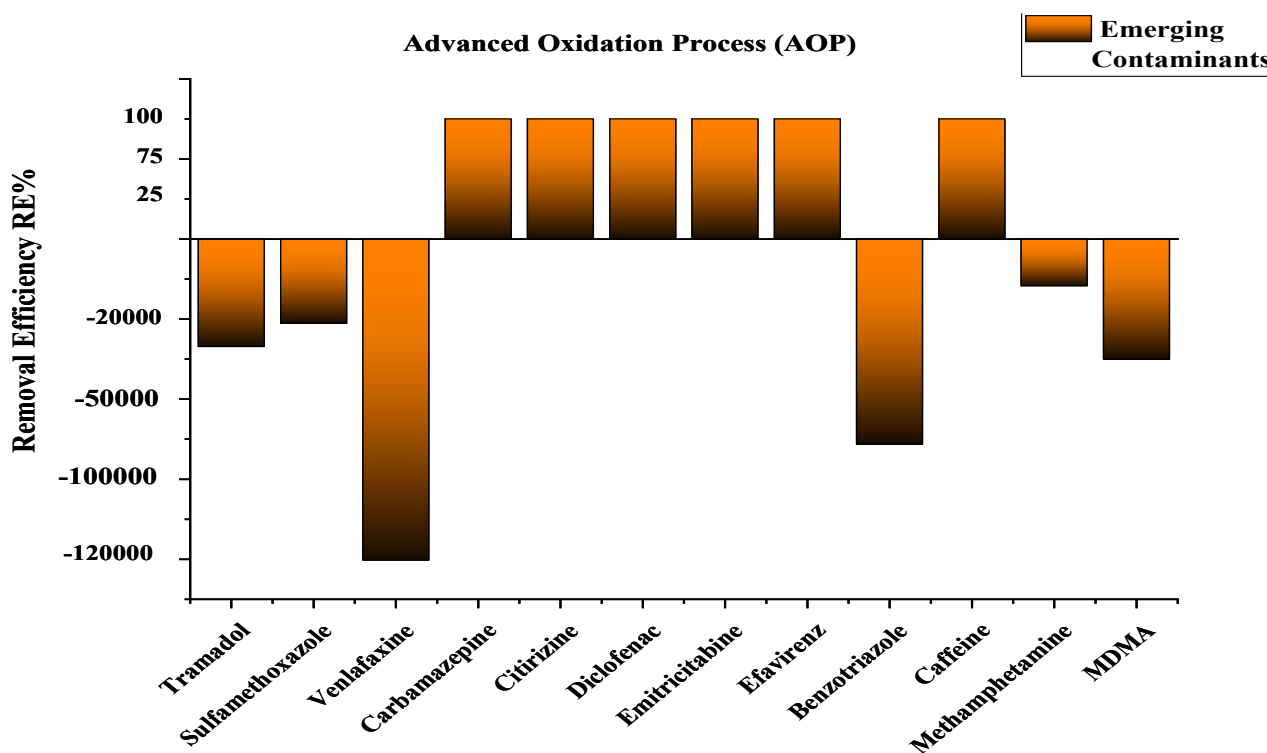


Figure 4.8 Advanced oxidation processes show the removal of emerging contaminants from the feed water

The reduction in concentration between the inlet and outlet of the Fenton advanced oxidation process was determined to be above 95% for emtricitabine, efavirenz, 1.7 dimethylxanthine, naproxen, cetirizine, and carbamazepine, except for measurable levels of benzotriazole, sulfamethoxazole, tramadol, and venlafaxine. The duplicate failed to give an accurate reading based on the internal standard used for these chemicals. This problem only occurred in this sample.

The anomalies in the four compounds could have been attributed to analytical artefacts, which are inaccuracies in sample collection, preparation, or analysis. Contaminant interactions can also be considered a factor that led to these misleading results. However, the removal rate of emerging contaminants above 95% is based on the reaction between hydrogen peroxide (H_2O_2) and ferrous iron (Fe^{2+}) catalyst to generate $\cdot\text{OH}$ radicals. $\cdot\text{OH}$ radicals are nonselective in their behaviour and rapidly react with numerous species with rate constants on the order of 10^8 – $10^{10} \text{ M}^{-1}\text{s}^{-1}$. Hydroxyl radicals attack organic pollutants through four basic pathways: radical addition, hydrogen abstraction, electron transfer, and radical combination (*Deng and Zhao, 2015*). The radicals attack the functional groups of the contaminants to products that are no longer detected at the initial levels.

The AOP indicates successful degradation of these emerging contaminants. In a related study, reported removal of efficiencies for different pharmaceuticals at different pH (7.5 - 8), the recorded average removal efficiencies for trimethoprim, diclofenac, sulfamethoxazole, were 80%, 85%, 65% respectively. The findings from this research coincides with this study findings illustrating that AOPs can effectively remove emerging contaminants.

In a related study, *Ghazal et al., (2022)*, reported removal efficiencies for different pharmaceuticals at different pH (7.5–8). The recorded average removal efficiencies for trimethoprim, diclofenac, and sulfamethoxazole were 80%, 85%, and 65%, respectively. The findings from this research coincide with those from this study, illustrating that AOPs can effectively remove emerging contaminants.

Table 4.4 Shows measured chemical water parameters and heavy metals in comparison with WHO and South African National Standards (SANS241-2015 Standards).

