

Environmental Health Risk Assessment of Potential Emerging Contaminants Identified from Water Sources around Bloemfontein in the Free State Province of South Africa

Innocent Mugudamani

Thesis submitted in fulfilment of the requirements for the degree

**DOCTOR OF PHILOSOPHY:
ENVIRONMENTAL HEALTH**

in the

Department of Life Sciences
Faculty of Health and Environmental Sciences

at the

Central University of Technology, Free State

Promoter: Prof SA Oke
Co-promoter: Dr TP Gumede

BLOEMFONTEIN
July 2024

DECLARATION

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

SIGNATURE OF THE STUDENT

July 2024

DATE

ABSTRACT

Background: The existence of emerging contaminants namely pharmaceuticals, personal care products, steroids hormones and pesticides in water sources is largely unregulated by legislation and they do not have to be extremely tenacious to cause environmental health effects as their decay is counterbalanced by their incessant introduction. The accumulation and detection of levels of these emerging contaminants in water sources has reduced water quality that makes water risky for aquatic and human life. Their quantity is likely to upsurge in water sources as a result of the rise in population density, which is a serious concern to our communities. Exposure to emerging contaminants has been reported to lead to health implications such as endocrine disruption, immunotoxicity, neurological disorders, reductions in fertility, spontaneous abortions, birth defects, poisoning of genes, sexual organs annoyance, resistance of antibiotics and congenital disorders, even at low concentrations.

Aim: The aim of this study was to assess the environmental and health risks of potential emerging contaminants identified from water sources around Bloemfontein in the Free State province of South Africa.

Methodology: In order to identify and monitor the presence of emerging contaminants in water sources around Bloemfontein, samples ($n=72$) were collected randomly by using the grab sampling method from various water sources such as rivers ($n=5$), dams ($n=5$), treated drinking water ($n=2$), wastewater influent ($n=3$) and wastewater effluent ($n=3$) during the spring, summer, autumn and winter seasons. The solid phase extraction cartridges were used for extraction of samples. The analysis was performed on a high performance liquid chromatography linked to a hybrid triple quadrupole ion trap mass spectrometer. Environmental risk assessment of individual compounds were estimated by a risk quotient (RQ) method, while risk quotient mixture (RQmix) and toxic unit sum (TUsum) methods were adopted to assess mixture risks of targeted emerging contaminants. The human health risk assessment method was adopted to estimate the carcinogenic and non-carcinogenic risks of selected pesticides. Moreover, multivariate statistical methods such as the Pearson coefficient correlation, the principal component analysis, and the hierarchical cluster analysis were used to trace the sources of pollution in water sources around Bloemfontein.

Results: The results of qualitative screening revealed the occurrence of various classes of emerging contaminants such as stimulants, non-steroidal anti-inflammatory drugs, Illicit drugs, lipid regulators, antiepileptics, antibiotics, antidepresents, antidiabetics, betablockers,

antivirals, diuretics, herbicides, fungicides and insecticides in rivers, dams, treated drinking water, wastewater influents and effluents around Bloemfontein. From these groups of emerging contaminants, herbicides and stimulants were the most commonly detected contaminants. The quantitative analysis of targeted compounds such as acetaminophen, carbamazepine, ibuprofen, triclosan, atrazine, metolachlor, simazine, terbutylazine, 17-alpha-ethinyl-estradiol, estradiol, progesterone and testosterone showed the mean concentrations of 17-alpha-ethinyl-estradiol to be the highest in all water sources in all seasons. Generally, the autumn season recorded the highest mean concentrations of emerging contaminants in all selected water sources except in treated drinking water. The results of the environmental risk assessment indicated that the majority of targeted compounds have the possibility to contribute to high risks. The risks of simazine, ibuprofen, 17-alpha-ethinyl-estradiol, atrazine and carbamazepine were most remarkable on all aquatic species in all water sources. Moreover, both RQmix and TUsum proved that the mixture of the targeted compounds is likely to contribute to high environmental risks. In addition, the non-carcinogenic risks of all selected herbicides in all water sources showed RQ values below one for the entire population, signifying that the population is safe. Atrazine is the only contaminant that showed high carcinogenic risk to the adult group in river water during the summer season. Multivariate statistical analysis pinpointed wastewater effluent discharge, illegal dumping, domestic sewage overflow, stormwater runoff and agricultural runoff as the possible sources of emerging contaminants in water sources around Bloemfontein.

Conclusion: Assessing the environmental health risks of emerging contaminants in water sources around Bloemfontein for the first time brings to an end the dearth of data on emerging contaminant pollution and its associated risk in the region. The project has shed light that water sources around Bloemfontein are vulnerable to pollution by emerging contaminants as a result of anthropogenic activities and their occurrence is likely to cause high ecological and human health risks. The outcomes of this study may be relevant for the prioritisation of hazardous substances in addressing suitable monitoring campaigns and any necessary countermeasures to be adopted for water sustainability, environmental and human health protection. This work may also facilitate the management of existing and future sources of emerging contaminant pollution in water sources around Bloemfontein.

Keywords: Emerging contaminants, environmental health, environmental risk, human health risk, pesticides, risk assessment, source apportionment, water sources

DEDICATION

This work is dedicated to my Lord and Saviour Jesus Christ who is the pioneer of this work, and giver of my life, strength, astuteness, and discernment. To Him be the glory.



ACKNOWLEDGEMENT

My sincere appreciation goes to Prof Saheed Adeyinka Oke for giving me the opportunity to be part of Water Research Commission Project (No. 2022/20240789) under his supervision. His inimitable way of mentoring, encouragement, useful suggestions, unceasing support and tolerance have kept me motivated during the course of my doctoral journey. I will forever be appreciative.

I would like to express my deepest gratitude to my co-supervisor, Dr Thandi Patricia Gumede, for all her efforts to see me being successful, her invaluable encouragement, positive reproach, clarifications, guidance, critical discussions and forever insisting on the highest level of quality and integrity to make this project a success.

Special acknowledgements are extended to Dr Samson Senbore, for his unceasing support and encouragement throughout my studies. I appreciate Dr Gabre Kemp from the Department of Microbiology and Biochemistry at the University of Free State, for his assistance with laboratory work. I thank Mr Jaco Swart for sharing his statistical knowledge and skills, and Mr Phaṭhutshedzo Ntshifhefhe, for his GIS insights.

Thanks to the Central University of Technology for the postgraduate grant (GLA 39628) and the Water Research Commission, South Africa (Project number 2022/20240777), for their monetary provision that assisted me in achieving this magnificent project. Without their monetary provisions, this work would be impossible.

Finally, a vote of thanks goes to my treasured family for their words of inspiration, steadfast love, care and prayers.

TABLE OF CONTENTS

DECLARATION.....	ii
ABSTRACT	iii
DEDICATION.....	v
ACKNOWLEDGEMENT	vi
TABLE OF CONTENTS	vii
LIST OF FIGURES	xiv
LIST OF TABLES.....	xvi
ABBREVIATIONS AND ACRONYMS	xix
LIST OF MEASUREMENTS	xxi
CONCEPTUAL DEFINITIONS.....	xxii
CONTRIBUTION OF THE STUDY.....	xxvi
Chapter 1	
INTRODUCTION	1
1.1 Background of the study	1
1.2 Problem statement.....	3
1.3 Aim and objectives.....	3
1.4 Research hypothesis	4
1.5 Research questions	4
1.6 Justification and significance of the study	4
1.7 Scope of the study	5
1.8 Limitation of the study	6
1.9 Thesis outline.....	6
Chapter 2	
OVERVIEW OF EMERGING CONTAMINANTS IN WATER SOURCES: A GLOBAL OUTLOOK.....	8
Abstract.....	8
2.1 Introduction.....	9
2.1.1 Water sources	10
2.1.1.1 Surface water as a water source.....	11
2.1.1.2 Groundwater as a water source.....	11
2.1.1.3 Wastewater as a water source.....	12
2.2 Methodology	13
2.3 Results and discussion	13
2.3.1 Emerging contaminants	13

2.3.1.1	Herbicides	14
2.3.1.2	Pharmaceuticals	15
2.3.1.3	Personal care products.....	15
2.3.1.4	Steroid hormones	16
2.3.1.5	Flame retardants	16
2.3.1.6	Illicit drugs and non-controlled drugs	17
2.3.1.7	Food additives	18
2.3.1.8	Nanomaterials	18
2.3.2	Sources and pathways of emerging contaminants.....	19
2.3.2.1	Point source of emerging contaminants.....	20
2.3.2.2	Non-point source of emerging contaminants.....	21
2.3.3	Emerging contaminants in water sources	22
2.3.4	Case studies: Global perspective	22
2.3.4.1	Pharmaceuticals and personal care products in surface water, groundwater and drinking water.....	22
2.3.4.2	Pharmaceuticals and personal care products in wastewater influent and effluent.....	48
2.3.4.3	Herbicides in surface water, groundwater and drinking water	58
2.3.4.4	Herbicides in wastewater influent and effluent.....	63
2.3.4.5	Steroid hormones in surface water, groundwater and drinking water	63
2.3.4.6	Steroid hormones in wastewater influent and effluent	65
2.3.5	Case studies: South African perspective	65
2.3.5.1	Pharmaceuticals and personal care products in surface water, groundwater and drinking water.....	66
2.3.5.2	Pharmaceuticals and personal care products in wastewater influent and effluent.....	73
2.3.5.3	Herbicides in surface water, groundwater and drinking water	80
2.3.5.4	Herbicides in wastewater influent and effluent.....	83
2.3.5.5	Steroid hormones in surface water, groundwater and drinking water	83
2.3.5.6	Steroid hormones in wastewater influent and effluent	84
2.3.6	Analytical procedure for detection of emerging contaminants	84
2.3.6.1	Sample preparation and extraction process.....	85
2.3.6.2	Chromatography analysis	86
2.3.6.3	Detection systems	86
2.3.6.4	Ionisation sources.....	87
2.3.7	Other analytical techniques	87

2.3.7.1	Capillary electrophoresis technique	87
2.3.7.2	Bio-analytical techniques	88
2.3.8	Removal mechanisms and advance treatment of emerging contaminants in water sources	88
2.3.8.1	Removal mechanism	88
2.3.8.2	Biodegradation	88
2.3.8.3	Sorption	89
2.3.8.4	Photolysis	89
2.3.8.5	Volatilisation	90
2.3.9	Advance treatment of emerging contaminants in water sources	90
2.3.9.1	Pressure-driven membrane filtration	90
2.3.9.2	Direct oxidation	91
2.3.9.3	Sand filtration.....	91
2.3.9.4	Activated carbon.....	91
2.3.10	Environmental health impacts of emerging contaminants	92
2.3.11	Mitigation of risks associated with emerging contaminants	93
2.4	Conclusion.....	94
2.5	Recommendation.....	94
Chapter 3		
DESCRIPTION OF THE STUDY AREA: BLOEMFONTEIN		95
3.1	Study location	95
3.2	Environmental attributes	97
3.2.1	Climate	97
3.2.2	Geology and soil.....	97
3.2.3	Topography	99
3.2.4	Land use	99
3.2.5	Water resources	100
3.2.5.1	Surface water	100
3.2.5.2	Groundwater	100
3.2.5.3	Treated drinking water	101
3.2.5.4	Wastewater treatment.....	101
3.3	Socio-economic status.....	101
3.3.1	Population	101
3.3.2	Municipal economy	103
3.3.3	Health care system.....	104
3.3.4	Housing and development	104
3.3.5	Water supply and sanitation	105

3.3.6	Waste management	105
Chapter 4		
METHODOLOGY		107
4.1	Sample collection and handling.....	107
4.1.1	Collection of river samples.....	110
4.1.1.1	Renosterspruit	110
4.1.1.2	Bloemspruit	110
4.1.1.3	Koringspruit	110
4.1.1.4	Modder River (Lekatlong)	110
4.1.1.5	Klein Modder River	111
4.1.2	Collections of dam samples.....	111
4.1.2.1	Maselspoort Dam	111
4.1.2.2	Mockes Dam.....	111
4.1.2.3	Krugersdrift Dam	111
4.1.2.4	Seroalo Dam.....	112
4.1.2.5	Rustfontein Dam.....	112
4.1.3	Collection of treated drinking water.....	112
4.1.3.1	Rustfontein water treatment plant	112
4.1.3.2	Maselspoort water treatment plant.....	113
4.1.4	Collection of wastewater influent and effluent samples	113
4.1.4.1	Bloemfontein north-east wastewater treatment plant influent and effluent.....	113
4.1.4.2	Botshabelo wastewater treatment plant influent and effluent	113
4.1.4.3	Bloemspruit wastewater treatment plant influent and effluent	114
4.2	Laboratory analysis.....	114
4.2.1	Reagents and materials.....	114
4.2.2	Sample preparation and extraction	114
4.2.3	Sample analysis	115
4.2.3.1	Unknown analytes	115
4.2.3.2	Selection of target analytes.....	115
4.2.3.3	Analysis of targeted compounds.....	116
4.2.3.4	Method verification and quality control	117
4.3	Removal efficiency of emerging contaminants in wastewater treatment plants	118
4.4	Multivariate statistical analysis	118
4.5	Environmental risk assessment of emerging contaminants	118
4.5.1	Individual risk assessment.....	118
4.5.2	Mixture risk assessment	119

4.5.3	Human health risk assessment.....	120
4.5.4	Non-carcinogenic risk assessment	121
4.5.5	Carcinogenic risk assessment	122
Chapter 5		
INVESTIGATION AND MONITORING OF EMERGING CONTAMINANTS IN WATER SOURCES		123
5.1	Introduction	123
5.2	Non-target screening of emerging contaminants in water sources	125
5.2.1	Screening of emerging contaminants in rivers	127
5.2.2	Screening of emerging contaminants in dams and reservoirs	129
5.2.3	Screening of emerging contaminants in wastewater treatment plants.....	130
5.2.4	Screening of emerging contaminants in treated drinking water	132
5.3	Selection of target analytes	132
5.4	Quantitative analysis of emerging contaminants in water sources.....	133
5.4.1	Occurrence of emerging contaminants in rivers	133
5.4.2	Occurrence of emerging contaminants in dams/reservoirs	138
5.4.3	Occurrence of emerging contaminants in wastewater treatment plants	142
5.4.3.1	Occurrence of emerging contaminants in wastewater influents.....	142
5.4.3.2	Occurrence of emerging contaminants in effluents	145
5.4.3.3	Removal efficiency of emerging contaminants in wastewater treatment plants.....	147
5.4.4	Occurrence of emerging contaminants in treated drinking water.....	152
5.5	Conclusion	156
Chapter 6		
ENVIRONMENTAL HEALTH RISK ASSESSMENT OF EMERGING CONTAMINANTS IN WATER SOURCES		157
6.1	Introduction	157
6.2	Environmental risk assessment of emerging contaminants in water sources	159
6.2.1	Individual risk assessment.....	159
6.2.1.1	Environmental risk assessment of individual emerging contaminant in rivers.....	160
6.2.1.2	Environmental risk assessment of individual emerging contaminant in dams.....	163
6.2.1.3	Environmental risk assessment of individual emerging contaminants in wastewater effluents	167
6.2.1.4	Environmental risk assessment of individual emerging contaminants in treated drinking water.....	171
6.2.2	Mixture risk assessment	175

6.2.2.1	Mixture environmental risk assessment of emerging contaminants in rivers	175
6.2.2.2	Mixture environmental risk assessment of emerging contaminants in dams	177
6.2.2.3	Mixture environmental risk assessment of emerging contaminants in wastewater effluents	179
6.2.2.4	Mixture environmental risk assessment of emerging contaminants in treated drinking water.....	181
6.3	Human health risk assessment of selected pesticides in water sources.....	182
6.4	Conclusion	190
Chapter 7		
SOURCE APPORTIONMENT OF EMERGING CONTAMINANT POLLUTION IN WATER SOURCES AND THEIR MITIGATION STRATEGIES.....		191
7.1	Introduction	191
7.2	Pollution source profiling	193
7.3	Identification of pollution source with Pearson correlation coefficient analysis.....	194
7.3.1	Identification of pollution source in rivers	194
7.3.2	Identification of pollution sources in dams and or reservoirs	197
7.3.3	Identification of pollution source in wastewater treatment plants.....	200
7.3.4	Identification of pollution source in treated drinking water	205
7.4	Identification of pollution sources using hierarchical cluster analysis.....	208
7.4.1	Identification of pollution source in rivers	208
7.4.2	Identification of pollution sources in dams and or reservoirs	212
7.4.3	Identification of pollution sources in wastewater treatment plants	215
7.4.4	Identification of pollution source in treated drinking water	221
7.5	Identification of pollution source using principal component analysis	228
7.5.1	Identification of pollution source in rivers	228
7.5.2	Identification of pollution sources in dams and or reservoirs	233
7.5.3	Identification of pollution sources in wastewater treatment plants	237
7.5.4	Identification of pollution source in treated drinking water	244
7.6	Mitigation measures to prevent water pollution for sustainable management and environmental health protection	246
7.6.1	Wastewater effluent discharged in nearby streams.....	248
7.6.2	Illegal dumping of domestic waste near water bodies	248
7.6.3	Emission from domestic sewage overflow	249
7.6.4	Emission from urban stormwater runoff	249
7.6.5	Emission from agricultural activities	249
7.7	Conclusion	250

Chapter 8

CONCLUSIONS AND RECOMMENDATIONS 251

8.1 Conclusions 251

8.1.1 Investigation and monitoring of potential emerging contaminants in water sources..... 251

8.1.2 Environmental risk assessment of emerging contaminants..... 252

8.1.3 Human health risk assessment of selected pesticides in water sources 252

8.1.4 Sources of emerging contaminants in water sources and possible mitigation measures 253

8.2 Recommendations 253

REFERENCES 255

Appendix A

COLLECTION AND HANDLING OF SAMPLES 301

Appendix B

MULTIPLE REACTION MONITORING CHROMATOGRAPHY 305

Appendix C

TARGET ANALYTES MULTIPLE REACTION MONITORING TRANSITION VALUES ... 311

Appendix D

TOXICITY DATA 312

Appendix E

LIST OF PUBLICATIONS..... 316

Appendix F

LABORATORY ANALYSES 326

Appendix G |APPROVED AND LINGUISTICALLY REVISED TITLE 332

Appendix H

TECHNICAL EDITING CONFIRMATION LETTER..... 333

LIST OF FIGURES

Figure 2.1	Sources and pathways of emerging contaminants in the environment	19
Figure 3.1	Geographical location of the study area	96
Figure 3.2	Geological map of the study area.....	98
Figure 3.3	Racial composition of Mangaung Metropolitan Municipality	102
Figure 3.4	Gender distribution in Mangaung Metropolitan Municipality	102
Figure 3.5	Age distribution in Mangaung Metropolitan Municipality	103
Figure 3.6	Economic drivers of Mangaung Metropolitan Municipality	104
Figure 4.1	Sampling points within the study area	108
Figure 5.1	Screening of emerging contaminants in water sources around Bloemfontein.....	127
Figure 5.2	Detection of analytes per water source in Bloemfontein	127
Figure 5.3	Seasonal concentrations of emerging contaminants in rivers	136
Figure 5.4	Seasonal concentrations of emerging contaminants in dams	140
Figure 5.5	Schematic presentation of the selected wastewater treatment plants.....	142
Figure 5.6	Seasonal concentrations of emerging contaminants in influents	145
Figure 5.7	Seasonal concentrations of emerging contaminants in effluents	147
Figure 5.8	Efficiency of wastewater treatment plants in removing emerging contaminants	149
Figure 5.9	Seasonal concentrations of emerging contaminants in treated drinking water	154
Figure 6.1	Seasonal mixture risks of emerging contaminants on aquatic species in rivers.....	177
Figure 6.2	Seasonal mixture risks of emerging contaminants on aquatic species in dams.....	179
Figure 6.3	Seasonal mixture risks of emerging contaminants in wastewater effluent on aquatic species	180
Figure 6.4	Seasonal mixture risks of emerging contaminants in treated drinking water on aquatic species.....	182
Figure 6.5	Seasonal variation of non-carcinogenic risks in various water sources	183
Figure 6.6	Seasonal variation of carcinogenic risks in various water sources.....	184
Figure 7.1	Cluster diagram showing similarities of emerging contaminants in rivers during the wet season	210