Parameter	Treatment Units along the Technology						WHO	SANS241 - 2015
	PST	MBR	BWRO	UF	SWRO	AOP		
	Influent	Effluent	Effluent	Effluent	Effluent	Effluent	Guideline Limit	GuidelinLimit
pH	7.02	7.34	6.55	7.34	6.33	7.11		5 to \leq 9.7
Temperature	27.54	27.52	27.50	27.5	27.50	27.69		
Conductivity	1101	814	24	821	2344	82		\leq 170
TDS (S)	0.718	0.53	0.015	0.533	0.533	0.054		\leq 1200
Ammonia (mg/L).	9.92	0	0	0.14	0	0		\leq 1.5

DO (mg/L).	0.26	2.70	2.5	2.5	3.0	3.0		
TON (mg/L).	0,2304	8,21	0,82	0.024	9,54	0,74		
Copper (µg/L).	32	< 5	<5	38	<1	<1	2000	≤ 2000
Arsenic	2	1	< 1	17	< 1	< 1		≤10
Lead (µg/L).	< 0.5	< 0.5	< 0.5	< 1	< 0.5	< 0.5	10	≤ 10
Mercury (µg/L).	< 1	< 1	< 1	< 2	<1	<1	6	≤ 6
Chromium (µg/L).	2	2	<1	3	< 0.5	< 0.5	50	≤50
Cadmium (µg/L).	<0.5	<0.5	<0.5	9.1	<0.5	<0.5	3	≤ 3

The acronyms of treatment units are, PST - primary settling tank; MBR - Membrane bioreactor; BWRO - Brackish water reverse osmosis; UF - Ultrafiltration; RRO - Remix reverse osmosis; AOP -Advance oxidation process.

4.4.1 PH

The pH level of the water in treatment units 6BV139 and 3BV362 is comparatively lower than that of other treatment units within the technology. It thereafter stayed nearly consistent, ranging from 7.02 to 7.34. pH has a general effect on EC clearance. For example, pH influences biological processes in MBRs, and maintaining an optimum pH range is critical for optimal microbial activity and treatment efficacy. The pH range for MBR systems is normally between 6.5 and 8.5; however, this might vary depending on the application. As a result, the pH of the feed water to the MBR was within the range observed in prior experiments where ECs were removed from the wastewater matrix. For RO processes, this is typically between 6.5 and 8.0, but this can vary depending on the membrane manufacturer's specifications. For RO operations, the pH is normally between 6.5 and 8.0; however, this might vary based on the membrane manufacturer's requirements. The pH of AOP is typically less than 7 to promote the formation of hydroxyl radicals. Hydroxyl radicals are commonly seen in acidic environments. As a result, the measured pH for AOP may have an effect on EC removal.

4.4.2 Temperature

The temperature of the water stayed nearly constant throughout the treatment technique, ranging from 27.50 to 27.69 degrees Celsius. Temperature has an effect on MBR effectiveness since various microorganisms have different optimum temperature ranges. Mesophilic bacteria, which are most typically employed in MBRs, function well at temperatures ranging from 20°C to 40°C. The optimal operating temperature for a RO membrane should be between 25 and 35 degrees Celsius. Temperature can influence the rejection or removal of dissolved salts by the RO membrane. Higher temperatures, in general, can result in lower salt rejection due to increased water flow and greater ion diffusion through the membrane. Temperature is a crucial parameter in AOP because it impacts the reaction kinetics in the formation of hydroxyl radicals, which then react with ECs to be removed. According to Taoufik *et al.*, (2020), the ideal temperature for AOP should be between 10 and 400°C for effective removal of micropollutants. As a result, the temperature measured for all feed waters was within the stipulated efficiency range.

4.4.3 Conductivity

Water conductivity measurement is an important parameter in monitoring and assessing water quality. The capacity of water to conduct an electric current is referred to as conductivity, and it is an indication of the presence and quantity of dissolved ions, salts, and other conductive compounds in water. The conductance of the wastewater influent to the MBR was initially recorded at a high level of 1101 μS , which subsequently decreased to 814 μS . The reduction in conductance may be attributed to biotic, abiotic, and membrane filtration processes. However, the effectiveness of filtration is more evident in the brackish reverse osmosis system, where the permeate water conductance was measured at 24 μS . The rejection of the brackish water reverse osmosis system is emphasised in the reject water or concentrate of the system. The high conductance observed in SWRO systems is typically attributed to the presence of seawater and a mixture of concentrate from BWRO processes. Conductivity measurements can offer significant insights into the effectiveness of reverse osmosis (RO) processes in eliminating such pollutants.

4.4.4 Heavy metal removal

This section reports heavy metal removal along the REMIX Water Treatment Plant (RWTP) treatment units. The acronyms of treatment units are PST - primary settling tank; MBR - Membrane bioreactor; BWRO - Brackish water reverse osmosis; UF - Ultrafiltration; RRO - Remix reverse osmosis; AOP -Advance oxidation process.

Table 4.5 Measured heavy metal concentration at various outlets of treatment units in RWTP.

Parameter	PST	MBR	BWRO	UF	RRO	AOP	WHO, (2004)
Copper ($\mu\text{g/L}$)	32	< 5	<5	38	<1	<1	1500
Arsenic ($\mu\text{g/L}$)	2	1	< 1	17	< 1	< 1	50
Lead ($\mu\text{g/L}$)	< 0.5	< 0.5	< 0.5	< 1	< 0.5	< 0.5	50
Mercury ($\mu\text{g/L}$)	< 1	< 1	< 1	< 2	<1	<1	1
Chromium ($\mu\text{g/L}$)	2	2	<1	3	< 0.5	< 0.5	50
Cadmium ($\mu\text{g/L}$)	<0.5	<0.5	<0.5	9.1	<0.5	<0.5	5

The concentration of heavy metals at various treatment steps in RWTP is shown in Table 4.5. The influent wastewater had a copper concentration of 32 $\mu\text{g/L}$ and concentrations of 2 $\mu\text{g/L}$ for chromium and arsenic. The concentrations of cadmium and lead were found minimum as 0.25

$\mu\text{g/L}$ and $0.3 \mu\text{g/L}$, respectively, compared to other heavy metals. The concentrations of heavy metals in the two influents of RWTP was efficiently removed in the treatment process. The concentration of arsenic and copper in seawater was higher than that observed in wastewater. This could be as a result of industrial activities or agricultural practices in kwaZulu Natal province where manufacturing, and smelting Industries have potential to release arsenic or copper based chemicals into the rivers, rivers then discharges these pollutants directly into the sea. Some farmers in agricultural practices in the province especially sugar cane use copper based herbicides (glyphosate) and pesticides (nordox) that can be washed off into the sea through rivers during rainy season (Mesquita et.al 2023). A 87.5% copper removal rate was attained in RWTP. Heavy metal removal efficiency exceeding 90% were observed in reverse osmosis systems (BWRO and RRO). The concentration of copper in the BWRO effluent decreased to below the stipulated guideline WHO limit of $50 \mu\text{g/L}$ in the outlet of final treatment step. Overall, the results show the combination of staged treatment units were adequate to remove heavy metals up to the acceptable limits advised by WHO, 2017).

4.5 Risk analysis of emerging contaminants

This section aims to report the level of human health risk for emerging contaminants that have been estimated in the final effluent of the REMIX demonstration plant. The risk quotient (RQ) is a measure used to assess the potential risk of a pollutant to human health. It is calculated by dividing the measured concentration by the estimated drinking water equivalent level of the emerging contaminant. In case of wastewater reuse systems, the human health risk assessment associated with produced drinking water is important. Human health risk evaluation was performed for emerging contaminants in the effluent of RWTP. For estimation of human health risk of ECs, risk quotient (RQ) was used based on the ratio of average daily intakes (ADIs) of targets ECs through reclaimed water and maximum therapeutic doses of respective ECs (Swartz et al., 2018).