Figure 7.2	Cluster diagram showing similarities of emerging contaminants in rivers during the dry season.....	211
Figure 7.3	Cluster diagram showing similarities of emerging contaminants in dams during the wet season.....	214
Figure 7.4	Cluster diagram showing similarities of emerging contaminants in dams during the dry season.....	215
Figure 7.5	Cluster diagram showing similarities of emerging contaminants in wastewater influent during the wet season.....	217
Figure 7.6	Cluster diagram showing similarities of emerging contaminants in wastewater influent during the dry season	218
Figure 7.7	Cluster diagram showing similarities of emerging contaminants in wastewater effluent during the wet season.....	220
Figure 7.8	Cluster diagram showing similarities of emerging contaminants in wastewater effluent in the dry season	221
Figure 7.9	Cluster diagram showing similarities of emerging contaminants in treated drinking water during the wet season	223
Figure 7.10	Cluster diagram showing similarities of emerging contaminants in treated drinking water during the dry season.....	224
Figure 7.11	PCA results of the first two principal components in rivers during the wet season (spring and summer).....	231
Figure 7.12	PCA results of the first two principal components in rivers during the dry season (autumn and winter).....	232
Figure 7.13	PCA results of the first two principal components in dams during the wet season (spring and summer).....	236
Figure 7.14	PCA results of the first two principal components in dams during the dry season (autumn and winter).....	237
Figure 7.15	PCA results of the first two principal components in influents during the wet season (spring and summer)	240
Figure 7.16	PCA results of the first two principal components in influent during the dry season (autumn and winter).....	241
Figure 7.17	PCA results of the first two principal components in effluent during the wet season (spring and summer)	243
Figure 7.18	PCA results of the first two principal components in effluent during the dry season (autumn and winter).....	244
Figure 7.19	PCA results of the first two principal components in treated drinking water ...	246
Figure 7.20	Exemplification of major routes of emerging contaminants in water sources around Bloemfontein.....	247

LIST OF TABLES

Table 2.1	Occurrence and concentration levels of pharmaceuticals and personal care products in international surface water, groundwater and drinking water	33
Table 2.2	Occurrence and concentration levels of pharmaceuticals and personal care products in international wastewater influents and effluents	53
Table 2.3	Occurrence and concentration levels of herbicides in international surface water, groundwater, and drinking water	60
Table 2.4	Occurrence and concentration levels of endocrine disrupting compounds in international surface water, groundwater and drinking water	64
Table 2.5	Occurrence and concentration levels of pharmaceuticals and personal care products in South African surface water, groundwater and drinking water	67
Table 2.6	Occurrence of pharmaceuticals and personal care products in South African wastewater influent and effluents	77
Table 2.7	Occurrence of herbicides in South African surface water, groundwater and drinking water.....	82
Table 4.1	Sampling sites at various water sources around the study area	109
Table 4.2	Measurement of linearity and limit of quantification.	117
Table 5.1	Qualitative non-target screening and occurrence (%) of emerging contaminants in water sources around Bloemfontein	126
Table 5.2	Composition of influent and effluent samples	131
Table 5.3	Occurrence of emerging contaminants in rivers	137
Table 5.4	Occurrence of emerging contaminants in dams	141
Table 5.5	Concentration of emerging contaminants in wastewater influents	150
Table 5.6	Concentration of emerging contaminants in wastewater effluents	151
Table 5.7	Removal efficiency of emerging contaminants from wastewater treatment plants	152
Table 5.8	Concentration of emerging contaminants in treated drinking water	155
Table 5.9	Concentration of pesticides in treated drinking water with guidelines values	155
Table 6.1	Acute and chronic risks of individual contaminants in rivers	162
Table 6.2	Acute and chronic risks of individual contaminant in dams.....	165
Table 6.3	Acute and chronic risks of individual contaminants in effluents	169

Table 6.4	Acute and chronic risks of individual contaminants in treated drinking water	173
Table 6.5	Acute and chronic mixture risks of contaminants in rivers	177
Table 6.6	Acute and chronic mixture risks of contaminants in dams	178
Table 6.7	Acute and chronic mixture risks of contaminants in wastewater effluents	180
Table 6.8	Acute and chronic mixture risks of contaminants in treated drinking water	182
Table 6.9	Non-carcinogenic risks of selected pesticides in various water sources	186
Table 6.10	Carcinogenic risks of selected pesticides in various water sources	188
Table 7.1	Sampling points around the study area	193
Table 7.2	Correlation coefficients among emerging contaminants during the wet season in rivers	195
Table 7.3	Correlation coefficients among emerging contaminants during the dry season in rivers	196
Table 7.4	Correlation coefficients among emerging contaminants during the wet season in dams	198
Table 7.5	Correlation coefficients among emerging contaminants during the dry season in dams	199
Table 7.6	Correlation coefficients among emerging contaminants during the wet season in influents	200
Table 7.7	Correlation coefficients among emerging contaminants during the dry season in influents	201
Table 7.8	Correlation coefficients among emerging contaminants during the wet season in effluents	203
Table 7.9	Correlation coefficients among emerging contaminants during the dry season in effluents	204
Table 7.10	Correlation coefficients among emerging contaminants during the wet season in treated drinking water	206
Table 7.11	Correlation coefficients among emerging contaminants during the dry season in treated drinking water	207
Table 7.12	Simplified analysis of clusters identified for emerging contaminants in water sources around Bloemfontein	225
Table 7.13	Principal component analysis of emerging contaminants in rivers	230
Table 7.14	Principal component analysis of emerging contaminants in dams	235
Table 7.15	Principal component analysis of emerging contaminants in wastewater influents	239
Table 7.16	Principal component analysis of emerging contaminants in wastewater effluents	242

Table 7.17	Principal component analysis of emerging contaminants in treated drinking waters.....	245
------------	---	-----

ABBREVIATIONS AND ACRONYMS

2,4-D	2,4-Dichlorophenoxyacetic acid
ADD	Average daily dose
BLD	Below limit of detection
CHE	Collaborative on Health and the Environment
CSF	Chemical Safety Facts
DEET	N-diethyl-meta-toluamide
EC ₅₀	Effective concentration
GC	Gas chromatography
HQ	Hazard quotient
HPLC	High performance liquid chromatography
IDP	Integrated Development Plan
IS	Internal standard
LC ₅₀	Lethal concentration
LOD	Limit of detection
LOQ	Limit of quantification
LC	Liquid chromatography
LC-MS	Liquid chromatography-mass spectrometry
LOEC	Lowest observed effect concentration
MCPA	Methyl4-chlorophenoxyacetic acid
MEC	Measured environmental concentration
MeOH	Methanol
MMM	Mangaung Metropolitan Municipality
MS	Mass spectrometry
ND	Not detected
NOEC	No observable effect concentration
NSAIDs	Non-steroidal anti-inflammatory drugs
PCA	Principal component analysis
PNEC	Predicted non-effect concentration
RF	Removal frequency
RQ	Risk quotient

RQmix	Risk quotient mixture
±SD	Standard deviation
SPE	Solid phase extraction
TRC	Total carcinogenic risk
TU	Toxic unit
TUsum	Toxic unit summation
USEPA	Unites State Environmental Protection Agency
WHO	World Health Organisation
WSA	Water Service Authority
WWTP	Waste Water Treatment Plants

LIST OF MEASUREMENTS

°C	Degree Celsius
%	Percentage
ha	Hectare
kg	Kilogram
ℓ	Litre
m	Metre
mℓ	Millilitre
msl	Mean sea level
km	Kilometre
km ²	Square kilometre
Ma	Mega Annum
m/s	Metre per second
mg	Milligram
mg/kg	Milligram per kilogram
mg/kg/d	Milligram per kilogram per day
mg/ℓ	Milligram per litre
m ²	Square metre
m ³	Cubic metre
ng	Nanogram
ng/ℓ	Nanogram per litre
nm	Nanometre
ppb	Particles per billion
ppm	Particles per million
psi	pounds per square inch
μg/ℓ	Microgram per litre
μm	Micrometre
Σ	Sum
V	Voltage

CONCEPTUAL DEFINITIONS

Acute toxicity, in this study, describes the adverse effects of an emerging contaminant that results either from a single exposure or from multiple exposures in a short period of time (USEPA, 2004).

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

Analyte: In this study, an analyte refers to a potential emerging contaminant that was the subject of chemical analysis.

Chronic toxicity, in this study, is defined as the development of adverse effects as a result of long-term exposure to an emerging contaminant (USEPA, 2004).

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

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

Environmental risk assessment is the process for evaluating how likely it is that the environment may be impacted as a result of exposure to one or more environmental stressors, which in this study is emerging contaminants (Duarte et al. , 2022).

Emerging contaminants are man-made or naturally occurring organic compounds that are not commonly investigated or regulated by legislation but have the possibility to trigger serious implications to the environment and public health (Morin-Crini et al., 2022).

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

Herbicides are chemical substances widely used in agricultural production and other areas such as in forestry, parks, golf courts and sports grounds (Wang et al., 2022; Medkova et al., 2023).

Human health risk assessment is defined as the process of estimating the nature and likelihood of adverse health effects in humans who may have been exposed to emerging contaminants in water sources or may be exposed in the future (Kamunda et al., 2018).

Non-target screening is an analytical analysis that permits the finding of unknown compounds with no necessity of any prior information (Abafe et al., 2023).

Pharmaceuticals are considered to be recommended, non-prescription, and animal salutary medications utilised to inhibit, or for treatment of ailments in human beings and mammals (Pei et al., 2022).

Personal care products are regarded as chemical compounds utilised mostly to increase grooming throughout day-to-day life (Huang et al., 2023).

River: A river is a body of water that resembles a ribbon and moves downward under the influence of gravity (Adeleye, 2016).

Steroid hormone: Natural or synthetic compounds widely used as contraceptives and for growth promotion in humans and animals (La Merrill et al., 2020).

Surface water: The water found on the earth's surface is known as surface water. It consists of marshes, lakes, rivers, reservoirs and streams with a small percentage (0.26%) of the world's freshwater (Tufenkji et al., 2002; Bella-Atangana et al., 2023).

Target analysis, in this study, refers to the identification of known emerging contaminants that are carefully chosen before the sample analysis and for which analytical standards are commercially obtainable (Čelić et al., 2020).

Treated drinking water, in this study, refers to tap water that has undergone processing to meet a specified end use.

Wastewater treatment plants is characterised as a facility that combines a number of physical, biological and chemical processes to clean up wastewater and turn it into effluent that can be recycled back into the water cycle (Gosset et al., 2021; Nannou et al., 2022).

Water sources, in this study, refers to rivers, dams, treated drinking water, wastewater treatment influents and effluents (Malewandja, 2018; Ojemaye, 2020).

CONTRIBUTION OF THE STUDY

The study contributed immensely to the discipline of environmental health by expanding the limited knowledge and understanding of the presence and risks of emerging contaminants in water sources around Bloemfontein and the Free State province as a whole. The research is unique since it is the first study to focus on environmental and health risks of emerging contaminants in the Free State province. The project yielded a large data set that may aid regulators in identifying priority actions for the management and sustainability of water bodies around Bloemfontein. The study will not only raise awareness on the presence of emerging contaminants and their potential health impacts but communicate risks to the relevant stakeholders for analysis and making decisions regarding risk mitigation. Additionally, it will serve as a starting point for future research and add to the body of knowledge on earlier studies conducted outside the Free State region. Several research outputs from this study were disseminated for possible use at international, national, provincial and local level through publications of a book, book chapter and journal articles. The results of the study were also presented at international conferences as listed below:

Books

1. Oke, S.A and Mugudamani, I. (2023). *An overview of emerging contaminants in water sources: A global outlook*. BP International, 2023, pp. 1–100.
<https://doi.org/10.9734/bpi/mono/978-81-19761-78-4>

Book chapter

2. Mugudamani, I., Oke, S.A., Gumede, T.P., Senbore, S. (2024). Monitoring of emerging contaminants in selected wastewater treatment works around Bloemfontein, South Africa: Initiative for environmental protection. In: Xu, H. (Eds.), *The 6th International Symposium on Water Resource and Environmental Management*. WREM 2023. Environmental Science and Engineering. Springer, Cham. https://doi.org/10.1007/978-3-031-55989-1_3

Journal articles

3. Mugudamani, I., Oke, S.A., Gumede, T.P., Senbore, S. (2024). Risk assessment of emerging contaminants in urban and natural water sources around Bloemfontein, South Africa: Implication for environmental sustainability. *Current Analytical Chemistry*, 20(8), 1–21.
<https://doi.org/10.2174/0115734110306162240527050732>
4. Mugudamani, I., Oke, S.A., Gumede, T.P., Senbore, S. (2023). Herbicides in water sources: Communicating potential risks to the population of Mangaung Metropolitan Municipality, South Africa. *Toxics*, 11, 538. <https://doi.org/10.3390/toxics11060538>

5. Oke, S.A., Mugudamani, I., Gumede, T.P., Senbore, S. (2023). Environmental risk assessment of exposure to selected emerging contaminants in dams and wastewater effluent around the City of Bloemfontein, South Africa. *Journal of Harbin Engineering University*, 44(12): 1077–1082.
<https://harbinengineeringjournal.com/index.php/journal/article/view/2407/1574>

Conference/Abstract presentation

6. Oke, S.A., Gumede, T.P., Senbore S., Mugudamani, I. (2023). The investigation and monitoring of emerging contaminants from point sources on the Modder River catchment system in Free State, South Africa (Abstract presented at *Persistent, Emerging and Organic Pollution in the Environment (PEOPLE 2023)-international conference on collaborative solution to environmental problems under climate change*, 7–11 August 2023. Montreal, Quebec, Canada).
7. Oke, S.A., Gumede, T.P., Senbore S., Mugudamani, I. (2023). Environmental risk assessment of exposure to selected emerging contaminants in dams and wastewater effluent around the city of Bloemfontein, South Africa. *International Conference on Global Warming, Climate Change and Pollution Control (GWCCPC-23)*. Montreal, Canada, 14th - 15th December 2023.

Manuscripts under review

8. Oke, S.A; Mugudamani I. Water quality and emerging contaminants pollution in the Modder River catchment in Free State, South Africa. *Discover Water*.
9. Mugudamani, I., Oke, S.A., Kemp, G. Qualitative screening of emerging contaminants in urban and natural waters of Mangaung District of the Free State province of South Africa. *Discover Environment*.

Chapter 1

INTRODUCTION

This chapter gives the background information regarding this study. The problem statement, aim and objectives, hypothesis, research questions, justification and significance, as well as the scope and study limitations are discussed, ending with a short presentation of the outline of the thesis.

1.1 Background of the study

Water is a valuable and limited resource that is essential for the survival of all known life forms (Bonecker et al., 2020). Dams, rivers, wetlands and lagoons are important water sources for both human welfare and aquatic life (Isah et al., 2013). They are critical for domestic use, agricultural endeavours, industrial growth, leisure and aquatic habitation and reproduction (Ma et al., 2020). The majority of urban areas such as Bloemfontein were built on or near freshwater sources (Bonecker et al., 2020). As a result of industrialisation and population growth, various organic chemicals from manufacturing, wastewater treatment plants (WWTPs), agricultural practises and household tasks find their way into water sources, contaminating and degrading their quality (Wang et al., 2015). The recent advances in methods of detection of organic chemicals in water sources has steered the detection of a high quantity of contaminants together with their end products, which formerly were unidentified in water sources and are currently recognised as emerging contaminants (Vasilachi et al., 2021).

Emerging contaminants are natural or synthetic tenacious organic substances that are not typically examined in the environment but have the possibility to cause effects on the surrounding areas and people's health (Vasilachi et al., 2021). Emerging contaminants comprise an extensive collection of organic substances, such as pesticides, personal and domestic care products, pharmaceuticals, steroid hormones and brominated flame retardants that are used universally and are essential for contemporary civilisation (Odendaal et al., 2015; Karpinska and Kotowska, 2021). The presence of these emerging contaminants in water sources may cause acute or chronic effects such as carcinogenic, mutagenic and teratogenic effects, depending on their concentration and exposure level. Their mixtures in water sources may also be extremely hazardous to human and aquatic life (Visca et al., 2021). Galindo-Miranda et al. (2019) also stated that the end products of these compounds are frequently more noxious than the original compounds.

The existence of emerging contaminants in water sources not only endangers aquatic and human life, but also restricts access to safe water for drinking, and impedes public and monetary development (Ma et al., 2020). The countries with the most limited access to drinking water are primarily those in sub-Saharan Africa, including South Africa (World Health Organization [WHO], 2017). Water resources in South Africa are scarce and unevenly distributed. It is expected that competition for water among users will intensify in the near future. South Africa currently uses mostly surface water, with groundwater accounting for only 15% of total water consumption (Sililo et al., 2001; WHO, 2017). The issue of emerging pollutants is a constant challenge (Vasilachi et al., 2021), because their numbers are increasing all the time (Patel et al., 2019). Given their incessant introduction into the water resources and the effect on aquatic life and human health, continuous monitoring of these compounds in water sources is seriously needed, particularly in water-stressed countries such as South Africa.

In South Africa, most studies on emerging contaminants only monitor known or targeted compounds in aqueous environments (Matongo et al., 2015; Sorensen et al., 2015; Wood et al., 2015; Agunbiade and Moodley, 2016; Wanda et al., 2017; Archer et al., 2017; Madikizela and Chimuka, 2017; Sibeko et al., 2019; Mhuka et al., 2020; Ncube et al., 2021; Spath et al., 2021), with few reports in the country focusing on qualitative analysis of a wide range of emerging contaminants (Odendaal et al., 2015; Rimayi et al., 2019; Afafe et al., 2023). Monitoring of emerging contaminants based on target compounds, according to Brack et al. (2019), fails to account for the majority of unforeseen and unknown chemicals that may also cause adverse environmental health risks. They further stated that qualitative screening of unknown analytes allows for comprehensive detection and such information can be used for target analysis in pollution monitoring studies. The majority of these quantitative and qualitative studies were conducted in specific provinces such as Gauteng and KwaZulu-Natal, with data in the Free State province being scarce. Moreover, in the Free State province, which is the host of the city of Bloemfontein, there is no published work on environmental health risks of emerging contaminants.

Therefore, this study, which is the first in Bloemfontein, was piloted with the aim to assess the environmental health risks of emerging contaminants in various water sources, namely rivers, dams, treated drinking water and wastewater treatment plants (WWTPs). This aim was achieved by (i) investigating and monitoring emerging contaminants based on qualitative and quantitative analysis; (ii) assessing the environmental health risks of emerging contaminants; and (iii) determining their possible sources in order to put forward possible mitigation measures. Monitoring and assessing risks of emerging contaminants in

water sources around Bloemfontein will not only raise awareness on their concentrations and the potential health impacts but communicate risks to relevant stakeholders for analysis and making decisions regarding risk mitigation. Furthermore, it is essential for the management and sustainability of the water bodies in this region of Free State. Additionally, it will serve as a starting point for future research and add to the body of knowledge on earlier studies conducted outside the Free State region.