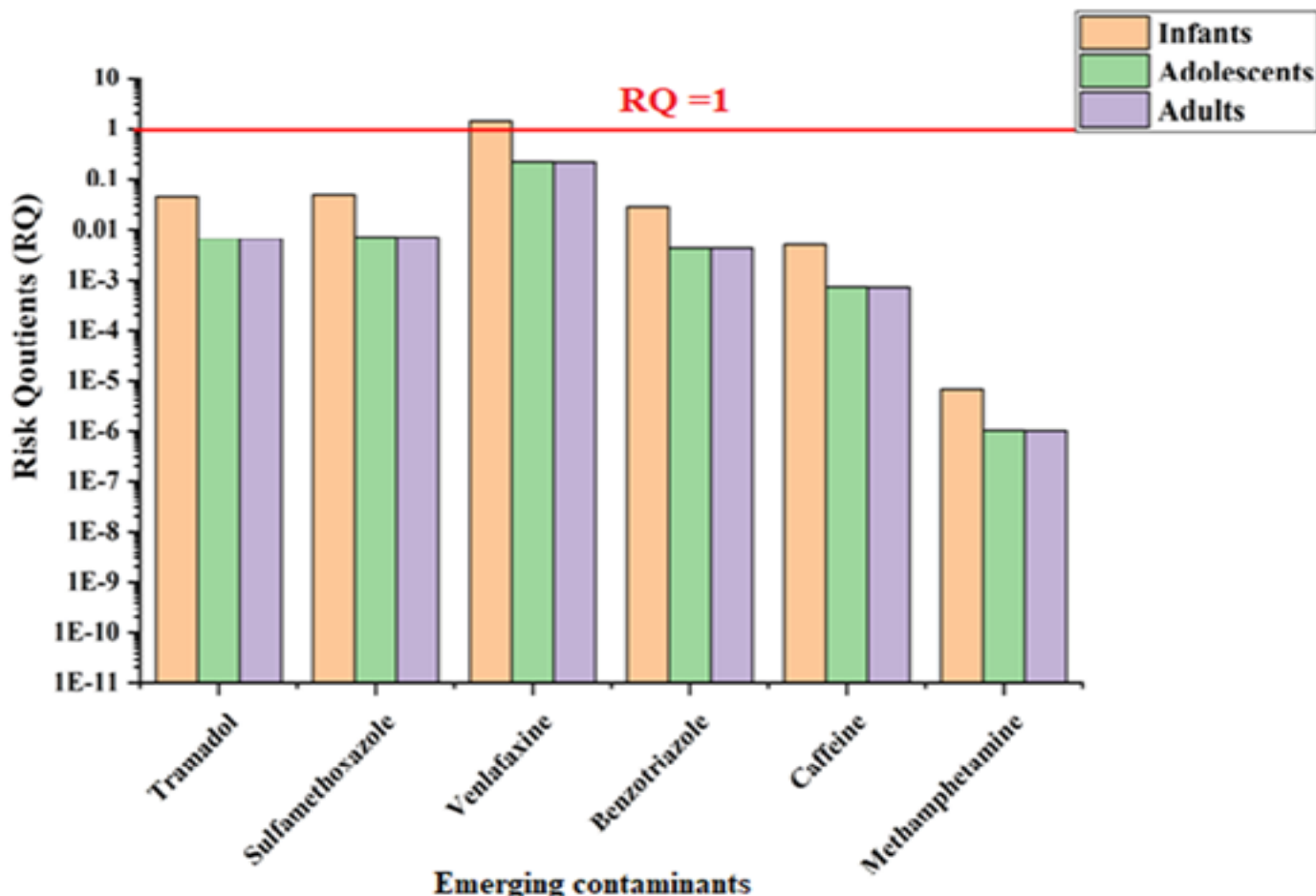


Figure 4.9 Deterministic risk assessment of the targeted emerging contaminants

The calculated values of DWEL and ADIs are shown in appendix A and calculated RQ of ECs is shown in Figure 4.10. Risk Quotient (RQ) values for the targeted emerging contaminants were below 1 showing negligible risk to human health when considered individually. The RQ value less than 1 depicts the efficiency of the RWTP in removal of ECs and thereby can be used as benchmark for the general information of the public for acceptance of reclaimed water. Reclaimed water is most often less accepted by consumers for the health risks associated with it (Gul et al., 2021). In absence of regulatory standards for ECs, the RQ can be used as an indicator to represent the safety of the drinking water produced from wastewater reuse technologies (Ranjan *et al.*, 2022). The anomaly recorded for venlafaxine was slightly above one, this anomaly is possibly attributed to matrix effects and ion suppression during sample analysis.

4.5.1 Human Health Risk Analysis for Heavy Metals

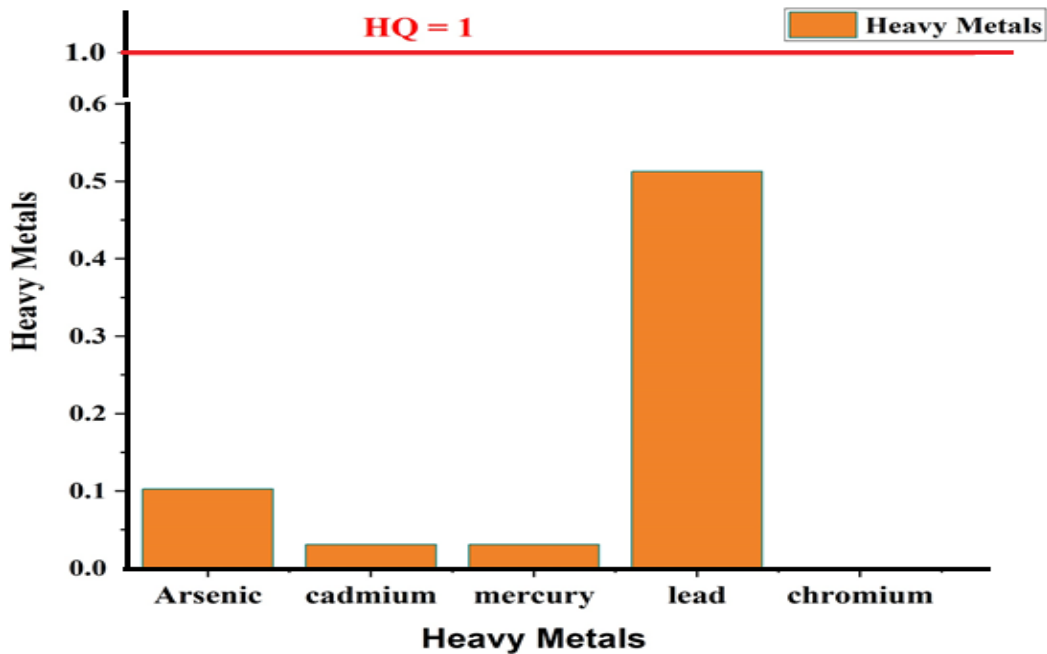


Figure 4.10 Estimated hazard quotients of heavy metals for young people weighing 15 kg with an assumed daily water intake of one litre.

The heavy metal contamination in the reclaimed water from wastewater can increase human health risks through ingestion. In the present work, non-carcinogenic and carcinogenic effects caused by oral ingestion were explored. The HQ values of heavy metals which were 0.1, 0.03, 0.03, 0.51, and 1.02×10^{-5} for arsenic, cadmium, mercury, lead, and chromium, respectively (figure 4.11).

The calculated values of unknowns for calculating HQ and reference dosages of heavy metals are mentioned in appendix B, All the investigated heavy metal HQs were below the threshold limit, with lead having the highest, followed by arsenic. From the total computation of the heavy metals, it can be concluded that there is a negligible non-carcinogenic risk to the consumers using reclaimed water from RWTP.

Heavy metals such as lead, chromium, and arsenic possess the potential to elevate the carcinogenic risk in human populations. Prolonged exposure to trace amounts of these toxic metals may

consequently engender a heightened susceptibility to various forms of cancer (*Mahommadi, et.al. 2019*). This study evaluated the cumulative exposure of lead, chromium, and arsenic due to produced drinking water, treating them as carcinogenic agents. This assessment was carried out through the calculation of chronic daily intake (CDI) values for each heavy metal appendix B.

Table 4.6 ILCR estimates of heavy metals based on their concentration in the reclaimed water from the wastewater and sea water.