1.2 Problem statement

Organic substances (e.g. emerging contaminants) are an essential part of everyday life, with over 100 000 different chemicals produced and used by industries (Sanchez and Egea, 2018). Organic chemicals, according to Bwapwa and Jaiyeola (2019), enable the development of new technologies while also improving living standards and quality of life. They are regularly used for domestic purposes, agricultural activities, industrial applications, as well as human and animal healthcare (Llamas et al., 2020). Despite their importance in daily life, many chemicals (e.g. emerging contaminants) are discharged into the aqueous environment (Sanchez and Egea, 2018) after they have served their primary purpose (Wilkinson et al., 2017; Bagheri, 2021). The issue of emerging contaminant pollution is a constant challenge (Vasilachi et al., 2021), because their numbers are increasing all the time (Patel et al., 2019). Their presence in water sources may cause acute or chronic effects such as carcinogenic, mutagenic and teratogenic effects, depending on their concentration and exposure level (Visca et al., 2021). Galindo-Miranda et al. (2019) also stated that the transformation products of these compounds are frequently more toxic than the original compounds. Moreover, their mixtures in water sources may also be extremely hazardous to human and aquatic life (Visca et al., 2021). Therefore, due to incessant introduction of these contaminants into the aqueous environment, and the associated environmental health risks, their continuous monitoring in water sources is seriously needed, particularly in provinces such as the Free State where information on emerging contaminants is dearth. To fill in the gap, the study assessed the environmental and health risks of potential emerging contaminants in rivers, dams, treated drinking water and WWTPs around the city of Bloemfontein.

1.3 Aim and objectives

The aim of this study was to assess the environmental health risks of potential emerging contaminants identified from water sources around Bloemfontein in the Free State province

of South Africa. The following specific objectives were framed to achieve the aim of the study:

- To compile a comprehensive overview of emerging contaminants in water sources around the world.
- To investigate and monitor potential emerging contaminants in water sources around Bloemfontein in the Free State province.
- To assess individual and a mixture of environmental risks of emerging contaminants in selected water sources.
- To assess carcinogenic and non-carcinogenic risks ensuing from exposure to pesticides in selected water sources.
- To identify possible sources of the targeted emerging contaminants in water sources and put forward control measures based on their sources identified in this study.

1.4 Research hypothesis

The study hypothesised that emerging contaminants are present in water sources around Bloemfontein, and their concentrations have a potential to contribute to environmental and human health risks.

1.5 Research questions

The research sought to address the following questions:

1. What are the potential emerging contaminants in water sources around Bloemfontein?
2. Does the concentration level of emerging contaminants in water sources around Bloemfontein have the potential to contribute to environmental and human health risks?
3. What are the sources of potential emerging contaminants in water sources around Bloemfontein?
4. Are there any possible mitigation measures to control emerging contaminant pollution in water sources?

1.6 Justification and significance of the study

The introduction of new chemicals, their expanding uses for health, agriculture and households, and the limited effectiveness of traditional purification processes used in wastewater treatment have caused the continuous discharge of emerging contaminants into

soil and water sources (Llamas et al., 2020; Bagheri, 2021; Karpinska and Kotowska, 2021). The existence of organic emerging contaminants in water sources at residual quantities ranging from nanograms to micrograms per litre can have detrimental impacts on aquatic animals and human health (Barbosa et al., 2018; Ghernaout and Elboughdiri, 2019; Reyes et al., 2021). These include eco-toxicological effects such as chemo-sensitisation; endocrine disruption; disruption of the production of platelets, red and white blood cells; antibiotic resistance of microorganisms and insomnia (Wanda et al., 2017; Pei et al., 2022). As of yet, there is not any long-term solutions put up to deal with the issues brought on by emerging contaminant pollution in many places of the world, including South Africa (Wanda et al., 2017). Therefore, it is critical to monitor their occurrence in water sources and assess their associated risks. In South Africa, studies on quantitative analysis of emerging contaminants (Matongo et al., 2015; Sorensen et al., 2015; Wood et al., 2015; Agunbiade and Moodley, 2016; Archer et al., 2017; Madikizela and Chimuka, 2017; Wanda et al., 2017; Sibeko et al., 2019; Ncube et al., 2021; Mhuka et al., 2020; Spath et al., 2021) and qualitative analysis of emerging contaminants (Odendaal, et al., 2015; Rimayi et al., 2019; Abafe et al., 2023) were conducted mostly in specific provinces such as Gauteng and KwaZulu-Natal, with a dearth of information in the Free State province. Monitoring and assessing the risks of emerging contaminant in water sources around Bloemfontein will not only raise awareness on their concentrations and the potential health impacts but communicate risks to relevant stakeholders for analysis and making decisions regarding risk mitigation (Vasilachi et al., 2021). This will also reduce the level of pollution and improve the quality of water resources around the city of Bloemfontein thus addressing sustainable development goal number six (clean water and sanitation). Furthermore, assessing the risks of emerging contaminants in water sources is essential in protecting aquatic ecosystem and other living organisms which is in agreement with sustainable development goal number fourteen (life below water). The outcomes of this project will also serve as a starting point for subsequent research and add to knowledge from earlier studies conducted in South Africa and other regions of the world.

1.7 Scope of the study

Although water sources may contain several pollutants, the study focused only on emerging contaminants (pharmaceutical, personal care products, steroid hormones and pesticides) identified from rivers, dams, treated drinking water, as well as wastewater influent and effluent during all seasons of the year.

1.8 Limitation of the study

Although this study closed an important data gap on emerging contaminant pollution, their sources and possible risks in Bloemfontein, it has some limitations:

- This study was limited to the water sources around Bloemfontein and areas such as Botshabelo and Thaba Nchu.
- The potential emerging contaminants in groundwater as a source of water were not monitored in this study.
- The physicochemical, hydro-chemical and microbiological parameters were not analysed in this study.
- The study also monitored only a few groups of emerging contaminants as a result of lack of finances and laboratory standards for some compounds.
- The main challenges in risk assessment included limited occurrence of data about toxicological tests assays, chronic and acute toxicity data of some emerging contaminants. The predicted non-effect concentration values are centred on presently accessible data and may vary as more dependable data becomes accessible.
- Because of a lack of slope factors and reference doses of some organic contaminants, the human health risk assessment was conducted only for the identified pesticides.
- Moreover, this study did not seek to implement the means of mitigation, but only to inform local inhabitants, WWTP managers, farmers and relevant authorities of the sources of emerging contaminants to their water sources and also the possibilities around decreasing the ill-effects of emerging contaminants through various mitigation treatments.

1.9 Thesis outline

This thesis is made up of eight separate chapters outlined as follows:

Chapter 1: Introduction

Chapter 1 covers the background to the problem, problem statement, research questions, research hypotheses, aims and objectives, significance, scope and limitations of the study.

Chapter 2: An overview of emerging contaminants in water sources: A global outlook

The chapter is published as a complete book under Book Publisher International, which provides an overview of emerging contaminants in water sources around South Africa and other parts of the world.

Chapter 3: Description of the study area: Bloemfontein

It describes the area where the study was conducted, the study location, environmental attribute and socio-economic status.

Chapter 4: Methodology

This chapter provides detailed information on the methods adopted to gather the data required to answer the research questions of the study. Information on collection of samples and laboratory analysis are discussed. The chapter also describes the methods used to determine the removal efficiency of WWTPs, sources and risks of emerging contaminants.

Chapter 5: Investigation and monitoring of emerging contaminants in water sources

This chapter describes the investigation and monitoring of emerging contaminants in rivers, dams, treated drinking water and WWTPs, which was achieved by conducting both non-target screening and quantitative analysis of emerging contaminants.

Chapter 6: Environmental health risk assessment of emerging contaminants in water sources

The results and discussion of the risks ensuing from exposure to emerging contaminants in water sources are presented in this section. It discusses the results of individual and a mixture of environmental risks of emerging contaminants in water sources around Bloemfontein. The results of human health risks of selected pesticides are also covered in this chapter.

Chapter 7: Source apportionment of emerging contaminant pollution in water sources and their mitigation strategies

The sources of emerging contaminants in water sources around Bloemfontein are presented and discussed in this segment. Possible mitigation strategies related to the sources of emerging contaminants are also discussed.

Chapter 8: Conclusions and recommendations

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

Chapter 2

OVERVIEW OF EMERGING CONTAMINANTS IN WATER

SOURCES: A GLOBAL OUTLOOK

This chapter provides an overview of emerging contaminants in water sources at a global scale and has been published as a book. For the sake of the thesis, only minor changes were made to grammar and spelling.

Oke, S.A. and Mugudamani, I. 2023. *An overview of emerging contaminants in water sources: A global outlook*. India/United Kingdom: BP International. <https://doi.org/10.9734/bpi/mono/978-81-19761-78-4>

Abstract

Advance in methods of detection for some organic chemicals in water sources has steered the screening and quantification of a high quantity of contaminants collectively with their end products, which formerly were not identified in water sources and are currently recognised as emerging contaminants. The accumulation and discovery of levels of these emerging contaminants in water sources has reduced water quality and made it unsafe for aquatic and human life. Exposure to these organic contaminants may trigger serious health effects. The aim of this chapter is to give a comprehensive review of global occurrence of emerging contaminants in various water sources such as surface water, groundwater, treated drinking water and wastewater influent and effluent. The chapter introduces the audience to concepts of water sources, emerging contaminants, point sources and nonpoint sources of emerging contaminants. It offers a glimpse of international and South African case studies on the occurrence of emerging contaminants, specifically herbicides, pharmaceuticals, steroid hormones and personal care products in water sources as well as in WWTPs. The analytical and removal methods of emerging contaminants in water sources are also covered. Moreover, information on possible environmental health impacts ensuing from exposure to emerging contaminants and their possible mitigation measures (such as classification and labelling methods; point source separation methods; and regulating the release of emerging contaminants) are discussed. It can be concluded that emerging contaminants pollution is a global problem. The occurrence of emerging contaminants around the world (Africa, America, Asia, Europe and Oceania) is likely to upsurge in water sources and WWTPs as a result of the rise in population, which is a public health concern. Therefore, more studies that report on the widespread of emerging contaminants in water sources and their associated environmental health risks are needed to help regulators in establishing priority measures for management of water resources.

Keywords: Emerging contaminants; herbicides; pharmaceuticals and personal care products; steroid hormones; water sources

2.1 Introduction

The increase in the universal inhabitants (to 8.0 billion as of 2022), manufacturing activities (pharmaceuticals) and the usage of chemical goods in households (plastics, cosmetic products, toothpaste, toys), tourism, industrial manufacturing, agricultural activities, as well as in human and animal health care are producing considerable volumes of chemical waste that pollute our surroundings (Torres-Padron et al., 2020). Pollution caused by chemicals is regarded as one of the world's utmost threats to the aquatic ecosystem and human life (Barton-Maclaren et al., 2022) and water as an indispensable resource for life in the world, is most vulnerable to these types of pollution. The advancement in methods of detection of some organic chemicals in the water sources recently has steered the detection of high quantity of contaminants together with their end products, which formerly were unidentified in water sources and are currently recognised as emerging contaminants (Vasilachi et al., 2021).

Emerging contaminants are regarded as natural or man-made organic chemicals commonly not scrutinised in water sources or controlled by regulation, however, have the prospect to trigger serious implications to aquatic and human life (Miraj et al., 2016; Morin-Crini et al., 2022). Many of these organic chemicals include herbicides, personal care products, steroid hormones and pharmaceuticals (Liu et al., 2020a; Medkova et al., 2023). Pharmaceuticals are considered to be recommended, non-prescription and animal salutary medications are utilised to inhibit or for treatment of ailments in human being and mammals, whereas personal care products are regarded as chemical compounds utilised mostly to increase grooming throughout day-to-day life (cosmetics, fragrance, skin care, dental products) (Liu et al., 2020b).

Steroid hormones are natural or synthetic compounds widely used as contraceptives and for growth promotion in humans and animals (Bexfield et al., 2019). Herbicides are chemical substances widely used in agricultural production (e.g. crop farming) (Wang et al., 2022) and other areas such as in forestry, parks, golf courts and sports ground (Slevanovic et al., 2019; Mugudamani et al. 2023) to either kill or severely injure undesirable plants (Casida, 2019; Ganaie et al., 2023). These organic contaminants enter the water sources at a very low level ranging from nanograms per litre (ng/l) to hundred micrograms per litre ($\mu\text{g/l}$) (Li et al., 2015) via several pathways such as WWTPs, roadways runoff, agricultural runoff, recreational

activities, deposition from atmosphere, animal feeding activities, sewage seepage and landfill tank leachates (Selwe et al., 2022; Liu et al., 2023).

The existence of emerging pollutants in water sources is largely unregulated by legislation and they do not have to be extremely tenacious to cause environmental health effects as their decay is counterbalanced by an incessant introduction (Llamas et al., 2020). The accumulation and detection of levels of these emerging contaminants in water sources has reduced water quality and made water risky for aquatic and human life (Gozzo et al., 2023). The quantity of these emerging contaminants is likely to upsurge in water sources as a result of the rise in population density (Tijani et al., 2013), which is a community health problem. Organic pollutant exposure has been testified to lead to health implications such as endocrine disruption, immunotoxicity, neurological disorders, reductions in fertility, spontaneous abortions, birth defects, poisoning of genes, sexual organ annoyance, resistance of antibiotics and congenital disorders, even at low concentrations (Ramirez-Malule et al., 2020).

The rise in usage of synthetic compounds around the world, their level of occurrence in an aqueous environment and possible ecological and health implications highlight the need for constant monitoring and reporting of emerging contaminants in water sources (Selwe et al., 2022). Therefore, an extensive review that scrutinises the current state of emerging contaminants in water sources is necessary. In this chapter, the concepts of water sources, emerging contaminants and their pathways are discussed. Furthermore, analytical procedures, removal mechanisms, adverse health effects and mitigation measures of emerging contaminants are examined.

2.1.1 Water sources

The most crucial resource on earth is water and it represents 70% of the globe (Malewandja, 2018). It is a necessity for existence of all living organisms (e.g. animals and human beings) (Inyinbor et al., 2018). Water offers sustenance and enables the circulation of oxygen within living cells such as mitochondria (Moses, 2006). It also serves as a habitation for aquatic organisms and a reproduction home for some terrestrial organisms (Fawell and Nieuwenhuijsen, 2003). According to Adeleye (2016), continuous safe and clean water supplies are requirements for a decent and healthy living. Rivers, dams, lakes, canals and groundwater are the main sources of required fresh water which are recharged by rainwater (Ojemaye, 2020). Furthermore, wastewater may be a viable water resource, which when effectively managed, is crucial for future water security (Edokpayi et al., 2017).

2.1.1.1 Surface water as a water source

Any body of water that is exposed to the atmosphere and susceptible to runoff from the land is referred to as surface water. As it accumulates on the ground or in a stream, river, lake, reservoir or ocean, surface water is the most easily accessible type of water (Tufenkji et al., 2002). The WHO's (2017) approximations are that 144 million persons around the globe are dependent on surface water for survival. Drinking water and other public uses such as irrigation and the thermoelectric power industry to cool electricity-generating equipment are the main uses of surface water. It is very likely that surface water sources will contain microorganisms because the same surface water serves as a natural habitat for numerous living things. Additionally, surface water sources are frequently susceptible to contamination from humans, animals, storms or heavy rains (Bwire et al., 2020).

In addition, anthropogenic pollution is transported through rivers and lakes far from populated areas. This pollution can enter water resource systems as "point" discharges from industrial and/or urban activities, typically through a discharge pipe or as "diffuse" pollution from many sources within the hydrological catchment area (Jonsson, 2005). Particularly for society, the "effluent transport" function of rivers present a probable threat to downstream ecosystems and community health. The utility of the available water volume is significantly decreased by biological, chemical, thermal and possibly radiological pollution of the world's water resources (Blackstock and Richards, 2007).

2.1.1.2 Groundwater as a water source

Water that is found underground in voids and fissures in rock, sand and soil is known as groundwater. It is a scarce but important resource, making up about 37% of the non-ocean water on Earth, compared to 63% of ice and less than 0.5% of surface water (rivers, lakes). The hydrologic cycle includes groundwater as a key player because it interacts with surface water bodies and the atmosphere. The ocean, lakes, rivers and springs are fed by groundwater discharge (Trenberth et al., 2007). Rain and snow melt and seeps into the voids and crevices beneath the surface of the land and replenishes or recharges groundwater supplies. Water and air are present in the open spaces or pores of the unsaturated zone, which is immediately below the surface of the land. Underlying the unsaturated zone is the saturated zone, which is a region where water fills all of the pores and rock fractures (Beckie, 2013).

In many countries, groundwater is already preferred as a source of drinking water because it is more dependable than surface water (Carrard et al., 2019). It is typically free of the majority of pathogens and less susceptible to surface-derived contamination than surface

water. Since there is no land used for surface impoundments, losses due to evaporation are minimal. A stable, dependable supply can be provided by large aquifers. Around 50% of the world's drinking water is derived from groundwater (Zektser and Evertt, 2004). The majority of groundwater contamination begins at the surface of the land. Pollutants can easily enter groundwater supplies in areas where the material above the aquifer is permeable. Landfills, septic tanks, leaky underground petrol tanks and excessive fertiliser and pesticide use are among the sources of groundwater pollution. Groundwater will no longer be suitable for drinking if it is contaminated. In addition, contaminated surface water that recharges an aquifer will contaminate the groundwater (Beckie, 2013).

2.1.1.3 Wastewater as a water source

When significant amounts of solids, particulate matter, microorganisms, nutrients, heavy metals and micropollutants have negatively contaminated water, it is regarded as waste. In order to prevent further contamination of water sources, it must be treated before being released into another body of water. Every day, a large amount of wastewater is produced worldwide from a variety of sources. Industrial, municipal, stormwater, surface runoff and agricultural activities are some of the sources of wastewater. Rain and runoff that travels through street gutters and is eventually treated at a wastewater facility are referred to as stormwater. Municipal wastewater is the term for the liquid waste discharged by both residential and commercial properties that is contaminated with washing water, urine, faeces, and other substances (Warwick et al., 2013).

The different dissolved chemicals, and occasionally colours, found in industrial wastewater come from a variety of industrial processes, including food processing, the iron and steel industry, mines and quarries and textile factories. A high concentration of organic matter from animal and vegetable sources, microorganisms and different chemicals used to control pests and diseases are all present in agricultural effluents. Before being discharged into another body of water, wastewater must be treated to prevent further contamination of water sources. Before wastewater can be recycled or safely released into the environment, it needs to be properly treated (Adeleye, 2016).

Consequently, this can be accomplished using a range of wastewater treatment techniques, such as secondary treatment, waste stabilisation ponds and artificial or constructed wetlands (Edokpayi et al., 2017). Water security in the future depends on the wise management of wastewater, which is a usable water resource. Reclaimed and treated wastewater can be used for a variety of tasks, including flushing toilets, industrial processes, irrigation of gardens and other areas (Garcia and Pargament, 2015).

2.2 Methodology

This chapter aimed at comprehensively reviewing the literature related to emerging contaminants in water sources and their associated risks around the world. Theses, dissertations, essays, original articles, reviews, scientific reports and book chapters were used to retrieve relevant information. The information was mostly sourced from works focusing on surface water, groundwater and drinking water. Published articles or studies targeting wastewater treatment plants were also considered in this study. Keywords such as emerging contaminants, pharmaceuticals, herbicides, steroid hormones, water sources, personal care products and health impacts were used for literature search. Moreover, words such as analytical procedure, removal mechanisms and risk mitigations were also used during the literature search. The retrieved articles, student reports, scientific reports and book chapters only written in English were then scrutinised and only articles that reported primarily on emerging contaminants were included.

2.3 Results and discussion

After thorough analysis of theses, dissertations, essays, original articles, reviews, scientific reports and book chapters, only studies focusing on the occurrence of emerging contaminants in water sources such as surface water, groundwater, drinking water and wastewater influents and effluents were selected. Some of the concepts related to emerging contaminant pollution are discussed under (1) emerging contaminants; (2) sources and pathways of emerging contaminants; (3) their occurrence in water sources; (4) a global perspective; (5) a South African perspective on water sources; (6) analytical procedure for detection of emerging contaminants; (7) other analytical techniques; (8) removal mechanisms; (9) advanced treatment of emerging contaminants; (10) environmental health impacts of emerging contaminants; and (11) mitigation of risks associated with emerging contaminants.

2.3.1 Emerging contaminants

Organic compounds that were not recognised as important in freshwater and are currently being detected due to the improvement of analytical techniques, are referred to as emerging contaminants (Miraj et al., 2020). They are well known as man-made or naturally occurring organic compounds or microorganisms not presently examined in the environment or regulated by legislation; however, they possess the possibility to trigger serious implications to the environment and public health (Miraj et al., 2016).

Ojemaye (2016) described emerging contaminants as a sub-group of microcontaminants occurring in the environment at low level with perfect chemical properties, arrangements, application ranges and effects. The author further stated that emerging contaminants are compounds introduced late into the environment; compounds that were existing in the environment for a long period but were then only recently identified owing to the development of new analytical devices and chemical compounds whose adverse health implications are just showing.

Emerging pollutants in general are categorised as either nanomaterial; pharmaceutical; food additives; pesticides; personal care products; industrial chemicals; illicit and non-controlled drugs or endocrine disrupting compounds (Lodeiro et al., 2019). Their hastily growing use in homes, hospices, manufacturing, transport and farming activities leads to their introduction into surface water, groundwater and WWTPs at an increasing level (Oluwole et al., 2020). Depending on consumption patterns and places, their concentration can vary hourly, daily, seasonally, geographically, chronologically and socio-economically (Patel et al., 2019).

Pollution of water sources by organic chemicals is a serious community hazard that necessitates continuous monitoring (Malewandja, 2018). Many types of emerging contaminants are mostly identified in water sources. To deliver pragmatic and valued evidence, the study was confined only to the occurrence of herbicides, pharmaceuticals, steroid hormones and personal care products in water sources, including wastewater influent and effluent. The international and South African case studies are also covered in this chapter.

2.3.1.1 Herbicides

Pesticides are chemicals or chemical compounds manufactured with the intention to destroy, prevent, or control pests, unwanted kinds of plants or animals. The Food and Agricultural Organisation of the United Nations (2006), described pesticides as chemicals used in the production, processing, storage, transport of food, farm produce, animal feedstuffs, wood and wood commodities or chemicals used to control insects and pests in animal bodies. Generally, pesticides are aimed at controlling the growth of unwanted weeds or the presence of pests, insects and bacterial strains that may interfere with agricultural activities or cause the spread of diseases (Mugudamani et al., 2023). They are classified as herbicides, insecticides and fungicides. The widely known type of pesticides is herbicides and account for roughly 80% of all pesticides in application (Ojemaye et al., 2020).

Herbicides are chemical substances widely used in agricultural production (Wang et al., 2022) and other areas such as in forestry, parks, golf courts and sports ground (Slevanovic

et al., 2019) to either kill or severely injure undesirable plants (Casida, 2019). Herbicides may be classified as alachlor, metolachlor, butachlor, simazine, atrazine, 2,4-Dichlorophenoxyacetic acid (2,4-D), terbutylazine, atraton, prometryn, terbutryn, diuron, propyzamide, haloxyfop, 2-methyl-4-chlorophenoxyacetic acid (MCPA) and oxyfluorfen (Ojemaye, 2020; Wang et al., 2022).

2.3.1.2 Pharmaceuticals

They are anthropogenic or natural chemical compounds used as a life supplement, to diagnose, treat, or prevent an ailment in both persons and animals. In people and animal bodies, pharmaceuticals are known to have dissimilar chemical structures, behaviour, applications and metabolism (Jiang et al., 2013). They are designed as specific bioactive compounds which interact with receptors in the human body and in animals or to target specific infectious organisms and induce specific biological responses at low doses (Galus et al., 2013a). According to Kanama et al. (2018), pharmaceuticals are used for alteration of physiology and biochemical processes in humans and animals in order to treat, diagnose or prevent ailments. They are classified as non-steroidal anti-inflammatory drugs (NSAIDs) (i.e. acetaminophen); antibiotics (such as ampicillin); beta-blockers (such as atenolol); lipid regulators (such as clofibrate); antiepileptic drugs (such as carbamazepine); anti-psychotic (such as thioridazine); antivirals (such as lamivudine) and human indicators or psychomotor stimulants (such as caffeine).

The widespread usage of pharmaceuticals by human beings and for animals has contributed to their detection in the environment (Kummerer, 2010). These pollutants are firm and manufactured to be robust, which make it impossible to be broken down by the current wastewater treatment processes. Furthermore, their polar and non-volatile nature leads to their partial elimination in wastewater treatment plants and subsequently in their discharge into the natural water resources (Baker and Kasprzyk-Hordern, 2013). They are regarded as pseudo-persistent contaminants, which frequently enter the water environment at concentrations stretching from $\text{ng/l}-1$ to low $\mu\text{g/l}-1$ (Gogoi et al., 2018). Their frequent release may cause health effects to aquatic organisms and humans (Lindberg et al., 2007).

2.3.1.3 Personal care products

Personal care products are considered to be chemical compounds found mostly in customer products sold for human body use (Barceló and Petrovic, 2007). Jiang et al. (2013) indicated that personal care products are manufactured for external human body use and not for ingestion in most cases. These chemicals are found mostly in cosmetics, skin care, dental products, hair care products, sunscreen agents, soaps, antibacterial products, fragrances

and insect repellents (Barceló and Petrovic, 2007). They are classified into compounds such as fragrance (e.g. polycyclic musks), preservatives (e.g. parabens), antiseptics (e.g. triclosan) and sun screen (e.g. benzophenone) (Ojemaye, 2020).

Personal care products are non-recommended products and as a result they are overused and directly discharged into the aqueous environment. Their direct discharge into the environment is mainly through consistent usage in showering, spraying, washing of clothes, swimming, sunbathing and improper disposal (Miraj et al., 2016). They are released into wastewater and advance toward WWTPs in their original or biologically transformed structures (Gogoi et al., 2018). Effluents and surface water have been found to contain concentrations of personal care products and their metabolites as a consequence of their lipophilic nature and non-biodegradability (Jiang et al., 2013).

2.3.1.4 Steroid hormones

Steroid hormones are natural or synthetic compounds widely used as contraceptives and for growth promotion in humans and animals (Bexfield et al., 2019). Steroid hormones can be classified into estrogens, androgens, progestogens, glucocorticoids and mineralocorticoids. Natural steroids mainly originated from the excretion (faeces and urine) of humans, livestock, and aquaculture. Some natural and synthetic steroids have also been used as pharmaceuticals in human daily life for many reasons, such as contraception and human therapy and as growth promoters in farm animals to inhibit and treat sicknesses, stimulate development and maximise productivity. These steroids and their metabolites may pose high risks to aquatic organisms at very low environmental concentrations as they are constantly introduced into the environment (Ying et al., 2013). These compounds have the ability to mimic or hinder hormones, altering normal bodily functions (Gogoi et al., 2018), consequently causing serious medical implications such as cancer, reproductive impairment, cognitive deficits and obesity (La-Merrill et al., 2020).

2.3.1.5 Flame retardants

Flame retardants are defined as substances that can delay or prevent combustion (Roca, 2016). Chemical Safety Facts (CSF, 2021) described flame retardants as chemicals that are added in flammable materials to inhibit fire ignition or slow its blow-out. Flame retardants are classified based on their chemical structures and properties (Collaborative on Health and the Environment [CHE], 2019). For the flame retardants to work effectively, different chemistries with various properties and molecular structures are regularly mixed (Kasprzyk-Hordern, 2008). According to Rocca (2016), flame retardants fall into groups such as halogenated

organics, phosphorus-based, nitrogen-based, other inorganic compounds and mineral compounds.

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

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

2.3.1.6 Illicit drugs and non-controlled drugs

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

2.3.1.7 Food additives

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

Furthermore, drugs, sanitary products, personal care and pharmaceutical products also contain certain amounts of artificial sweeteners. They are regarded as emerging contaminants as a result of their persistent occurrence and world-wide presence in various water matrices. Artificial sweeteners may cause serious toxic effects in the ecosystem, plant growth and aquatic organisms because of the incapability of current wastewater treatment processes to completely eliminate them. Depending on their concentration level, persistence and bioaccumulation potential, artificial sweeteners may cause serious toxic effects in the ecosystem, plant growth and aquatic organisms (Naik et al., 2021).

2.3.1.8 Nanomaterials

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

The European Commission (2011) categorised nanomaterials as natural, incidental or engineered. Engineered nanoparticles consist of carbon-based and inorganic forms, partly with a functionalised surface (Bundschuh et al., 2018). Inorganic compounds such as titanium dioxide and nano-silver, as well as organic compounds such as carbon nanotubes, are classified as nanoparticles (Lin et al., 2010). Carbon nanotubes are used in the manufacturing of tennis racquets, whereas titanium dioxides are used as a sunscreen in cosmetics. Silver nanoparticles are used to decrease smell in outfits such as socks,

2.3.2.1 Point source of emerging contaminants

The point source of contamination signifies any detectable source of contamination from which contaminants are released (Mandaric, 2018). Household waste, hospital wastewater outflows, industrial activities, agricultural activities and wastewater effluents, which are frequently being released to the streams and rivers, are some of the examples of point source pollution (Stefanakis and Becker, 2016). Emerging contaminants are classified as either natural or man-made chemical compounds. Natural chemical compounds such as hormones are emitted from excretion of vertebrates and invertebrates groups, whereas man-made chemical compounds are produced by manufacturing industries (Janna, 2011). In factories or manufacturing industries such as pharmaceuticals and personal care product industries, mining, rubber industries, corrosion inhibitors and pesticide industries, contaminants of emerging concern are manufactured regularly or utilised as a raw material to make other substances (Moon et al., 2007). Furthermore, effluents are also discharged into the environment from these manufacturers or industries that contain various substances, such as pharmaceuticals, personal care products, flame retardants, alkylphenols and polycyclic aromatic hydrocarbons, phthalates and pesticides (Janna, 2011).

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

Another significant point source of various emerging contaminants is households. Many pharmaceuticals and personal care products such as trimethoprim, ibuprofen, diazepam, metoprolol, polycyclic and macrocyclic musk or benzophenone are frequently discarded from household solid waste or flushed down in the toilet (Stefanakis and Becker, 2016). Dumping of pharmaceuticals with household solid waste consequently leads to the introduction of these chemical compounds in landfills leachates which also pollute groundwater. Moreover, in regions where the water table is too high, water pollution with pharmaceuticals and

personal care products from onsite wastewater disposal systems such as septic tanks may occur (Stefanakis and Becker, 2016; Pal et al., 2010).

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

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

2.3.2.2 Non-point source of emerging contaminants

According to Darradi et al. (2012), a nonpoint source contamination can be defined as a diffuse pollution in nature that occurs over a wide geographic scale. They are not connected to a particular source and cannot be readily defined in a specially or temporally obvious way (Ncube et al., 2021). Although nonpoint sources are associated with lighter loads of contaminants (Lapworth et al., 2012), they are responsible for most of the surface contamination and are hence a serious threat to the aquatic ecosystems (Darradi et al., 2012). Urban runoff may be regarded as a nonpoint source of emerging contaminants. Urban run-off occurs because of impermeable surfaces such as roads, housing and construction sites, which are typical features of urbanisation. It carries contaminants straight into surface water, particularly during rainy seasons (Gerber, 2019).

Other examples of nonpoint sources are sediments from mining activities, loose river banks, poorly managed construction sites and forestry. Livestock bacteria and nutrient, atmospheric deposition and hydro-modifications are also regarded as nonpoint sources of pollution. Furthermore, farming and forestry activities may contribute to diffusion of micro-pollutants in the surface water and groundwater through leakages from manures used as fertilisers and

washing away of pesticides used in agriculture and forestry (Mandarić, 2018). Discharge of nonpoint source contaminants into the water environment is a serious threat to the entire biosphere of an aquatic environment (Wu and Chen, 2013; Mandarić, 2018).

2.3.3 Emerging contaminants in water sources

Almost one-third of all available freshwater is used for anthropogenic purposes, including industry, agriculture and domestic use, which simultaneously result in their contamination by numerous different organic contaminants. Organic substances, together with their derivatives, are eventually introduced into different water sources after serving their primary purpose in these industries (Bagheri, 2021). Once these chemicals enter the water sources, they put pressure on the quality of water bodies, raising concerns about the risks on ecosystems and the population (Liu et al., 2014). Most of these contaminants are detected in various water matrices such as hospital discharges, wastewater influents and effluents, surface water, groundwater and drinking water and are traceable in every continent due to human activities (Ort et al., 2010).

Manufacturing plants, hospitals, sewage deterioration, rainfall, sampling uncertainties and analytical procedures all have a role in the production of these chemical compounds. Depending on consumption patterns and places, their concentration can vary hourly, daily, seasonally, geographically, chronologically and socio-economically (Ort et al., 2010). Emerging pollutants in water matrices are detected differently in different nations and even different locations of the same country (Ebele et al., 2017). To deliver a pragmatic and valued evidence, the study was confined only to the occurrence of herbicides, pharmaceuticals, steroid hormones and personal care products in water sources, including wastewater influents and effluents. Some of the case studies related to the quantities of emerging contaminants, such as pharmaceuticals, personal care products, herbicides and steroid hormones, are presented in this section.

2.3.4 Case studies: Global perspective

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

Pharmaceuticals are a broad category of chemical pollutants that come from human consumption, excretion and veterinary use. Most of the pharmaceuticals identified in surface water, groundwater and drinking water are classified as NSAIDs, antibiotics, beta-blockers, antiepileptics, antipsychotic, lipid regulators, antivirals and psychomotor stimulants (Ngqwala and Muchesa, 2020). The primary classes of personal care products are antiseptics,

fragrances, insect repellents, preservatives and UV fillers. Several studies have detected the concentration of pharmaceuticals and personal care products in various water matrices in different concentrations (Petersen, 2016) and some of the scenarios of the occurrence of pharmaceuticals and personal care products in international surface water, groundwater and drinking water are discussed below and summarised in Table 2.1.

Non-steroidal anti-inflammatory drugs

NSAIDs are drugs utilised as antipyretic, anti-inflammatory and analgesic agents. Muscle soreness, dysmenorrhea, rheumatic diseases, pyrexia, gout and migraines are all routinely treated with them. Additionally, in some cases of acute trauma, they are employed as opioid-sparing medicines. Aspirin, diflunisal, salsalate, naproxen, ibuprofen, diclofenac, indomethacin, meloxicam, piroxicam, meclofenamate and mefenamic acid are some of the medications that are included under NSAIDs (Ghlichloo and Gerriets, 2022). The occurrence of these drugs has been detected in the surface water, groundwater and drinking water of many countries. In Lagos, Nigeria, Ogah et al. (2020) conducted a study on pharmaceuticals in the environment focusing on the quantities of selected drugs in several water matrices and reported concentrations of NSAIDs such as diclofenac in borehole water as 0.39 mg/l, treated drinking water as 0.17 mg/l and well water as 0.73 mg/l. In Montana, United States, a study was conducted in the Helena valley groundwater to detect pharmaceuticals, personal care products, endocrine disruptors and microbial indicators of faecal contamination and reported the maximum concentration of diclofenac in groundwater as 46 ng/l (Miller and Meek, 2006).

In Germany, Ferrari et al. (2004) in their study of environmental risk assessment of six human pharmaceuticals reported the occurrence of diclofenac in surface water at a mean concentration of 1.2 µg/l. A pilot study along the Skaneateles Lake in New York State, United States, reported ibuprofen at a concentration ranging from not detected (ND) to 1.16 ng/l in treated drinking water (Subedi et al., 2015). Wilkinson et al. (2017) conducted a study on spatial distribution of organic contaminants in three rivers of Southern England bound to suspended particulate material and dissolved in water, and recorded the concentrations of acetaminophen and diclofenac in the upper stream at mean concentrations of 20.8 ng/l and 11.4 ng/l, respectively. A study in the Mississippi River in New Orleans, Louisiana in the United States, revealed contamination by ibuprofen (<1–34 ng/l), acetaminophen (25–65 ng/l) and naproxen (<1–135 ng/l) (Zhang et al., 2006).

Choi et al. (2008) looked at the concentrations of several pharmaceutical residues in surface water of the Han River, Korea, and detected the concentration of acetaminophen as 34.8 ng/l. In a nationwide reconnaissance of contaminants of emerging concern in source

and treated drinking water of the United States conducted in two phases, maximum concentration of tramadol was detected in source water as 23.04 ng/l during phase two (Glassmeyer et al., 2016). Fairbairn et al. (2015), in the United States focused on sediment–water distribution of contaminants of emerging concern in a mixed-use watershed and detected acetaminophen in surface water stretching from 0.99–7.0 ng/l. Another study detected several pharmaceuticals such as mefenamic acid (ND–326 ng/l) and indomethacin (ND–33.5 ng/l) in surface water from the Mankyung River, South Korea (Kim et al., 2009b).

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

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

Chen et al. (2008) reported concentrations of ketoprofen (110–620 ng/l), ibuprofen (<12–30 ng/l) and diclofenac (24–62 ng/l) in Taiwanese rivers. Another study in Lagos, Nigeria, reported maximum concentrations of acetylsalicylic acid (0.13 µg/l), diclofenac (0.27 µg/l), fenoprofen (<0.02 µg/l), ibuprofen (8.84 µg/l), ketoprofen (<0.02 µg/l) and naproxen (0.03 µg/l) in surface water (Olarinmoye et al., 2016). In urban water bodies around southern Brazil, mean concentrations of various steroid hormones and NSAIDs in the Cancela-Tamandaí and João Goulart catchments were detected (Pivetta and Gastaldini, 2019). Among the NSAIDs, diclofenac, ibuprofen and paracetamol were detected in the Cancela-Tamandaí at a mean concentration of 0.060 µg/l, 1.266 µg/l and 2.975 µg/l, correspondingly. In the João Goulart catchments, their respective mean concentrations were

0.069 µg/l, 0.515 µg/l and 0.426 µg/l. In Hanoi, Vietnam, concentrations of ketoprofen (<40–330 ng/l), ibuprofen (100–1 100 ng/l), diclofenac (<140–310 ng/l) and naproxen (80–380 ng/l) were reported in surface water (Tran et al., 2014).

Furthermore, in China (Beijing) concentrations of ibuprofen (<LOD–17.17 ng/l), antipyrine (0.15–0.22 ng/l) and aminopyrine (0.17–0.64 ng/l) were detected among the NSAIDs in treated drinking water (Cai et al., 2015). The study also detected concentrations of naproxen (<LOD–3.12 ng/l) and diclofenac (<LOD–2.37 ng/l) in treated drinking water. In groundwater around northern China, maximum concentrations of ibuprofen in unconfined aquifers were detected as 24.50 ng/l and 42.99 ng/l during the wet and dry season, respectively (Wu et al., 2020).

Antibiotics

Both human and animal health depends heavily on antibiotics. They are produced to treat pathogen-caused illnesses. They included compounds such as amoxicillin, erythromycin, fluoroquinolones, sulfamethoxazole, tetracycline, trimethoprim, doxycycline, ciprofloxacin, ofloxacin, lincomycin, norfloxacin, azithromycin, oxytetracycline and florfenicol. As the current sewage treatment works are unable to completely eliminate these compounds, they end up entering natural surface water, groundwater and drinking water (Viana et al., 2021). Choi et al. (2008) reported a mean concentration of sulfamethoxazole (26.9 ng/l) in the Han River, Korea. Sulfamethoxazole was also reported in German's surface water at a mean concentration of 0.48 µ/l (Ferrari et al., 2004).

In Cape Cod, Massachusetts, United States, a maximum concentration of sulfamethoxazole was reported as 113 ng/l in well water (Schaidler et al., 2014). Miller and Meek (2006), reported a maximum concentration of sulfamethoxazole in groundwater as 490 ng/l in Montana, United States. In Mankyung River, South Korea, pharmaceuticals such as clarithromycin and erythromycin were detected at concentrations ranging from ND to 443 ng/l and ND to 137 ng/l, respectively (Kim et al., 2009b). In the United States, the maximum concentration of sulfamethoxazole in source water was 161.1 ng/l. while in treated drinking water it was 8.2 ng/l (Glassmeyer et al., 2016). Another study conducted in the Nairobi River Basin in Kenya, reported maximum concentrations of sulfamethoxazole, trimethoprim and ciprofloxacin as 13.8 mg/l, 2.6 mg/l, and 0.5 mg/l, respectively (Ngumba et al., 2016). In Beijing, China, the concentration of sulfamethoxazole in treated drinking water ranged from <LOD to 1.81 ng/l among antibiotics (You et al., 2015).