Metals	CDI	Cancer slope factor*	ILCR
Arsenic	3.08×10^{-5}	1.5	0.0000462
Cadmium	1.54×10^{-5}	6.2	0.00009548
Lead	15.4×10^{-5}	0.0085	0.000001309
Chromium	3.08×10^{-5}	0.5	0.00000154

* *USEPA, 2016*

The incremental cancer risk was also calculated for lead, cadmium, arsenic, and mercury (Table 4) while copper was considered non-human carcinogen. Lead, cadmium, arsenic, and mercury have the potential to cause either or both acute and chronic toxicity in humans. The ILCR for arsenic is 0.0000462 this means that for every unit of exposure to arsenic at this concentration in the drinking water, there is an estimated additional cancer risk of 0.0000462 or approximately 0.00462% over a person's lifetime. For cadmium, lead, chromium ILCR was as follows: 0.00009548, 0.000001309, 0.0012936 respectively showing negligible cancer risk of people consuming the reclaimed water in their lifetime in comparison with the standard proposed the thresholds of 10^{-4} to 10^{-6} for an independent carcinogenic element (*Mohammadi et al., 2019*). An ILCR exceeding 1×10^{-4} is classified as detrimental, signifying a noteworthy cancer risk that warrants concern (*Mahommadi, et.al.2019*). Conversely, an ILCR lower than 1×10^{-6} is deemed negligible, allowing the cancer risk to be disregarded. Among heavy metals under investigation,

the ILCR for arsenic, cadmium lead and chromium were 4.62×10^{-5} , 9.5×10^{-5} , and 1.3×10^{-6} 1.54×10^{-6} respectively implying that there is minimal cancer risk to humans consuming reclaimed water over their lifetime. The findings of this research underscore the potential of RWTP to produce safe water for human consumption.

4.6 Hazard Analysis and Identification of Critical Control Points (HACCP)

Conducting was risk assessment is a necessary step in the entire technology process of the RWTP. HACCP involves the identification of potential risks, followed by an assessment of their significance and the controls in place within the system to systematically manage those risks. This process begins with the membrane biological treatment (secondary treatment unit) of the wastewater treatment system, it then extends to the seawater intake, and concludes with the final treatment unit process of the RWTP technology. At every stage of the process, the potential risks to water quality were assessed, and corresponding measures were implemented to prevent any hazards from contaminating the water. The Codex principles are used utilised to identify potential hazards to water quality and corresponding controls to prevent their entry into the water at each stage of the process. Figure 4.11 illustrates the Codex conceptual approach to the RWTP.

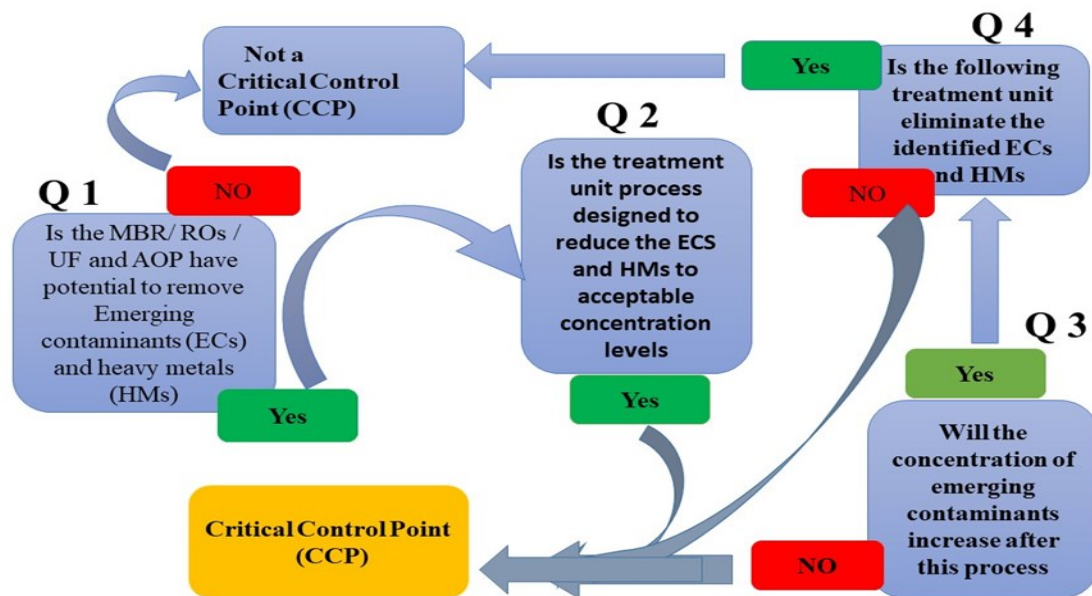


Figure 4.11 Codex Alimentarius principles for identifying critical control points in HAACP System (Tsoukalas and Tsitsifli, 2018).

Table 4.7 Application of critical control points decision tree for the REMIX water treatment plant

Process Step	Hazard	Q1*	Q2*	Q3*	Q4*	Q5*
Membrane biological reactor (MBR)	Emerging contaminants and Heavy metals	Yes	No	Yes	Yes	No
Brackish Reverse Osmosis (BWRO)	Emerging contaminants and Heavy metals	Yes	Yes	Yes	No	Yes
Ultrafiltration filter (UF)	Emerging contaminants and Heavy metals	Yes	No	Yes	Yes	No
REMIX Tank	Emerging contaminants and Heavy metals	No	No	No	No	No
Seawater Reverse Osmosis (SWRO)	Emerging contaminants and Heavy metals	Yes	Yes	Yes	Yes	Yes
Advanced Oxidation Process (AOP)	Emerging contaminants and Heavy metals	Yes	No	Yes	No	Yes

Q1: Are there some preventive measures for the recognition hazard?*

Q2: Is the step specifically planned to eliminate or reduce the likely happening of the hazard to an acceptable level?*

Q3*: Could contamination take place or increase to unacceptable levels?