Lin et al. (2015) reported concentrations of various antibiotics in Taiwan, such as sulfadiazine (0.1–14.4 ng/l), sulfamethoxazole (0.2–1 820 ng/l), sulfathiazole (0.7–3.0 ng/l),

sulfamethazine (1.6–28.9 ng/l), sulfahamonomethoxine (0.6–1.8 ng/l), sulfadimethoxine (0.8–4.3 ng/l), erythromycin-H₂O (54.8 ng/l), clarithromycin (6.9 ng/l), nalidixic acid (1.6–16.4 ng/l), flumequine (2.4–6.6 ng/l), pipemidic acid (10.2 ng/l), norfloxacin (9.3 ng/l), ofloxacin (0.9–11.8 ng/l), dimetridazole (1.8 ng/l) and metronidazole (26.2 ng/l) in groundwater.

In Bangladesh, Hossain et al. (2018) reported concentrations of sulfadiazine (< LOD–0.58 ng/l), sulfamethazine (< LOD–4.19 ng/l), sulfamethoxazole (< LOD–7.24 ng/l), sulfamethizole (< LOD–11.35 ng/l), trimethoprim (< LOQ–17.20 ng/l), erythromycin (< LOD–6.46 ng/l), tylosin (< LOD–16.68 ng/l) and metronidazole (0.05–13.51 ng/l) in rivers. In Chongqing, China, rivers were found to be polluted by antibiotics such as erythromycin-H₂O (1.41–156 ng/l), roxithromycin (0.6–88.4 ng/l), azithromycin (2.6–166.5 ng/l), sulfamethazine (ND–3.7 ng/l), sulfamethoxazole (0.44–115.3 ng/l), sulfadiazine (0.36–26.7 ng/l), trimethoprim (0.4–20.5 ng/l), ofloxacin (3.1–114.1 ng/l), norfloxacin (ND–92.4 ng/l) and moxifloxacin (ND–6.4 ng/l) (Yan et al., 2015).

A study in rivers within the tropical urban catchment of Singapore reported concentrations of the antibiotic chloramphenicol ranging from <0.07 to 1.53 ng/l (You et al., 2015). Another study in mangrove ecosystems of Singapore detected concentrations of lincomycin (0.04–1.36 ng/l), chloramphenicol (0.003–0.70 ng/l), sulfadiazine (0.04–0.80 ng/l), sulfamerazine (0.03–0.24 ng/l) and sulfamethazine (0.6–6.26 ng/l) in surface water (Bayen et al., 2016). A pilot study conducted along the Skaneateles Lake in New York, United States, reported sulfamethoxazole ranging from ND to 0.39 ng/l, among the antibiotics in treated drinking water (Subedi et al., 2015).

In Lusaka, Zambia, Ngumba et al. (2018) detected the antibiotics trimethoprim, sulfamethoxole, ciprofloxacin, tetracycline, doxycycline and amoxicillin at mean concentrations of 2 410 ng/l, 11 800 ng/l, 400 ng/l, 2 200 ng/l, 2 730 ng/l and 2 500 ng/l, respectively. In Kenya, Kairigo et al. (2020) reported mean concentrations of norfloxacin, trimethoprim, ciprofloxacin, sulfamethoxole in upstream surface water as 1.6 µg/l, 3.8 µg/l, 2.5 µg/l and 96.9 µg/l, respectively.

In Lagos, Nigeria, Ogah et al. (2020) detected concentrations of ofloxacin in borehole water and treated drinking water as 0.24 mg/l and 0.08 mg/l, respectively. Another study in Lagos, Nigeria, detected maximum concentrations of antibiotics such as chloramphenicol (0.36 µg/l), chlortetracycline (<0.05 µg/l), clarithromycin (<0.05), doxycycline (<0.05 µg/l), erythromycin (1.00 µg/l), sulfadiazine (0.04 µg/l), sulfadimidine (<0.01 µg/l), sulfa-

methoxazole (1.50 µg/l), tetracycline (<0.05 µg/l) and trimethoprim (0.40 µg/l) in surface water (Olarinmoye et al., 2016).

Lin et al. (2020) reported concentrations of the antibiotics sulfamethoxole, enrofloxacin, oxytetracycline and florfenicol in river samples in China, ranging from ND to 39.6 ng/l, ND to 45.8 ng/l, 85.0 to 375.9 ng/l and ND to 287.5 ng/l, respectively. In North China, maximum concentrations of various antibiotics in groundwater during the wet and dry season were reported as erythromycin (1.55 and 1.71 ng/l); sulfamonomethoxine (3.43 and 12.39 ng/l); sulfathiazole (3.86 and 2.24 ng/l); sulfisoxazole (1.51 and 16.73 ng/l); sulfamerazine (2.49 and 0.69 ng/l); sulfamethazine (0.49 and 0.83 ng/l); sulfamethoxazole (19.29 and 11.01 ng/l); chloramphenicol (0.55 and 0.16 ng/l) and trimethoprim (1.03 and 3.23 ng/l) (Wu et al., 2020).

Beta-blockers

Beta-blockers are frequently used for the treatment of cardiovascular illnesses such as hypertension, cardiac arrhythmias, tachycardia, thyrotoxicosis, hypertrophic subaortic stenosis or ischemic heart disease. Additionally, they are used to treat acute panic feelings in anxious circumstances, as well as ocular pressure in glaucoma treatment and migraine prophylaxis. The wastewater treatment plants do not entirely eliminate these chemicals and as a result, they are found in surface water, groundwater and drinking water in many different nations. Atenolol, propranolol, metoprolol, bisoprolol and betaxolol are the most used beta-blockers (Iancu et al., 2020). In the United States metoprolol in source water and treated drinking water were detected at maximum concentrations of 35.7 ng/l and 18.4 ng/l, correspondingly (Glassmeyer et al., 2016).

In Germany, a study by Ferrari et al. (2004) reported propranolol at a mean concentration of 0.59 µg/l in surface water. A study conducted in groundwater in Taiwan detected concentrations of beta-blockers such as atenolol (3.6 ng/l) and acebutolol (0.7 ng/l) (Lin et al., 2015). In surface water of the Mankyung River in South Korea, beta-blockers such as atenolol (ND–690 ng/l) and propranolol (ND–40.1 ng/l) were detected (Kim et al., 2009b). In Chongqing, China, the beta-blocker metoprolol was detected at concentrations ranging from 0.46 to 17.3 ng/l in river water (Yan et al., 2015). In the Skaneateles Lake in New York State, United States, atenolol was detected at concentrations ranging from ND to 19.5 ng/l among the beta-blockers in treated drinking water (Subedi, 2015).

Antiepileptics

Patients with epilepsy are treated with antiepileptic drugs. Carbamazepine is the most popular and commonly used antiepileptic medication. Pharmaceuticals are not effectively

removed from wastewater, thus they are released into rivers together with wastewater effluent, where they may seep into groundwater or be absorbed by water treatment facilities. There have been instances of carbamazepine in drinking water despite the use of sophisticated water treatment techniques (Rezka et al., 2015). In Cape Cod, Massachusetts, United States, Schaidler et al. (2014) detected anticonvulsants such as phenytoin and carbamazepine in well water at maximum concentrations of 66 ng/l and 72 ng/l, respectively. Another study conducted in Helena valley groundwater in Montana, United States, reported detection of carbamazepine and dilantin in groundwater with maximum concentrations of 22 ng/l and 420 ng/l, respectively (Miller and Meek, 2006).

Ferrari et al. (2004), in their study conducted in Germany on environmental risk assessment of six human pharmaceuticals in an aquatic environment detected carbamazepine at a mean concentration of 1.1 µg/l. Lin et al. (2015) conducted a study in Taiwanese groundwater and detected carbamazepine with concentrations ranging from 0.4 to 37.9 ng/l. In the United States, maximum concentrations of carbamazepine were reported as 269 ng/l and 586 ng/l in source water and treated drinking water, respectively, during Phase 1. During Phase 2, carbamazepine was detected in source water at a maximum concentration of 35.7 ng/l and in treated drinking water at a maximum concentration of 26.50 ng/l (Glassmeyer et al., 2016).

In the Mississippi, Louisiana, United States, carbamazepine ranging from 43 to 114 ng/l was reported as surface water contaminants (Zhang et al., 2006). In South Korea, the Mankyung River was contaminated by carbamazepine with a concentration ranging from ND to 595 ng/l (Kim et al., 2009b). In Bangladesh, Hossain et al. (2018) reported the concentration of carbamazepine ranging from <LOD to 8.80 ng/l among the antiepileptic drugs in the Old Brahmaputra River. Antiepileptic drug carbamazepine was detected in drinking water at concentrations ranging from 0.41 to 10.3 ng/l in Chongqing, China (Yan et al., 2015).

In the mangrove ecosystems of Singapore, concentrations of carbamazepine ranging from 0.06 to 4.63 ng/l in surface water was reported (Bayen et al., 2016). Tran et al. (2014) detected carbamazepine ranging from <0.144 to 0.53 ng/l in surface water around Hanoi, Vietnam. In Lagos, Nigeria, a study detected a maximum concentration of carbamazepine in surface water as <0.01 µg/l (Olarinmoye et al., 2016). Furthermore, a study in Beijing, China, detected concentrations of carbamazepine ranging from 0.37 to 1.15 ng/l in drinking water and 0.51 to 38.24 ng/l in treated drinking water (Cai et al., 2015).

Antipsychotics

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

A study by Ferrari et al. (2004) in the Guandu River, Rio de Janeiro, Brazil, reported concentrations of bromazepam, clonazepam and diazepam in all samples of surface water at maximum concentrations of 42 ng/l, 198 ng/l and 335 ng/l, respectively. A study in a tropical urban catchment of Singapore reported a concentration of an antipsychotic drug such as sulpiride ranging from <0.1 to 1.23 ng/l in river water (You et al., 2015). Another study in Singapore's mangrove ecosystems detected concentrations of antipsychotics such as risperidone (0.03–0.21 ng/l) in surface water (Bayen et al., 2016). In Lagos, Nigeria, a maximum concentration of antipsychotic drugs such as diazepam (<0.01 µg/l) was detected in surface water (Olarinmoye et al., 2016).

Lipid regulators

The high usage of blood lipid regulators has led to the introduction of chemical compounds such as bezafibrate, clofibric acid, gemfibrozil, fenofibric acid, simvastatin, etofibrate and atorvastatin in aquatic environments. The majority of fibrates were excreted unaltered (Rosal et al., 2010). Lipid lowering agents such as bezafibrate (ND–31.4 ng/l), clofibric acid (ND–17.2 ng/l), gemfibrozil (ND–1.4 ng/l), simvastatin (2.3–16.7 ng/l) and atorvastatin (ND–0.6 ng/l) were detected in river water in Chongqing, China (Yan et al., 2015).

Lin et al. (2015) reported concentrations of lipid regulators and cholesterol-lowering drugs such as clofibric acid and bezafibrate, ranging from 0.1 to 1.0 ng/l and 0.1 to 256.7 ng/l, respectively, in groundwater in Taiwan. Another study conducted in the Pearl River Delta in Guangzhou, South China, revealed the presence of acidic pharmaceuticals such as clofibric acid in water samples with maximum concentrations of 248 ng/l (Peng et al., 2009). In the mangrove ecosystems of Singapore, a study detected concentrations of lipid regulators such as gemfibrozil ranging from 0.77 to 17.7 ng/l in surface water (Byen et al., 2016). A study conducted in the Mississippi River in Louisiana, United States, revealed the prevalence of clofibric acid at concentrations ranging from 3 to 27 ng/l (Zhang et al., 2006). A preliminary

study in Hanoi, Vietnam, detected lipid regulators such as clofibric acid (<0.05 ng/l) and gemfibrozil (<0.05 ng/l) in surface water (Tran et al., 2014).

Olarinmoye et al. (2016) in Lagos, Nigeria, detected a maximum concentration of lipid regulators such as bezafibrate (<0.02 µg/l), clofibric acid (0.04 µg/l), etofibrate (<0.02 µg/l), fenofibrate (<0.04 µg/l) and gemfibrozil (<0.02 µg/l) in surface water. In treated drinking water around Beijing, China, concentrations of bezafibrate ($<\text{LOD}$ – 0.16 ng/l) and clofibric acid ($<\text{LOD}$ – 1.37 ng/l) were detected among the lipid regulators, whereas in a drinking water treatment plant only bezafibrate was detected, ranging from 0.31 to 0.85 ng/l (Cai et al., 2015).

Human indicators or psychomotor stimulants

As one of the most common psychoactive chemicals taken globally, caffeine is a human indicator or psychomotor stimulant that is found in coffee, tea, soft drinks and chocolate. Because it stimulates the central nervous system and has the short-term effect of revitalising the body and regaining attention, caffeine is widely ingested. Numerous countries have reported the occurrence of caffeine in natural waters (Edwards et al., 2015). A study in the United States detected and reported maximum concentrations of caffeine in source water and treated drinking water during Phase 1 as 124 ng/l and 88 ng/l, respectively. Furthermore, caffeine was detected in source water at a maximum concentration of 90.89 ng/l during Phase 2 (Glassmeyer et al., 2016).

The concentrations of caffeine in the Han River in Korea, was detected as 268.7 ng/l (Choi et al., 2008). In urban groundwater sources of Zambia, a maximum concentration of caffeine (1.7 ng/l) was detected during the wet season (Sorensen et al., 2015). Lin et al. (2015) conducted a study in groundwater in Taiwan, targeting the occurrence of pharmaceuticals, hormones and perfluorinated compounds, and reported caffeine as the only psychostimulant at concentrations ranging from 1.2 to 930.7 ng/l. In the United States, a study detected caffeine in surface water at concentrations ranging from 0.84 to 250 ng/l (Fairbairn et al., 2015).

Rivers within a tropical urban catchment in Singapore reported concentrations of caffeine ranging from 33.9 to 644.5 ng/l (You et al., 2015). Another study in the Singapore mangrove ecosystems reported concentrations of caffeine ranging from 5 to $1\,389$ ng/l in surface water (Bayen et al., 2016). In the Mississippi River in New Orleans, Louisiana, United States, a study revealed the concentration of caffeine ranging from <1 to 38 ng/l (Zhang et al., 2006). In the Skaneateles Lake in New York, United States, caffeine in treated drinking water was detected at concentrations ranging from ND to 11.1 ng/l (Subedi et al., 2015). In North China, human indicators such as caffeine was detected in groundwater at maximum

concentrations of 782.62 ng/l and 461.87 ng/l during wet and dry season, respectively (Wu et al., 2020).

Antivirals

Antivirals are medications that are primarily used to treat the human immunodeficiency virus (HIV), including abacavir, nevirapine, zidovudine, lamivudine and stavudine. Acyclovir and penciclovir for the treatment of herpes infections are also included, as are medications like ribavirin for the treatment of Hepatitis C and oseltamivir for the treatment of influenza A and B. Similar to other medications, these substances are partially digested in patients and then eliminated through the urine or faeces. Therefore, they can pollute the environment through discharges from wastewater treatment plants (Prasse et al., 2010). Because of probable ecosystem changes and the emergence of antiviral resistance, the environmental release of antiviral medications is highly concerning (Nannou et al., 2020). In the Nairobi River Basin of Kenya, a study was conducted to determine the occurrence of antibiotics and antivirals and reported maximum concentrations of lamivudine, nevirapine and zidovudine in river water as 5.4 mg/l, 4.8 mg/l and 7.7 mg/l, respectively (Ngumba et al., 2016). In the Chunga River in Lusaka, Zambia, Ngumba et al. (2020) reported nevirapine, zidovudine and lamivudine among the antiretroviral drugs at average concentrations of 210 ng/l, 1 280 ng/l and 49 700 ng/l, respectively. In Kenya, the mean concentrations of lamivudine, zidovudine and nevirapine in upstream surface water were reported as 219.6 µg/l, 2.1 µg/l and 0.9 µg/l, respectively (Kairigo et al., 2020).

Antiseptics

An antiseptic is a chemical that inhibits or retards microbial growth. In hospitals and other health care facilities, antiseptics are widely utilised for a variety of topical and hard-surface applications (Mcdonnell and Russell, 1999). Even in tiny amounts, the release of these chemicals into aquatic environments may have harmful consequences on aquatic organisms and public health (Das et al., 2014). In China, Lin et al. (2020) detected triclosan in river samples at concentrations ranging from 61 to 660 ng/l. In North China, maximum concentrations of triclosan in groundwater during the wet and dry season were detected as 18.05 ng/l and 109.90 ng/l, respectively (Wu et al., 2020). A pilot study along the Skaneateles Lake in New York State, United States, reported antiseptics such as triclosan and triclocarban in treated drinking water at concentrations ranging from ND to 1.93 ng/l and ND to 20.2 ng/l, respectively (Subedi et al., 2015). Another study in the Mississippi River in New Orleans, Louisiana, United States, revealed concentrations of triclosan ranging from 9 to 26 ng/l (Zhang et al., 2006). In Zambia, triclosan in groundwater was detected at maximum concentrations of 0.02 ng/l and 0.03 ng/l during the dry and wet season, respectively (Sorensen et al., 2015).

Insect repellent

To ward off mosquitoes, ticks, flies and other biting insects, people use insect repellents. Insect repellents, which are rinsed off skin during recreation, bathing and doing laundry, is one of the emerging contaminants that puts a lot of strain on stream ecosystems (Campos et al., 2016). Fairbairn et al. (2015) conducted a study in South Fork of the Zumbro River in South-eastern Minnesota and detected N, N-diethyl-meta-toluamide (DEET) with concentrations ranging from 7.2 to 110 ng/l and a mean concentration of 27 ng/l in surface water. In China, a study reported the occurrence of DEET in surface water at concentrations ranging from 0.8 to 10.2 ng/l (Sun et al., 2015).

These case studies cited above demonstrated that the water sources of many countries contain pharmaceuticals and personal care product pollutants. Since these medications are an integral part of modern lifestyles around the world, their introduction into water sources is inevitable. Emissions of medical, industrial, agricultural or household wastes or improper disposal of pharmaceuticals and personal care product wastes may introduce these compounds in rivers, lakes, wells, groundwater, treated drinking water and WWTPs.

The inability of water treatment methods to remove these compounds may lead to the detection of organic substances such as antibiotics, antivirals, antiepileptics, antiseptics and NSAIDs in drinking water. Moreover, runoff from animal production farms after insufficient absorption and excretion from animal bodies may lead to their introduction in nearby water sources.

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

Pharmaceuticals and personal care products	Country	Concentration in various water matrices						References
		Surface Water		Groundwater		Drinking Water		
		Range	Mean	Range	Mean	Range	Mean	
Non-steroidal anti-inflammatory drugs (NSAIDs)								
Acetaminophen	United States	0.99–7.0 ng/l	3.5 ng/l					Fairbairn et al., 2015
	United States	25–65 ng/l						Zhang et al., 2006
	China	0.5–445.6 ng/l						Yan et al., 2015
	Singapore	<4–159 ng/l						You et al., 2015
	Taiwan			0.9–1036 ng/l				Lin et al., 2015
	Korea		34.8 ng/l					Choi et al., 2008
	England		20.8 ng/l					Wilknson et al., 2017
Antipyrine	China					0.15–0.22 g/l		Cai et al., 2015
Aminopyrine	China					0.17–0.64 g/l		Cai et al., 2015
Diclofenac	Germany		1.2 µg/l					Ferrari et al., 2004
	United States			46 ng/l				Miller and Meek, 2006
	England		11.4 ng/l					Wilknson, et al., 2017
	China	ND–1.5 ng/l						Yan et al., 2015
	Taiwan			2.1–33.2 ng/l				Lin et al., 2015
	Singapore	0.04–1.7 ng/l						Bayen et al., 2016
	Nigeria				0.39 mg/l		0.17 mg/l	Ogah, 2020
	Nigeria				0.73 mg/l			Ogah, 2020
	Vietnam	0.41–0.31 ng/l						Tran et al., 2014
	Nigeria	0.27 µg/l						Olarinmoye et al., 2016
	Brazil		0.060 µg/l					Pivetta and Gastaldini, 2019
	Brazil		0.069 µg/l					Pivetta and Gastaldini, 2019
	Taiwan	24–62 ng/l						Chen et al., 2008
	Vietnam	<140–310 ng/l						Tran et al., 2014.
	China					<LOD–2.37 ng/l		Cai et al., 2015
Paracetamol	Brazil		2.975 µg/l					Pivetta and Gastaldini, 2019
	Brazil		0.426 µg/l					Pivetta and Gastaldini, 2019
Ibuprofen	United States	<1–34 ng/l						Zhang et al., 2006
	South Korea	ND–414 ng/l						Chen et al., 2008
	China	0.86115.8 ng/l						Yan et al., 2015
	Taiwan			17.4–836.7 ng/l				Lin et al., 2015
	China	1417 ng/l						Peng et al., 2009
	Vietnam	0.10–0.58 ng/l						Tran et al., 2014
	United States					ND–1.16 ng/l		Subedi et al., 2015

Pharmaceuticals and personal care products	Country	Concentration in various water matrices						References
		Surface Water		Groundwater		Drinking Water		
		Range	Mean	Range	Mean	Range	Mean	
	Nigeria	8.84 µg/l						Olarinmoye et al., 2016
	Brazil		1.266 µg/l					Pivetta and Gastaldini, 2019
	Brazil		0.515 µg/l					Pivetta and Gastaldini, 2019
	Taiwan	<12–30 ng/l						Chen et al., 2008
	Vietnam	100–1000 ng/l						Tran et al., 2014
	China					<LOD–17.17 ng/l		Cai et al., 2015
	China			24.50 ng/l				Wu et al., 2020
	China			42.99 ng/l				Wu et al., 2020
	Vietnam	<0.04–0.45 ng/l						Tran et al., 2014
	Nigeria	< 0.02 µg/l						Olarinmoye et al., 2016
	United States	<1–135 ng/l						Zhang et al., 2006
	Taiwan	110–620 ng/l						Chen et al., 2008
	Vietnam	<40–330 ng/l						Tran et al., 2014
Naproxen	Taiwan				128.0 ng/l			Lin et al., 2015
	Singapore	<1–10.85 ng/l						You et al., 2015
	Vietnam	0.08–0.38 ng/l						Tran et al., 2014
	Nigeria	0.03 µg/l						Olarinmoye et al., 2016
	Vietnam	80–380 ng/l						Tran et al., 2014
Fenopropfen	Vietnam	<0.04–0.41 ng/l						Tran et al., 2014
	Nigeria	<0.02 µg/l						Olarinmoye et al., 2016
	South Korea	ND–326 ng/l						Kim et al., 2009b
	South Korea	ND–33.5 ng/l						Kim et al., 2009b
	Vietnam	<0.02–0.27 ng/l						Tran et al., 2014
Propyphenazone	Vietnam	<0.06 ng/l						Tran et al., 2014
Acetylsalicylic acid	Nigeria	0.13 µg/l						Olarinmoye et al., 2016
Antibiotics								
Amoxicillin	Zambia		2 500 ng/l					Ngumba et al., 2020
Chloramphenicol	Singapore	<0.07–1.53 ng/l						You et al., 2015
	Singapore	0.003–0.70 ng/l						Bayen et al., 2016
	Nigeria	0.36 µg/l						Olarinmoye et al., 2016
	China			0.55 ng/l				Wu et al., 2020
	China			0.16 ng/l				Wu et al., 2020
Chlortetracycline	Nigeria	<0.05 µg/l						Olarinmoye et al., 2016
Erythromycin	South Korea	ND–137 ng/l						Kim et al., 2009b
	Taiwan				54.8 ng/l			Lin et al., 2015
	Bangladesh	<LOD–6.46 ng/l						Hossain et al., 2018
	China	1.41–156 ng/l						Yan et al., 2015
	Nigeria	1.00 µg/l						Olarinmoye et al., 2016

Pharmaceuticals and personal care products	Country	Concentration in various water matrices						References
		Surface Water		Groundwater		Drinking Water		
		Range	Mean	Range	Mean	Range	Mean	
	China			1.55 ng/l				Wu et al., 2020
	China			1.71 ng/l				Wu et al., 2020
Clarithromycin	Taiwan				6.9 ng/l			Lin et al., 2015
	Nigeria	<0.05						Olarinmoye et al., 2016
Fluoroquinolones	China	ND–45.8 ng/l	15.4 ng/l					Lin et al., 2020
Sulfadimidine	Nigeria	<0.01 µg/l						Olarinmoye et al., 2016
Nalidixic acid	Taiwan			1.6–16.4 ng/l				Lin et al., 2015
Sulfamethoxazole	Germany		0.48 µ/L					Ferrari et al., 2004
	Taiwan			0.2–1820 ng/l				Lin et al., 2015
	United States			490 ng/l				Miller and Meek, 2006
	United States			113 ng/l				Schaider et al., 2016
	Korea		26.9 ng/l					Choi et al., 2008
	United States					8.2 ng/l		Glassmeyer et al., 2016
	Kenya	13.8 mg/l						Ngumba et al., 2020
	China	0.44–115.3 ng/l						Yan et al., 2015
	Bangladesh	<LOD–7.24 ng/l						Hossain et al., 2018
	United States					ND–0.39 ng/l		Subedi et al., 2015.
	Nigeria	1.50 µg/l						Olarinmoye et al., 2016
	China	ND–39.6 ng/l	20 ng/l					Lin et al., 2020
	China					<LOD–1.81 ng/l		Cai et al., 2015
	China			19.29 ng/l				Wu et al., 2020
	China			11.01 ng/l				Wu et al., 2020
Zambia			11 800 ng/l				Ngumba et al., 2016	
Kenya			96.9 µg/l				Kairigo et al., 2020	
Tetracycline	Kenya	2.6 mg/l						Ngumba et al., 2016
	Zambia		2 200 ng/l					Ngumba et al., 2016
	Nigeria	<0.05 µg/l						Olarinmoye et al., 2016
	Bangladesh	< LOQ–17.20 ng/l						Hossain et al., 2018
Trimethoprim	China	0.4–20.5 ng/l						Yan et al., 2015
	Zambia		2 410 ng/l					Ngumba et al., 2020
	Kenya		3.8 µg/l					Kairigo et al., 2020
	Nigeria	0.40 µg/l						Olarinmoye et al., 2016
	China			1.03 ng/l				Wu et al., 2020
	China			3.23 ng/l				Wu et al., 2020
Doxycycline	Zambia		2 730 ng/l					Ngumba et al., 2020
	Nigeria		< 0.05 µg/l					Olarinmoye et al., 2016
Tylosin	Bangladesh	<LOD–16.68 ng/l						Hossain et al., 2018
Clarithromycin	South Korea	ND–443 ng/l						Kim et al., 2009b

Pharmaceuticals and personal care products	Country	Concentration in various water matrices						References
		Surface Water		Groundwater		Drinking Water		
		Range	Mean	Range	Mean	Range	Mean	
Ciprofloxacin	Kenya Zambia Kenya	0.5 mg/l	400 ng/l 2.5 µg/l					Ngumba et al., 2016 Ngumba et al., 2020 Kairigo et al., 2020
Ofloxacin	Taiwan China Nigeria	3.1–114.1 ng/l			0.24 mg/l	0.9–11.8 ng/l	0.08 mg/l	Lin et al., 2015 Yan et al., 2015 Ogah, 2020
Sulfadiazine	Taiwan China Singapore Nigeria	0.36–26.7 ng/l 0.04–0.80 ng/l 0.04 µg/l		0.1–14.4 ng/l				Lin et al., 2015 Yan et al., 2015 Bayern et al., 2016 Olarinmoye et al., 2016
Sulfamonomethoxine	Taiwan China China			0.6–1.8 ng/l 3.43 ng/l 12.39 ng/l				Lin et al., 20152 Wu et al., 2020 Wu et al., 2020
Sulfathiazole	Taiwan China China			0.7–3.0 ng/l 3.86 ng/l 2.24 ng/l				Lin et al., 2015 Wu et al., 2020 Wu et al., 2020
Sulfamethizole	Bangladesh	<LOD–11.35 ng/l						Hossain et al., 2018
Sufisoxazole	China China			1.51 ng/l 16.73 ng/l				Wu et al., 2020 Wu et al., 2020
Sulfamethazine	Taiwan Bangladesh China Singapore China China	<LOD–4.19 ng/l ND–3.7 ng/l 06–6.26 ng/l		1.6–28.9 ng/l				Lin et al., 2017 Hossain et al., 2018 Yan et al., 2015 Bayen et al., 2016 Wu et al., 2020 Wu et al., 2020
Sulfadimethoxine	Taiwan			0.8–4.3 ng/l				Lin et al., 2015
Flumequine	Taiwan			2.4–6.6 ng/l				Lin et al., 2015
Pipemidic acid	Taiwan				10.2 ng/l			Lin et al., 2015
Lincomycin	Singapore	0.04–1.36 ng/l						Bayen et al., 2016
Dimetridazole	Taiwan				1.8 ng/l			Lin et al., 2015
Norfloxacin	Taiwan China Kenya	ND–92.4 ng/l	1.6 µg/l			9.3 ng/l		Lin et al., 2015 Yan et al., 2015 Kairigo et al., 2020
Moxifloxacin	China	ND–6.4 ng/l						Yan et al., 2015
Metronidazole	Taiwan Bangladesh	0.05–13.51 ng/l			26.2 ng/l			Lin et al., 2015 Hossain et al., 2018
Roxithromycin	China	0.6–88.4 ng/l						Yan et al., 2015
Sulfamerazine	Singapore	0.03–0.24 ng/l						Bayen et al., 2016

Pharmaceuticals and personal care products	Country	Concentration in various water matrices						References
		Surface Water		Groundwater		Drinking Water		
		Range	Mean	Range	Mean	Range	Mean	
	China			2.49 ng/l				Wu et al., 2020
	China			0.69 ng/l				Wu et al., 2020
Azithromycin	China	2.6–166.5 ng/l						Yan et al., 2015
Oxytetracycline	China	85.0–375.9 ng/l	213.1 ng/l					Lin et al., 2020
Florfenicol	China	ND–287.5 ng/l	153.1 ng/l					Lin et al., 2020
Antiseptics								
	United States	9–26 ng/l						Zhang et al., 2006
	Kenya			0.02 ng/l				Sorensen et al., 2015
	China	61–660 ng/l	189 ng/l					Lin et al., 2020
	Kenya			0.03 ng/l				Sorensen et al., 2015
	United States					ND–1.93 ng/l		Subedi et al., 2015
	China			18.05 ng/l				Wu et al., 2020
	China			109.90 ng/l				Wu et al., 2020
Triclocarban	United States					ND–20.2 ng/l		Subedi et al., 2015
N,N-Diethyltoluamide (DEET)	United States	7.2–110 ng/l						Fairbairn et al., 2015
	China	0.8–10.2 ng/l						Sun et al., 2015
Antihypertensives/Beta-blockers								
	South Korea	ND–690 ng/l						Kim et al., 2009b
	Taiwan				3.6 ng/l			Lin et al., 2015
	United States					ND–19.5 ng/l		Subedi et al., 2015
Acebutolol	Taiwan				0.7 ng/l			Lin et al., 2015
	United States					18.4 ng/l		Glassmeyer et al., 2016
	China	0.46–17.3 ng/l						Yan et al., 2015
	Germany		0.59 µg/l					Ferrari et al., 2004
	South Korea	ND–40.1 ng/l						Kim et al., 2009b
Anti-epileptics								
	Bangladesh	<LOD–8.80 ng/l						Hossain et al., 2018
	United States					586 ng/l		Glassmeyer et al., 2016
	United States					26.50 ng/l		Glassmeyer et al., 2016
	Germany		1.1 µg/l					Ferrari et al., 2004
	United States			72 ng/l				Schaidler et al., 2014
	United States	43–114 ng/l						Zhang et al., 2006
	United States			420 ng/l				Miller and Meek, 2006
	Singapore	0.06–4.63 ng/l						Bayen et al., 2016
	Taiwan			0.4–37.9 ng/l				Lin et al., 2015
	China	0.41–10.3 ng/l						Yan et al., 2015

Pharmaceuticals and personal care products	Country	Concentration in various water matrices						References
		Surface Water		Groundwater		Drinking Water		
		Range	Mean	Range	Mean	Range	Mean	
	South Korea	ND–595 ng/l						Yan et al., 2015
	Vietnam	<0.144–0.53 ng/l						Tran et al., 2014
	Nigeria	<0.01						Olarinmoye et al., 2016
	China					0.37–1.15 ng/l		Cai et al., 2011
	China					0.51–38.24 ng/l		Cai et al., 2015
Dilantin	United States			22 ng/l				Miller and Meek, 2006
Phenytoin	United States			66 ng/l				Schaider et al., 2014
Anti-psychotics								
Bromazepam	United States	42 ng/l						Ferrarri et al., 2004
Clonazepam	United States	198 ng/l						Ferrari et al., 2004
Sulpiride	Singapore	<0.1–1.23 ng/l						You et al., 2015
Risperidone	Singapore	03–0.21 ng/l						Bayen et al., 2016
Diazepam	United States	335 ng/l						Ferrari et al., 2004
	Nigeria	<0.01 µg/l						Olarinmoye et al., 2016
Lipid regulators								
Bezafibrate	China	ND–31.4 ng/l						Yan et al., 2015
	Taiwan			0.1–256.7 ng/l				Lin et al., 2015
	Nigeria	<0.02 µg/l						Olarinmoye et al., 2016
	China					0.31–0.85 ng/l		Cai et al., 2015
	China					<LOD–0.16 ng/l		Cai et al., 2015
Clofibrac acid	Germany		0.55 µg/l					Ferrari et al., 2004
	China	ND–17.2 ng/l						Yan et al., 2015
	United States	3–27 ng/l						Zhang et al., 2006
	China	248 ng/l						Peng et al., 2009
	Taiwan			0.1–1.0 ng/l				Lin et al., 2015
	Vietnam	<0.05 ng/l						Tran et al., 2014
	Nigeria	0.04 µg/l						Olarinmoye et al., 2016
	China					<LOD–1.37 ng/l		Cai et al., 2015
Gemfibrozil	China	ND–1.4 ng/l						Yan et al., 2015
	Singapore	0.77–17.7 ng/l						Bayen et al., 2016
	Vietnam	<0.05 ng/l						Tran et al., 2014
	Nigeria	<0.02 µg/l)						Olarinmoye et al., 2016
Simvastatin	China	2.3–16.7 ng/l						Yan et al., 2015
Atorvastatin	China	ND–0.6 ng/l						Yan et al., 2013
Etofibrate	Nigeria	<0.02 µg/l						Pivetta and Gastaldini, 2019
Fenofibrate	Nigeria	<0.04 µg/l						Olarinmoye et al., 2016

Pharmaceuticals and personal care products	Country	Concentration in various water matrices						References
		Surface Water		Groundwater		Drinking Water		
		Range	Mean	Range	Mean	Range	Mean	
Antivirals								
Lamivudine	Kenya	5.4 mg/l						Ngumba et al., 2016
	Zambia		49 700 ng/l					Ngumba et al., 2020
	Kenya		219.6 µg/l					Kairigo et al., 2020
Zidovudine	Kenya	7.7 mg/l						Ngumba et al., 2016
	Zambia		1 280 ng/l					Ngumba et al., 2020
	Kenya		2.1 µg/l					Kairigo et al., 2020
Nevirapine	Kenya	4.8 mg/l						Ngumba et al., 2016
	Zambia		210 ng/l					Ngumba et al., 2020
	Kenya		0.9 µg/l					Kairigo et al., 2020
Human indicators								
Caffeine	United States	0.84–250 ng/l	44 ng/l					Fairbairn et al., 2015
	United States	<1–38 ng/l						Zhang et al., 2006
	Singapore	33.9–644.5 ng/l						You et al., 2015
	Korea		268.7 ng/l					Choi et al., 2008
	Zambia			1.7 ng/l				Sorensen et l., 2015
	United States					88 ng/l		Glassmeyer et al., 2016
	Taiwan			1.2–930.7 ng/l				Lin et al., 2015
	Singapore	5–1389 ng/l						Bayen et al., 2016
	United States					ND–11.1 ng/l		Subedi et al., 2015
	China			782.62 ng/l				Wu et al., 2020
China			461.87 ng/l				Wu et al., 2020	

2.3.4.2 Pharmaceuticals and personal care products in wastewater influents and effluents

The international prevalence of pharmaceuticals and personal care products in wastewater influent and effluent is well researched as discussed below and summarised in Table 2.2.

Non-steroidal anti-inflammatory drugs

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

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

Another study conducted in Northern Taiwan by Fang et al. (2012) reported the concentrations of diclofenac (152–185 ng/l), ibuprofen (724–2 200 ng/l) and ketoprofen (128–184 ng/l) in wastewater influent samples. Their respective concentrations in wastewater effluent ranged from 100 to 131 ng/l, 552 to 1 600 ng/l and 68 to 128 ng/l. Wilkinson et al. (2017) conducted a study in a Southern England sewage treatment effluent

and reported that the mean concentrations of acetaminophen and diclofenac were 47.5 ng/l and 86.5 ng/l, respectively.

Antibiotics

In the peri-urban area of Chunga, Lusaka, Zambia, mean concentrations of trimethoprim (32 670 ng/l), sulfamethoxole (33 300 ng/l), ciprofloxacin (740 ng/l), norfloxacin (100 ng/l), tetracycline (220 ng/l), doxycycline (4 490 ng/l) and amoxicillin (3 270 ng/l) were reported in wastewater influent samples (Ngumba et al., 2020). The study also detected trimethoprim, sulfamethoxole, ciprofloxacin, norfloxacin, tetracycline, doxycycline and amoxicillin in wastewater effluent at mean concentrations of 1 770 ng/l, 30 040 ng/l, 230 ng/l, 80 ng/l, 4 590 ng/l, 5 280 ng/l and 5 580 ng/l, respectively (Ngumba et al., 2020). In a study conducted in low and middle-income countries, the mean concentrations of norfloxacin, trimethoprim, ciprofloxacin and sulfamethoxole were reported in effluent samples as 4.2 µg/l, 15.8 µg/l, 5.3 µg/l and 956.4 µg/l, respectively (Kairigo et al., 2020).

A study in Jordan reported concentrations of sulfamethoxazole (ND–0.9 ng/l) and erythromycin (0.5–1.1 ng/l) in wastewater influent samples. Furthermore, sulfamethoxazole (ND–0.3 ng/l) and erythromycin (ND–0.5 ng/l) were detected in wastewater effluent samples (Al-Tarawneh et al., 2014). In China, Lin et al. (2020) reported that wastewater influents were loaded with concentrations of sulfamethoxole, enrofloxacin, oxytetracycline and florfenicol in influent samples ranging from 2.7 to 40.8 ng/l, 50.1 to 135.2 ng/l, 203.6 to 348.5 ng/l and ND to 297.3 ng/l, respectively. They also mentioned that sulfamethoxole, enrofloxacin, oxytetracycline and florfenicol were also detected in wastewater effluents at concentrations ranging from ND to 14.0 ng/l, ND to 100.6 ng/l, 32.5 to 381.0 ng/l, and ND to 219.6 ng/l, respectively (Lin et al., 2020). In Southern India, antibiotics such as trimethoprim (68–400 ng/l), sulfamethoxazole (55–690 ng/l) and clindamycin (25–790 ng/l) were detected in wastewater influent samples. In wastewater effluent samples, the same study detected concentrations of sulfamethoxazole ranging from 120 to 420 ng/l and lincomycin ranging from 280 to 510 ng/l (Subedi et al., 2017).