Q4*: Will a subsequent step or action delete or reduce the hazard to an acceptable level?

Q5*: Critical Control Points

Table 4.7 illustrates an implementation of the CCP decision tree based on the Codex principles from wastewater, seawater and up to the last treatment unit of the RWTP. The utilisation of preparatory measures and HACCP principles has led to the development of a HACCP plan, which is delineated in Table 4.8 below. The HACCP plan comprises the treatment process steps: identification of hazards, implementation of preventive measures, determination of critical control points, establishment of a monitoring system, specification of critical limits for monitoring parameters at CCPs, and definition of requisite corrective actions.

Table 4.8 Hazard Identification and critical control points plan for the REMIX water treatment for potable reuse.

Process step	CCP	Hazards	Preventive measures	CCP Parameters/limits	Monitoring Procedures	Corrective Action
Membrane Biological Reactor (MBR)	CCP1	Biological membrane fouling, membrane degradation, Toxic shock, and Nutrient imbalance to organism's ratio.	Prevent excessive loading. Conduct regular maintenance of the system. Properly control the HRT by optimizing the flow rates and volumes of wastewater	Flux rate - (10-20 L/m ² /hr.) (Transmembrane pressure (TMP)- (0.1-0.5 bars) SRTs ≥ 20 HRT - (4-6) Food/microorganisms ratio (F/M) < 0.2	Mixed liquor suspended solids (MLSS) should be frequently monitored. Transmembrane pressure should be monitored across the membranes. BOD should be frequently evaluated since it is an indicator of efficiency	Clean the membrane. Conduct timed backwashing. Replace the damaged reaction and correct the feed water transmembrane water pressure.
Brackish Water Reverse Osmosis (BWRO)	CCP2	High concentration of salt, organic and inorganic compounds causing clogging/fouling	Regular check of the RO system for any leaks or damage in the pipes, fittings, and membranes. Regularly clean and replace filters the membrane. Ensuring proper sanitisation of the RO system to avoid bacterial growth. Check to ensure that the pressure is within the required range. Conduct regular water testing to ensure that the RO is producing high-quality water.	Chlorine (0.1 ppm) Turbidity (1NTU) TDS < 2000 ppm Feed pressure (30-69 bars). pH (3-11)	Frequent chemical analysis (TDS, COD, Nitrates, Heavy metals and identified persisting emerging contaminants such as ARVDS and illicit drugs Monitor the flow rate of the system to ensure if it is producing the expected amount of water	Modification and Replacing of the filter membrane. Ensure that the RO membrane is in good condition and has not been degraded. Use a food-grade sanitizer to clean the system.

Ultrafiltration (UF)	CCP3	Fouling, Scaling, Fluctuating feed water chemistry (pH, Temperature) impacts membrane filtration efficiency. Physical and chemical degradation of filter membranes.	Chemical treatment can help to prevent fouling of the membrane. Regular backwashing of the ultrafiltration system can help to remove any particulate matter that may have accumulated on the membrane surface. Proper training of personnel operating the system can help to prevent mechanical damage and ensure that the system operates efficiently.	pH (6-8.5) Flux rate (400-800) Recovery rate (70-95%) Pressure (14.5 - 1.45 psi). MWCO (1 to 100 kDa)	At all times ensure that proper pre-treatment, including filtration, softening, and pH adjustment is always done correctly. Install Automated control systems that monitor and control permeate flow rate, feed water flow rate, pressure drop, and other parameters.	Clean the membranes and do timed backwash during the operation. Ensure the transmembrane pressure is always at optimum. Check the system components. Ensure that all system components such as pumps, valves and instruments are working properly. Increase the cleaning frequency. Replacing and modifying membrane under the manufacturer's guidance.
Seawater Reverse Osmosis (SWRO)	CCP4	High concentration of salt, organic and inorganic compounds causing clogging/fouling	Regular check of the RO system for any leaks or damage in the pipes, fittings, and membranes. Regularly clean and replace filters the membrane. Ensuring proper sanitisation of the RO system to avoid bacterial growth. Check to ensure that the pressure is within the required range. Conduct regular water testing to ensure that the	Chlorine (0.1 ppm) Turbidity (1NTU) TDS < 2000 ppm Feed pressure (30-69 bars). pH (3-11)	Frequent chemical analysis (TDS, COD, Nitrates, Heavy metals and identified persisting emerging contaminants such as ARVDS and illicit drugs Monitor the flow rate of the system to ensure if it is producing the expected amount of water	Modification and Replacing of the filter membrane. Ensure that the RO membrane is in good condition and has not been degraded. Use a food grade sanitizer to clean the system

			RO is producing high quality water			
Advanced Oxidation Process (AOP)	CCP5	Catalyst deactivation, UV lamp fouling, Access, by product formation, Scaling	Avoid overuse of AOP: Overuse of AOP can lead to complexity, difficulty in debugging and a decrease in performance. The aspect-oriented design of the system by the manufacturer should always be followed. Regular maintenance of AOP code is important to keep it efficient and bug	pH (2-6) Temperature (10-40 °C)	The residence time should be sufficient to ensure that the oxidants have enough time to react with the impurities in the water. The intensity of the UV light used in the AOP process should be monitored to ensure that it is within the recommended range.	Dosage Control of reactants and catalyst should be carefully controlled to ensure the effective remove of contaminants. Optimum pH Control should be done regularly. Product monitoring. The intermediate reactive species needs to be monitored not to create harmful byproducts that may react with other compounds in the water