In Cyprus, Hapeshi et al. (2015) reported the prevalence of antibiotics such as erythromycin (BLD–428 ng/l) with an average concentration of 97 ng/l, ofloxacin (220–2 360 ng/l) with an average concentration of 615 ng/l, sulfamethoxazole (178–350 ng/l) with an average concentration of 305 ng/l and trimethoprim (30–130 ng/l) with an average concentration of 71 ng/l in wastewater influent. The same study also reported the occurrence of erythromycin (BLD–140 ng/l) with an average concentration of 32 ng/l, ofloxacin (BLD–353 ng/l) with an average concentration of 218 ng/l, sulfamethoxazole (BLD–290 ng/l) with an average

concentration of 76 ng/l, trimethoprim (BLD–4 ng/l) with an average concentration of 4 ng/l and azithromycin (BLD–70 ng/l) with an average concentration of 38 ng/l in wastewater effluent (Hapeshi et al., 2015).

Beta-blockers

In Southern India, antihypertensives and beta-blockers such as propranolol (42–62 ng/l), atenolol (2 100–3 800 ng/l), nordiazepam (5–17 ng/l), diltiazem (23–120 ng/l), desacetyl diltiazem (20–64 ng/l), verapamil (16–103 ng/l), norverapamil (65–550 ng/l), venlafaxine (11–77 ng/l) and bupropion (13–32 ng/l) were detected in wastewater influent samples. Furthermore, diazepam (6–100 ng/l), nordiazepam (13–20 ng/l), venlafaxine (12–18 ng/l), bupropion (13–16 ng/l), sertraline (8–21 ng/l), propranolol (36–52 ng/l), diltiazem (3–7 ng/l) and desacetyl diltiazem (28–65 ng/l) were identified in wastewater effluent (Subedi et al., 2017).

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

Antiepileptics

In Jordanian WWTPs, antiepileptic drugs, i.e. carbamazepine, was detected in both wastewater influent and effluent as 0.7–3.6 ng/l and 0.4–1.3 ng/l, respectively (Al-Tarawneh et al., 2014). Subedi et al. (2017), in two sewage treatment plants located in Southern India, detected the antiepileptic drug, carbamazepine, at concentrations ranging from 240 to 750 ng/l and 450 to 770 ng/l in wastewater influent and effluent, respectively. Hapeshi et al. (2015) detected carbamazepine in both wastewater influent and effluent at concentrations ranging from 460 to 4 023 ng/l and BLD to 5 520 ng/l, respectively, in Cyprus.

Antipsychotic

In Southern India, Subedi et al. (2017) reported concentrations of quetiapine ranging from 17 to 76 ng/l in wastewater influent samples. Furthermore, in wastewater effluent samples, quetiapine (16–24 ng/l) and aripiprazole (38–150 ng/l) were also reported among the antipsychotic drugs.

Lipid regulators

In a study in Cyprus, Hapeshi et al. (2015) detected lipid regulators such as bezafibrate (519–1 610 ng/l) with an average concentration of 1 104 ng/l, gemfibrozil (71–1 080 ng/l) with an average concentration of 476 ng/l, pravastatin (23–130 ng/l) with an average concentration of 70 ng/l in wastewater influent samples. The same study also detected bezafibrate (25–170 ng/l) with an average concentration of 108 ng/l, gemfibrozil (BLD–480 ng/l) with an average concentration of 139 ng/l and pravastatin (BLD–8 ng/l) with an average concentration of 8 ng/l in wastewater effluent samples.

Antivirals

A study conducted in the peri-urban area of Chunga in Lusaka, Zambia, reported mean concentrations of antiretroviral drugs such as nevirapine (680 ng/l), zidovudine (66 590 ng/l), and lamivudine (118 970 ng/l) in wastewater influent samples. Furthermore, in the same study, nevirapine, zidovudine and lamivudine were detected in wastewater effluent and reported at mean concentrations of 1 720 ng/l, 37 140 ng/l and 55 760 ng/l, respectively (Ngumba et al., 2020). In wastewater effluents collected in Kenya, Kairigo et al. (2020) reported mean concentrations of antiretroviral drugs such as lamivudine, zidovudine and nevirapine as 847 µg/l, 1.4 µg/l and 9.5 µg/l, respectively.

Antiseptics

The study conducted by Subedi et al. (2017) in southern India, detected and reported concentrations of triclocarban in both wastewater influents and effluents ranging from 1 300 to 4 300 ng/l and 300 to 860 ng/l, respectively. In China, antiseptic triclosan was detected in wastewater influents at concentrations ranging from 219 to 718 ng/l with an average concentration of 418 ng/l, and in wastewater effluent ranging from 37 to 620 ng/l, with an average concentration of 204 ng/l (Lin et al., 2020).

Although some drugs are prescribed, some may be bought without prescriptions. In urban areas, the high usage of medicinal drugs is predominant and as a result, they are detected at various concentrations in WWTPs around the world. Medicinal drugs are not completely metabolised and absorbed by our bodies. They escape the body through incomplete

absorption and excretion, as parts of human waste or as a result of the emissions of industrial, medical or household wastewater. They also end up in WWTPs after being disposed of using various techniques, like flushing down the toilet or draining in the washbasin. Moreover, conventional WWTPs were not designed to remove emerging contaminants in most urban cities around the world. This situation led to their detection in effluents as shown in the case studies above.

.

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

Pharmaceuticals and personal care products	Country	WWTP Influent		WWTP Effluent		References
		Range	Mean	Range	Mean	
Non-steroidal anti-inflammatory drugs (NSAIDs)						
Acetaminophen	England				47.5 ng/l	Wilkinson et al., 2017
	India	5 400–11 000 ng/l		330–1 200 ng/l		Subedi et al., 2017
	Cyprus	7 871–232 300 ng/l	11 5004 ng/l	BLD–650 ng/l	553 ng/l	Al-Tarawneh et al., 2014
Diclofenac	Germany				2.1 µg/l	Ferrari et al., 2004
	Taiwan	152–185 ng/l		100–131 ng/l		Fang et al., 2012
	England				86.5 ng/l	Wilkinson et al., 2017
	Cyprus	1 202–3457 ng/l	2 339 ng/l	BLD–2 950 ng/l	804 ng/l	Hapeshi et al., 2015
	Jordan	0.8–3.3ng/l		ND–1.1 ng/l		Al-Tarawneh et al., 2014
Ibuprofen	Cyprus	1680–5 315 ng/l	2801 ng/l	BLD–82 ng/l	43 ng/l	Hapeshi et al., 2015
	Taiwan	724–2 200 ng/l		552–1 600 ng/l		Fang et al., 2012
	Jordan	ND–5.7 ng/l		ND–2.2 ng/l		Al-Tarawneh et al., 2014
	India			270–1 940 ng/l		Subedi et al., 2017
Ketoprofen	Taiwan	128–184 ng/l		68–128 ng/l		Fang et al., 2012
	Cyprus	BLD–956 ng/l	900 ng/l	BLD–120 ng/l	89 ng/l	Hapeshi et al., 2015
Naproxen	Jordan	0.7–5.2 ng/l		ND–1.3 ng/l		Al-Tarawneh et al., 2014
	Cyprus	BLD–210 ng/l	90 ng/l			Hapeshi et al., 2015
Mefenamic acid	India			320–750 ng/l		Subedi et al., 2017
Indomethacin	Cyprus	1040–2040 ng/l	1411 ng/l	BLD–310 ng/l	68 ng/l	Hapeshi et al., 2015
	Cyprus	19–120 ng/l	73 ng/l	BLD–110 ng/l	23 ng/l	Hapeshi et al., 2015
Tramadol	United States	23.04 ng/l				Glassmeyer et al., 2016
Propyphenazone	Cyprus	BLD–10 ng/l	10 ng/l			Hapeshi et al., 2015
Antibiotics						
Amoxicillin	Zambia		3 270 ng/l		5 580 ng/l	Ngumba et al., 2020
Erythromycin	Jordan	0.5–1.1 ng/l		ND–0.5 ng/l		Al-Tarawneh et al., 2014
	Cyprus	BLD–428 ng/l	97 ng/l	BLD–140 ng/l	32 ng/l	Hapeshi et al., 2015
Fluoroquinolones	China	50.1–135.2 ng/l	92.2 ng/l	ND–100.6 ng/l	52.6 ng/l	Lin et al., 2020
Sulfamethoxazole	Germany				2 µg/l	Ferrari et al., 2004
	United States	161.1 ng/l				Glassmeyer et al., 2016
	China	2.7–40.8 ng/l	12.9 ng/l	ND–14.0 ng/l	2.2 ng/l	Lin et al., 2020
	Zambia		33 300 ng/l		30 040 ng/l	Ngumba et al., 2020
	Kenya			956.4 µg/l		Kairigo et al., 2020
	Jordan	ND–0.9 ng/l		ND–0.3 ng/l		Al-Tarawneh et al., 2014
	India	55–690 ng/l		120–420 ng/l		Subedi et al., 2017
	Cyprus	178–350 ng/l	305 ng/l	BLD–290 ng/l	76 ng/l	Hapeshi et al., 2015
Tetracycline	Zambia		220 ng/l		4 590 ng/l	Ngumba et al., 2020
Trimethoprim	Kenya				15.8 µg/l	Kairigo et al., 2020

Pharmaceuticals and personal care products	Country	WWTP Influent		WWTP Effluent		References
		Range	Mean	Range	Mean	
	Zambia		32 670 ng/l		1 770 ng/l	Ngumba et al., 2020
	India	68–400 ng/l				Subedi et al., 2017
	Cyprus	30–130 ng/l	71 ng/l	BLD–4 ng/l	4 ng/l	Hapeshi et al., 2015
Doxycycline	Zambia		4 490 ng/l		5 280 ng/l	Ngumba et al., 2020
Ciprofloxacin	Kenya				5.3 µg/l	Kairigo et al., 2020
	Zambia		740 ng/l		230 ng/l	Ngumbo et al., 2020
Ofloxacin	Cyprus	220–2360 ng/l	615 ng/l	BLD–353 ng/l	218 ng/l	Hapeshi et al., 2015
Lincomycin	India			280–510 ng/l		Subedi et al., 2017
Norfloxacin	Kenya				4.2 µg/l	Kairigo et al., 2020
	Zambia		100 ng/l		80 ng/l	Ngumba et al., 2020
Azithromycin	Cyprus			BLD–70 ng/l	38 ng/l	Hapeshi et al., 2015
Oxytetracycline	China	203.6–348.5 ng/l	287.5 ng/l	32.5–381.0 ng/l	194.9 ng/l	Lin et al., 2020
Florfenicol	China	ND–297.3 ng/l	216.6 ng/l	ND–219.6 ng/l	112.8 ng/l	Lin et al., 2020
Antiseptic						
Triclosan	China	219–718 ng/l	418 ng/l	37–620 ng/l	204 ng/l	Lin et al., 2020
Triclocarban	India	1 300–4 300 ng/l		300–860 ng/l		Subedi et al., 2017
Beta-blocker/Antihypertensive						
Atenolol	India	2 100–3 800 ng/l				Subedi et al., 2017
	Cyprus	2750–4740 ng/l	3733 ng/l	10–900 ng/l	466 ng/l	Subedi et al., 2015
Metoprolol	United States	37.8 ng/l				Glassmeyer et al., 2016
	Cyprus	196–610 ng/l	340 ng/l	20–210 ng/l	92 ng/l	Hapeshi et al., 2015
Propranolol	Germany				0.29 µg/l	Ferrari et al., 2004
	India	42–62 ng/l		36–52 ng/l		Subedi et al., 2017
	Cyprus	BLD–270 ng/l	45 ng/l	BLD–90 ng/l	40 ng/l	Hapeshi et al., 2015
Sotalol	Cyprus	336–950 ng/l	597 ng/l	BLD–330 ng/l	121 ng/l	Hapeshi et al., 2015
Nordiazepam	India	5–17 ng/l		13–20 ng/l		Subedi et al., 2017
Diltiazem	India	23–120 ng/l		3–7 ng/l		Subedi et al., 2017
Desacetyl diltiazem	India	20–64 ng/l		28–65 ng/l		Subedi et al., 2017
Verapami	India	16–103 ng/l				Subedi et al., 2017
Norverapamil	India	65–550 ng/l				Subedi et al., 2017
Venlafaxine	India	11–77 ng/l		12–18 ng/l		Subedi et al., 2017
Bupropion	India	13–32 ng/l		13–16 ng/l		Subedi et al., 2017
Diazepam	India			6–100 ng/l		Subedi et al., 2017
Sertraline	India			8–21 ng/l		Subedi et al., 2017
Famotidine	Cyprus	490–2 320 ng/l	1 181 ng/l	BLD–20 ng/l	20 ng/l	Hapeshi et al., 2015

Pharmaceuticals and personal care products	Country	WWTP Influent		WWTP Effluent		References
		Range	Mean	Range	Mean	
Ranitidine	Cyprus	28–640 ng/l	207 ng/l	BLD–30 ng/l	30 ng/l	Hapeshi et al., 2015
Anti-epileptics						
Carbamazepine	United States	269 ng/l				Glassmeyer et al., 2016
	United States	35.7 ng/l				Glassmeyer et al., 2016
	Germany				6.3 µg/l	Ferrari et al., 2004
	Jordan	0.7–3.6 ng/l		0.4–1.3 ng/l		Al-Tarawneh et al., 2014
	India	240–750 ng/l		450–770 ng/l		Subedi et al., 2017
	Cyprus	460–4023 ng/l	1 720 ng/l	BLD–5 520 ng/l	1 820 ng/l	Hapeshi et al., 2015
Anti-psychotic						
Quetiapine	India	17–76 ng/l		16–24 ng/l		Subedi et al., 2017
Aripiprazole	India			38–150 ng/l		Subedi et al., 2017
Lipid regulators						
Bezafibrate	Cyprus	519–1 610 ng/l	1 104 ng/l	25–170 ng/l	108 ng/l	Hapeshi et al., 2015
Clofibrac acid	Germany				1.6 µg/l	Ferrari et al., 2004
	Taiwan	104–109 ng/l		95–102 ng/l		Fang et al. 2012
Gemfibrozil	Cyprus	71–1080 ng/l	476 ng/l	BLD–480 ng/l	139 ng/l	Hapeshi et al., 2015
Pravastatin	Cyprus	23–130 ng/l	70 ng/l	BLD–8 ng/l	8 ng/l	Hapeshi et al., 2015
Antivirals						
Lamivudine	Zambia		118 970 ng/l		55 760 ng/l	Ngumba et al., 2020
	Kenya				847.1 µg/l	Kairigo et al., 2020
Zidovudine	Zambia		66 590 ng/l		37 140 ng/l	Ngumba et al., 2020
	Kenya				1.4 µg/l	Kairigo et al., 2020
Nevirapine	Zambia		680 ng/l		1 720 ng/l	Ngumba et al., 2020
	Kenya				9.5 µg/l	Kairigo et al., 2020
Human indicators						
Caffeine	United States	124 ng/l				Fairbairn et al., 2015
	United States	37.8 ng/l				Fairbairn et al., 2015

2.3.4.3 Herbicides in surface water, groundwater and drinking water

According to Casida (2019), pesticides are chemicals applied with the aim of killing or injuring life. They are classified based on the target species they act on. For example, herbicides are chemicals with the capability of either killing or severely injuring plants. Several studies have indicated that the wide spread use of agrochemicals such as herbicides have led to their introduction into various water matrices as summarised in Table 2.3 and discussed in this section. Atrazine was detected in groundwater in Kabwe, Zambia, at a maximum concentrations of 0.13 ng/l and 0.07 ng/l in dry and wet season, respectively. The same study also reported the maximum concentration of bromacil in groundwater as 0.09 ng/l in wet season while the concentrations of terbutryne in dry and wet season were as 0.03 ng/l and 0.02 ng/l, respectively (Sorensen et al., 2015).

In the South Fork of the Zumbro River watershed in south-eastern Minnesota, United States, herbicides such as atrazine and acetochlor were detected in surface water at concentrations ranging from 1.8 to 390 ng/l, with an average concentration of 40 ng/l, and 1.2 to 180 ng/l with an average concentration of 28 ng/l, respectively (Fairbairn et al., 2015). A survey was conducted in Hungary to monitor pesticide residues in surface water and groundwater. The study detected and reported concentrations of trifluralin, atrazine, metribuzin, alachlor, prometryn, ethofumesate, metolachlor, MCPA, 2,4-D, and glyphosate in surface water ranging from 800 to 10 000 ng/l, 500 to 15 000 ng/l, 100 to 1 000 ng/l, 1 to 10 ng/l, 100 to 10 000 ng/l, 10 to 30 ng/l, 1 to 56 000 ng/l, 5 to 300 ng/l, 10 to 1 000 ng/l and 500 to 1 000 ng/l, respectively (Szekacs et al., 2015).

A study by Mawussi et al. (2009) conducted in Southern Togo, detected 2,4-D in river water at concentrations ranging from 0.03 to 0.15 µg/l. In the semiarid region of Argentina, Mas et al. (2020) reported concentrations of herbicides such as 2,4-D, alachlor, glyphosate and imazethapyr in surface water ranging from 0.015 to 0.925 µg/l (0.084 µg/l), 0.063 to 0.326 µg/l (0.197 µg/l), 0.1 to 35 µg/l (1.251 µg/l) and 0.001 to 0.161 µg/l (0.015 µg/l), respectively. Pandey et al. (2019) conducted a study in Liberty Island of the Sacramento-San Joaquin Delta, California, United States, and reported the mean concentrations of glyphosate and fluoridone concentrations in water columns and sediment leachate as 0.2 ppb and 0.02 ppb, respectively.

In Brazil, a study was conducted during the rainy and dry season targeting herbicides in water bodies of the Samambaia River sub-basin. During the rainy season, the study detected atrazine, bentazon, carfentrazone-ethyl, clomazone, flumioxazin, fomesafen, glyphosate, linuron, metribuzin, S-metolachlor and sulfentrazone at concentrations ranging

from 0.0080 to 1.7484 $\mu\text{g}/\ell$, 0.0058 to 0.8310 $\mu\text{g}/\ell$, 0.0021 to 0.0325 $\mu\text{g}/\ell$, 0.0011 to 4.0621 $\mu\text{g}/\ell$, 0.0008 to 0.0828 $\mu\text{g}/\ell$, 0.0000 to 0.0040 $\mu\text{g}/\ell$, 0.6078 to 1.0628 $\mu\text{g}/\ell$, 0.0406 to 0.0599 $\mu\text{g}/\ell$, 0.0017 to 0.8217 $\mu\text{g}/\ell$, 0.1420 to 1.7800 $\mu\text{g}/\ell$ and 0.0852 to 0.8471 $\mu\text{g}/\ell$, respectively. Furthermore, the concentrations of atrazine, bentazon, carfentrazone-ethyl, clomazone, flumioxazin, fomesafen, glyphosate, linuron, metribuzin, S-metolachlor and sulfentrazone ranged from 0.0130 to 0.5914 $\mu\text{g}/\ell$, 0.0561 to 0.2500 $\mu\text{g}/\ell$, 0.0020 to 0.0364 $\mu\text{g}/\ell$, 0.0011 to 2.8621 $\mu\text{g}/\ell$, 0.0000 to 0.0078 $\mu\text{g}/\ell$, 0.0000 to 0.0126 $\mu\text{g}/\ell$, 0.8048 to 11.3328 $\mu\text{g}/\ell$, 0.0015 to 0.0109 $\mu\text{g}/\ell$, 0.0007 to 0.2897 $\mu\text{g}/\ell$, 0.0129 to 0.8430 $\mu\text{g}/\ell$ and 0.0000 to 0.1421 $\mu\text{g}/\ell$ in dry season, respectively (Correia et al., 2020).