4.6.1 Discussion of the HACCP System

The critical control points (CCPs) that have been identified as most significant are the membrane biological reactor, brackish reverse osmosis and ultrafiltration, seawater desalination, and advanced oxidation processes. Membrane biological reactor is critical in producing high quality feed water for reverse osmosis reducing fouling which can be a major drawback of the subsequent process (brackish reverse Osmosis). Reverse osmosis systems are known to have exceptional removal efficiencies in eliminating emerging polar and non-polar contaminants, viruses, heavy metals, and nutrient. The removal efficiency of reverse osmosis for emerging contaminants, as highlighted by *Swartz et al., (2018)*, ranges from 96% to 99%, which is excellent removal and it coincides with the findings in this study.

According to the analysis results, advanced oxidation processes exhibit the capacity to oxidise a wide variety of products. Hence, it is probable that any compound capable of bypassing the barrier membrane will be eliminated. The study demonstrates a noteworthy decrease in physical, biological, and chemical hazards during the treatment procedure. The effectiveness of reverse osmosis (RO) in eliminating contaminants from brackish and seawater Plant operators and managers have highlighted significant challenges in the filtration system of the RWTP. The issue of membrane fouling poses a significant challenge in MBR and RO systems, as it diminishes the efficacy of reclaimed water production and leads to increased plant downtime. Plant operators and managers have highlighted significant challenges in the filtration system of the RWTP. The issue of membrane fouling poses a significant challenge in MBR and RO systems, as it diminishes the efficacy of reclaimed water production and leads to increased plant downtime. Managing membrane fouling is a critical concern in the functioning of a membrane bioreactor (MBR). The fouling of membranes is considerably impacted by various factors such as hydrodynamic conditions, membrane type, and module configuration.

Additionally, the presence of higher-molecular-weight compounds, which may be generated by microbial metabolism or introduced during the sludge bulking process (e.g., polyelectrolytes), can also play a significant role. The proper monitoring and regular evaluation of the MBR are considered crucial for enhancing subsequent process efficiency. Therefore, it is imperative to closely monitor the parameters outlined in the HACCP plan. The successful completion of this task necessitates the provision of adequate skills and training to operators and managers.

The HACCP plan that has been developed may serve as an additional system for the REMIX Water Treatment Plant (RWTP) if the plant decides to adopt it as an operational system. According to *Damikouka et al., (2007)*, the development of a Hazard Analysis and Critical Control Points (HACCP) plan can identify potential areas for system improvement and increased efficiency. Hence, the implementation of appropriate and effective corrective measures for each Critical Control Point (CCP) to regulate and mitigate any potential hazards in every process unit is of utmost importance for the REMIX Water Treatment Plant (RWTP).

CHAPTER 5: CONCLUSION

The objective of this chapter is to provide a concise overview of the outcomes and consequences of investigating the removal of emerging contaminants, heavy metals, and water physiochemical parameters through the REMIX Water treatment procedure. This section concluded the findings of prioritisation and the HACCP system, very crucial steps in risk assessment for efficient production of water. It is important to acknowledge that this study was constrained to a single sampling occurrence throughout the complete treatment train technology as a result of an unmanageable shutdown beyond the researchers control.

The following are the conclusions drawn from this study:

- The concentration of emerging contaminants in wastewater is higher than that in seawater, with the exception of antiretroviral drugs. This is due to the widespread use of ARV drugs in the city, and numerous studies have reported elevated levels of these contaminants in both influents and effluents of wastewater treatment plants.
- The MBR effectively eliminated certain emerging contaminants, while others exhibited persistence under both biotic and abiotic MBR processes. The implementation of MBR as a pre-treatment technique for reverse osmosis has been found to be highly efficacious in mitigating fouling. The reverse osmosis system exhibited exceptional elimination efficiencies for all the contaminants assessed in this investigation. The mean elimination rate for emerging contaminants was found to be within the range of 97–99%. The observed trend is in line with the expected performance of reverse osmosis systems, which are recognised as highly effective unit processes for the elimination of heavy metals and emerging contaminants. The advanced oxidation process demonstrated effective elimination of the majority of emerging contaminants, with the exception of anomalous irregularities resulting from matrix effects and ion suppression during sample analysis.

A total of 20 compounds were subjected to a consensus approach utilising the OPBT criteria and QSARINS methodologies, resulting in the prioritisation of 4 compounds. These compounds will be closely monitored and evaluated to assess the technology's efficiency and performance. In addition, the originality of the study lies in the proposition of an alternative approach for the screening and prioritising of emerging contaminants in South Africa which eliminates the need for

in-vivo tests and experiments involving animals. For this objective, two criteria have been identified. The experimental evidence reveals that the REMIX Water Treatment Plant's barriers eliminated the targeted emerging pollutants with impressive efficacy and consistency.

The heavy metals and nutrients were successfully extracted, and their levels were found to be within the threshold limits set by WHO and SANS241-2015.

- For the average population of 65 kg, the risk and hazard quotients were below one, indicating a reasonable margin of safety for both heavy metals and emerging pollutants. Accordingly, the recovered water was deemed safe in terms of ongoing exposure to the study's targeted contaminants based on the findings of the human health impact assessment.
- Out of the seven treatment unit phases, five were chosen as the most crucial control points for the effective removal of emerging contaminants. Because of recent illness outbreaks in wealthy nations using traditional approaches, the HACCP system is now widely used. Understanding the risks associated with the RWTP process was the main goal of HACCP (Hazard Analysis and Critical Control Points), which was designed to ensure that more attention would be paid to these unit processes and that they would always be operating at their peak efficiency for the effective production of high-quality drinking water.

Overall, the Remix Water treatment plant proved to have the capacity to successfully remove chemicals based on their occurrence, persistence, bioaccumulation, and toxicity behaviour. Except for some anomalies incurred during sample analysis attributed to ion suppression and enhancement, the one sample event highlights the reduction in nutrients, heavy metals, and other contaminants along the multi-barrier treatment train, which was expected for such a sophisticated water treatment system.

CHAPTER 6: RECOMMENDATIONS

6.1 Introduction

The present chapter presents recommendations that provide guidance and suggestions to the stakeholders of the REMIX Water Treatment Plant under the eThekweni Municipality based on the research findings. This section holds significant importance as it facilitates the operators, plant managers, and decision-makers in identifying emerging contaminants and heavy metals and their potential impact on human health. It also guides the improvement and monitoring of treatment units to make informed decisions based on the relevant options available for the REMIX Water Treatment Plant.

The following are the recommendations proposed in this study:

- A further inquiry is required to assess the efficacy of the REMIX Water Treatment Plant (RWTP) in eliminating emerging contaminants, taking into account the seasonal fluctuations in wastewater. A minimum of three sampling events is recommended.
- The personnel responsible for designing, operating, and managing schemes must possess adequate skills and training. Adequate and relevant expertise and competencies are required for all individuals engaged in the planning, administration, execution, and evaluation of reclaimed water infrastructure. The treatment process's overall operation necessitates supervision by managers possessing adequate engineering and quality assurance expertise.
- All schemes shall be subjected to regulatory monitoring. It is imperative to implement autonomous regulatory monitoring and auditing protocols for the enhancement of potable water with the active participation of public health organisations. The implementation of surveillance and auditing procedures ensures that recycled water systems are managed and operated in compliance with high standards while also safeguarding public health.

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APPENDICES

Appendix A: Drinking water equivalent level for emerging contaminants

Compounds	Average daily Intake (ADI)	ADI Reference	Infants	Adolescents	Adults
Acetaminophen	3100	(Shafi et al., 2023)	15095,6522	99830,50847	100750
Tramadol	7100	(Shafi et al., 2023)	34573,913	228644,0678	230750
Codeine	350000	(Shafi et al., 2023)	1704347,83	11271186,44	11375000
Sulfamethoxazole	3800	(Shafi et al., 2023)	18504,3478	122372,8814	123500
Trimethoprim	4200	(Shafi et al., 2023)	20452,1739	135254,2373	136500
Venlafaxine	7100	(Shafi et al., 2023)	34573,913	228644,0678	230750
Carbamazepine	2900	(Shafi et al., 2023)	14121,7391	93389,83051	94250
Cetirizine	71	(Shafi et al., 2023)	345,73913	2286,440678	2307,5
Naproxen	7100	(Shafi et al., 2023)	34573,913	228644,0678	230750
Diclofenac	1400	(Shafi et al., 2023)	6817,3913	45084,74576	45500
Emtricitabine	200000	(Swartz et al., 2018)	973913,043	6440677,966	6500000
Efavirenz	600000	(Swartz et al., 2018)	2921739,13	19322033,9	19500000
Benzotriazole	295000	(Shafi et al., 2023)	1436521,74	9500000	9587500
Atrazine	30000	(Swartz et al., 2018)	146086,957	38644,0678	975000
1.7	15000	(Swartz et al., 2018)	73043,4783	966101,6949	487500
Dimethylxanthine					
Caffeine	180000	(Swartz et al., 2018)	876521,739	483050,8475	5850000
Methamphetamine	250000	(Swartz et al., 2018)	1217391,3	5796610,169	8125000
MDMA	300000	(Swartz et al., 2018)	1460869,57	8050847,458	9750000
Methaqualone	300000	(Swartz et al., 2018)	1460869,57	9661016,949	9750000
Cocaine	300000	(Swartz et al., 2018)	1460869,57	9661016,949	9750000
Benzoyllecgonine	300000	(Swartz et al., 2018)	1460869,57	9661016,949	9750000

Appendix B: Human health Risk Assessment

Chronic daily water intake and Hazard Quotients

7PG-801	IR	EF	ED	BW	AT	CDI	Reference dose	HQs
0.001	2	365	30	65	10950	3.07692E-05	0.0003	0.102564
0.0005	2	365	30	65	10950	1.53846E-05	0.0005	0.030769
0.001	2	365	30	65	10950	3.07692E-05	0.001	0.030769
0.005	2	365	30	65	10950	0.000153846	0.0003	0.512821
0.001	2	365	30	65	10950	3.07692E-05	3	1.03E-05

Incremental life time cancer risk estimates for heavy metals based on their concentration in the reclaimed water from the wastewater and sea water.

Metals	CDI	Cancer slope factor*	ILCR
Arsenic	3.08×10^{-5}	1.5	0.0000462
Cadmium	1.54×10^{-5}	6.2	0.00009548
Lead	15.4×10^{-5}	0.0085	0.000001309
Chromium	3.08×10^{-5}	0.5	0.00000154

* USEPA, 2016