Herbicides are substances that are used to control or manipulate unwelcome vegetation. The most frequent use of herbicides is in row-crop farming, where they are sprayed either prior to or during planting in order to reduce other vegetation and increase crop productivity. They may also be used on crops in the autumn to enhance harvesting. Runoff from farm areas may introduce these compounds in water sources. Moreover, herbicides are also used in other areas such as public squares, parks, at the road sides or residential areas to control unwanted weeds. As a result of their applications, runoff from these prominent areas may introduce them in rivers and groundwater. The application of herbicides to kill aquatic weeds in dams that are considered a source of water for water treatment plants may lead to the detection of some herbicides in treated drinking water.

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

Herbicides	Country	Concentration in various water matrices						References
		Surface Water		Groundwater		Drinking Water		
		Range	Mean	Range	Mean	Range	Mean	
2,4-Dichlorodiphenyldichloro-ethylene	Hungary	10–1 000 ng/l						Szekacs et al., 2015
	Togo	0.03–0.15 µg/l						Mawussi et al., 2009
	Argentina	0.015–0.925 µg/l	0.084 µg/l					Ma et al., 2020
Acetochlor	USA	1.2–180 ng/l	28 ng/l					Fairbairn et al., 2015
Alachlor	Hungary	1–10 ng/l						Szekacs et al., 2015
	Argentina	0.063–0.326 µg/l	0.197 µg/l					Mas et al., 2020
Atrazine	Zambia			0.13 ng/l				Sorensen et al., 2015
	USA	1.8–390 ng/l	40 ng/l					Fairbairn et al., 2015
	Hungary	500–15 000 ng/l						Szekacs et al., 2015
	Brazil	0.0080–1.7484 µg/l						Correia et al., 2020
Bentazon	Brazil	0.0058–0.8310 µg/l						Correia et al., 2020
Bromacil	Zambia			0.09 ng/l				Sorensen et al., 2015
Carfentrazone-ethyl	Brazil	0.0021–0.0325 µg/l						Correia et al., 2020
Clomazone	Brazil	0.0011–4.0621 µg/l						Correai et al., 2020
Ethofumesate	Hungary	10–30 ng/l						Szekacs et al., 2015
Flumioxazin	Brazil	0.0008–0.0828 µg/l						Correia et al., 2020
Fluridone	USA	0.02 ppb						Pandy et al., 2019
Fomesafen	Brazil	0.0000–0.0040 µg/l						Correia et al., 2020
Glyphosate	Hungary	500–1 000 ng/l						Szekacs et al., 2015
	USA	0.2 ppb						Pandey et al., 2019
	Argentina	0.1 –35 µg/l	1.251 µg/l					Mas et al., 2020
	Brazil	0.6078–1.0628 µg/l						Correia et al., 2020
Imazethapyr	Argentina	0.001–0.161 µg/l	(0.015 µg/l)					Mas et al., 2020
Linuron	Brazil	0.0406–0.0599 µg/l						Correia et al., 2020
MCPA	Hungary	5–300 ng/l						Szekas et al., 2015
Metolachlor	Hungary	1–56 000 ng/l						Szekacs et al., 2015
	Brazil	0.1420–1.7800 µg/l						Correia et al., 2020
Metribuzin	Hungary	100–1000 ng/l						Szekacs et al., 2015
	Brazil	0.0017–0.8217 µg/l						Correia et al., 2020
Prometryn	Hungary	100–10000 ng/l						Szekacs et al., 2015
Sulfentrazone	Brazil	0.0852–0.8471 µg/l						Correia et al., 2020
Terbutryne	Zambia			0.03 ng/l				Sorensen et al., 2015
Trifluralin	Hungary	800–10 000 ng/l						Szekacs et al., 2015

2.3.4.4 Herbicides in wastewater influents and effluents

A few studies were conducted to determine the concentration of herbicides in international influent and effluent samples. A study in Baoding city, Hebei province, China, reported average concentrations of atrazine, simetryn and prometryn in wastewater influents as 104.59 ng/l, 87.23 ng/l and 28.79 ng/l, respectively. In wastewater effluent samples their respective average concentrations were 89.04 ng/l, 77.83 ng/l and 27.50 ng/l, respectively (Wang et al., 2022).

2.3.4.5 Steroid hormones in surface water, groundwater and drinking water

Surface water such as rivers are an easy way to discharge industrial wastewater, while groundwater is frequently polluted though leakage from landfill leachate, thus threatening aquatic ecosystems and possibly human health. Emerging contaminants are an environmental pollutant of increasing concern, which compromise the suitability of drinking water. Numerous types of steroid hormones in various water matrices have progressively been detected in different locations throughout the world at different concentrations (Wee and Aris, 2019) as shown in Table 2.4. A nationwide reconnaissance of contaminants of emerging concern in source and treated drinking waters of the United States detected and reported estrone at a maximum concentration of 0.29 ng/l (Glassmeyer et al., 2016). In a study conducted in the Cancela-Tamandaí and João Goulart catchments in southern Brazil, the respective mean concentrations of 17-beta-estradiol, estriol, estrone, ethisterone and megestrol acetates were reported as 0.074 µg/l, 0.074 µg/l, 0.082 µg/l, 0.017 µg/l and 0.012 µg/l in the Cancela-Tamandaí catchment. Furthermore, their respective mean concentrations in the João Goulart catchment were recorded as 0.074 µg/l, 0.089 µg/l, 0.067 µg/l, 0.013 µg/l and 0.012 µg/l (Pivetta and Gastaldini, 2019).

A study conducted in the Mississippi River in New Orleans, Louisiana, United States, reported estrone and 17-beta-estradiol at a maximum concentration of <1–5 ng/l and 5 ng/l, respectively (Zhang et al., 2006). Lin et al. (2015) conducted a study in the groundwater of Taiwan and detected estrone at concentrations ranging from 1.0 to 14.7 ng/l and 17-alpha-ethinyl-estradiol at a concentration of 1 822.2 ng/l. In the mangrove ecosystems of Singapore, concentrations of steroid hormones such as estrone (E1) ranging from 0.02 to 2.9 ng/l were reported in surface water (Bayen et al., 2016). In Lagos, Nigeria, maximum concentrations of 16-alpha-hydroxyestrone (<0.01 µg/l), 17-alpha-ethinyl-estradiol (<0.01 µg/l), beta-sitosterol (0.67 µg/l), estriol (<0.01 µg/l) and estrone (<0.01 µg/l) were detected in surface water (Olarinmoye et al., 2016). In China, Lin et al. (2020) reported the concentration of estrone (E1), 17-beta-estradiol (E2), estriol (E3) and ethinyl-estradiol (EE2) in river samples ranging from ND to 128 ng/l, ND to 53 ng/l, ND to 58 ng/l and ND to 124 ng/l, respectively.

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

Steroid hormones	Country	Concentration in various water matrices						References
		Surface Water		Groundwater		Drinking Water		
		Range	Mean	Range	Mean	Range	Mean	
Oestrone (E1)	United States	<1–5 ng/l						Zhang et al., 2006
	Taiwan			1.0–14.7 ng/l				Lin et al., 2015
	Singapore	0.02–2.9 ng/l						Bayen et al., 2016
	Nigeria	<0.01 µg/l						Olarinmoye et al., 2016
	China	ND–128 ng/l	34 ng/l					Lin et al., 2020
	Brazil		0.082 µg/l					Pivetta and Gastaldini, 2019
	Brazil		0.067 µg/l					Pivetta and Gastaldini, 2019
17-beta-estradiol (E2)	United States	5 ng/l						Zhang et al., 2006
	Nigeria	0.67 µg/l						Olarinmoye et al., 2016
	China	ND–53 ng/l	24 ng/l					Lin et al., 2020
	Brazil		0.074 µg/l					Pivetta and Gastaldini, 2019
	Brazil		0.074 µg/l					Pivetta and Gastaldini, 2019
17-alpha-ethinyl-estradiol	Taiwan			1 822.2 ng/l				Lin et al., 2015
	Nigeria	<0.01 µg/l						Olarinmoye et al., 2016
16-alpha-hydroxyestrone	Nigeria	<0.01 µg/l						Olarinmoye et al., 2016
Ethinyl-estradiol (EE2)	China	ND–124 ng/l	26 ng/l					Lin et al., 2020
Estriol (E3)	Nigeria	<0.01 µg/l						Olarinmoye et al., 2016
	China	ND–58 ng/l	22 ng/l					Lin et al., 2020
	Brazil		0.074 µg/l					Pivetta and Gastaldini, 2019
	Brazil		0.089 µg/l					Pivetta and Gastaldini, 2019
Ethisterone	Brazil		0.017 µg/l					Pivetta and Gastaldini, 2019
	Brazil		0.013 µg/l					Pivetta and Gastaldini, 2019
Megestrol acetate	Brazil		0.012 µg/l					Pivetta and Gastaldini, 2019
	Brazil		0.012 µg/l					Pivetta and Gastaldini, 2019

Direct excretion of steroid hormones by animals into waterways, or discharges from cattle yard drains, may be attributed as possible sources of contamination rather than through normal agricultural situations. Moreover, discharge of effluents into rivers may lead to the occurrence of steroid hormones in surface water. Improper disposal of unused medicinal drugs may also lead to the detection of some steroid hormones in surface water and groundwater. Moreover, leakage from septic tanks in areas with high water tables may introduce these compounds in groundwater.

2.3.4.6 Steroid hormones in wastewater influents and effluents

A few studies have reported the concentration of steroid hormones in wastewater influents and effluents. In Southern England, a mean concentration of ethinyl-estradiol (0.932 ng/l) was recorded in sewage treatment effluent samples (Wilkinson et al., 2017). In a study conducted in China, the concentrations of estrone (E1), 17-beta-estradiol (E2), estriol (E3) and 17-alpha-ethinyl-estradiol (EE2) were detected in wastewater influent samples ranging from 22 to 142 ng/l, 31 to 88 ng/l, ND to 102 ng/l and ND to 110 ng/l, respectively. Furthermore, wastewater effluent samples were also found to have concentrations of estrone (E1), 17-beta-estradiol (E2), estriol (E3) and 17-alpha-ethinyl-estradiol (EE2), ranging from ND to 153 ng/l, ND to 123 ng/l, ND to 48 ng/l and ND to 33 ng/l, respectively (Lin et al., 2020).

All vertebrates naturally produce steroid hormones, which are incredibly significant hormones. As pharmaceuticals for both humans and animals, many synthetic steroid hormones are in common use. Both in humans and animals, these medications may only be partially absorbed. As a result of their use in agriculture to make animals fatter, they may be present in the water sources. They may enter surface water through animal waste. Human excretion results in the presence of steroid hormones in wastewater treatment processes. Because of the inability of WWTPs to remove them, they were also detected in effluents and subsequently in surface water such as rivers and dams receiving effluent.

2.3.5 Case studies: South African perspective

Water sources are crucial for human and animal survival. However, surface water, groundwater and treated drinking water can all become contaminated as a result of rise in usage of pharmaceuticals and personal care products and lack of proper medicinal disposal methods. Moreover, one of Africa's most active and varied agricultural sectors is found in South Africa. Crop production, animal production, horticulture and dairy farming are some of its agricultural pursuits. All these activities necessitate the use of pesticides. Pesticides may

enter water sources due to a variety of factors, including the discharge of effluent from wastewater treatment facilities, leachates from municipal landfills, run-off and leaching from contaminated soils and the careless disposal of pesticide containers. Low removal rates of emerging contaminants in wastewater treatment facilities has also contributed to the pollution of water sources. It is concerning to the public as there is a lack of regulations in South Africa regarding emerging contaminants in water sources. Lack of legislation may exacerbate their introduction into water sources which could affect aquatic life and human health. In this section, a few case studies are presented to illustrate the presence of pharmaceuticals, personal care products, steroid hormones and pesticides in water sources. Although these contaminants have been found in various water sources in South Africa, their concentrations vary as summarised in Tables 2.5, 2.6, and 2.7.

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

The most commonly detected pharmaceuticals and personal care products in South African water sources include the following (Table 2.5):

Non-steroidal anti-inflammatory drugs

Some NSAIDs that are mostly detected in various South African water matrices include acetaminophen, aspirin, diclofenac, ibuprofen, ketoprofen, naproxen, fenoprofen, mefenamic acid, paracetamol and codeine (Kanama et al., 2018; Archer et al., 2017; Agunbiade and Moodley, 2014; Agunbiade and Moodley, 2016; Ademoyegun, 2017; Mhuka et al., 2020). In a study conducted in surface water around the Gauteng province, the concentrations of acetaminophen, diclofenac, ibuprofen and ketoprofen ranged from 0.02 to 0.2 µg/l, 0.3 to 2.2 µg/l, 0.1 to 0.6 µg/l, and 0.01 to 0.8 µg/l, respectively (Archer et al., 2017). A study conducted in the Umgeni River water system, KwaZulu-Natal, targeting pharmaceuticals as emerging organic contaminants detected and reported concentrations of acetaminophen (5.8–58.7 µg/l), aspirin (2.2–10.0 µg/l), diclofenac (1.1–5.6 µg/l), ibuprofen (0.8–18.9 µg/l) and ketoprofen (0.4–8.2 µg/l) (Agunbiade and Moodley, 2014). Agunbiade and Moodley (2016) detected concentrations of aspirin (13.7–25.4 µg/l), diclofenac (0.6–8.2 µg/l), ibuprofen (0.4–0.7 µg/l) and ketoprofen (0.4–0.7 µg/l) in the Msunduzi River, KwaZulu-Natal. Mhuka et al. (2020) detected various NSAIDs such as diclofenac, fenoprofen, ibuprofen, ketoprofen, mefenamic acid and naproxen in the upper stream of Apies River samples at a high concentration of 81.98 ng/l, 67.98 ng/l, 8 651 ng/l, 8.853 ng/l, 91.15 ng/l and 137.9 ng/l, respectively.

Table 2.5 Occurrence and concentration levels of pharmaceuticals and personal care products in South African surface water, groundwater and drinking water

Pharmaceuticals and personal care products	Area	Concentration in various water matrices						References	
		Surface Water		Groundwater		Drinking Water			
		Range	Mean	Range	Mean	Range	Mean		
Non-steroidal anti-inflammatory drugs (NSAIDs)									
Acetaminophen	Gauteng	0.02–0.2 µg/l						Archer et al., 2017	
	KwaZulu-Natal	5.8–58.7 µg/l						Agunbiade and Moodley, 2014	
Aspirin	KwaZulu-Natal	2.2–10.0 µg/l						Agunbiade and Moodley, 2014	
	KwaZulu-Natal	13.7–25.4 µg/l						Agunbiade and Moodley, 2016	
Diclofenac	Gauteng	0.3–2.2 µg/l						Archer et al., 2017	
	KwaZulu-Natal	1.1–15.6 µg/l						Agunbiade and Moodley, 2014	
	KwaZulu-Natal	0.6–8.2 µg/l						Agunbiade and Moodley, 2016	
	Gauteng	5.642–81.98 ng/l	20.38 ng/l					Patterton, 2013	
Ibuprofen	Gauteng	0.1–0.6 µg/l						Archer et al., 2017	
	KwaZulu-Natal	0.8–18.9 µg/l						Agunbiade and Moodley, 2014	
	KwaZulu-Natal	0.4–0.7 µg/l						Agunbiade and Moodley, 2016	
	Gauteng	<LOD–8651 ng/l	3192 ng/l					Mhuka et al., 2020	
Ketoprofen	Gauteng	0.01–0.8 µg/l						Archer et al., 2017	
	KwaZulu-Natal	0.4–8.2 µg/l						Agunbiade and Moodley, 2014	
	KwaZulu-Natal	0.4–0.7 µg/l						Agunbiade and Moodley, 2016	
	Gauteng	<LOD–8.853 ng/l	4.289 ng/l					Mhuka et al., 2020	
Naproxen	Gauteng	0.2–1.9 µg/l						Archer et al., 2017	
	Gauteng	30.33–137.9 ng/l						Hendricks and Pool, 2012	
Fenoprofen	Gauteng	< LOD–67.98 ng/l						Mhuka et al., 2020	
Mefenamic acid	Gauteng	2.239–91.15 ng/l						12.87 ng/l	Mhuka et al., 2020
Antibiotics									
Ampicillin	KwaZulu-Natal	2.5–14.5 µg/l						Agunbiade and Moodley, 2014	
	KwaZulu-Natal	3.2–5.5 µg/l						Agunbiade and Moodley, 2016	
Chloramphenicol	KwaZulu-Natal	0.5–10.7 µg/l						Agunbiade and Moodley, 2014	
Erythromycin	KwaZulu-Natal	0.6–22.6 µg/l						Agunbiade and, 2016	
	KwaZulu-Natal	0.1–0.2 µg/l						Matongo et al., 2015	
	Gauteng	<LOD–6.59 ng/l	1.57 ng/l					Mhuka et al., 2020	
Fluoroquinolones	KwaZulu-Natal	0.7–16.9 µg/l						Agunbiade and Moodley, 2014	
	KwaZulu-Natal	2.4–14.3 µg/l						Agunbiade and Moodley, 2016	

Pharmaceuticals and personal care products	Area	Concentration in various water matrices						References
		Surface Water		Groundwater		Drinking Water		
		Range	Mean	Range	Mean	Range	Mean	
Nalidixic acid	KwaZulu-Natal	1.7–30.8 µg/l						Agunbiade and Moodley, 2014
	KwaZulu-Natal	12.4–23.5 µg/l						Agunbiade and Moodley, 2016
Streptomycin	KwaZulu-Natal	0.8–8.4 µg/l						Agunbiade and Moodley, 2014
Sulfamethoxazole	KwaZulu-Natal		3.68 µg/l					Agunbiade and Moodley, 2014
	KwaZulu-Natal	1.2–5.3 µg/l						Matongo et al., 2015
	Gauteng	<LOD–237.4 ng/l	103.5 ng/l					Mhuka et al., 2020
Tetracycline	KwaZulu-Natal	0.6–5.7 µg/l						Agunbiade and Moodley, 2014
Trimethoprim	KwaZulu-Natal		0.3 µg/l					Matongo et al., 2015
	Gauteng	6.9011–114.8 ng/l	49.76 ng/l					Mhuka et al., 2020
Tylosin	KwaZulu-Natal	0.2–22.0 µg/l						Agunbiade and Moodley, 2014
Clarithromycin	Gauteng	<LOD–5.480 ng/l	3.194 ng/l					Mhuka et al., 2020
Ciprofloxacin	North West	<LOD						Kanama et al., 2018
Ofloxacin	Gauteng	<LOD–4.65 ng/l						Mhuka et al., 2020
Norfloxacin	North West	<LOD						Kanama et al., 2018
Sulfadiazine	Gauteng	ND–1.77 ng/l	0.253 ng/l					Mhuka et al., 2020
Antiseptic								
Triclosan	Gauteng	0.4–0.9 µg/l						Madikizela et al., 2014
Beta-blockers								
Atenolol	KwaZulu Natal	1.0–39.1 µg/l						Agunbiade and Moodley, 2014
	Gauteng	0.1–0.5 µg/l						Archer et al., 2017
Metoprolol	Gauteng	ND–0.22 ng/l	0.048 ng/l					Mhuka et al., 2020
Anti-epileptics								
Carbamazepine	Free State					0.02–0.3 µg/l		Mhuka et al., 2020
	KwaZulu-Natal					0.01–0.02 µg/l		Patterton, 2013
	Gauteng					0.03–0.1 µg/l		Patterton, 2013
	North West	0.1–3.2 µg/l						Matongo et al., 2015
	Gauteng	0.2–0.3 µg/l						Archer et al., 2017
	Gauteng		1.75 ng/l					Wanda et al., 2017
	North West		52.35 ng/l					Wanda et al., 2017
	Mpumalanga		29 ng/l					Wanda et al., 2017
Gauteng	8.774–176.0 ng/l	58.51 ng/l					Mhuka et al., 2020	
Anti-psychotic								
Clozapine	North West	2.2–8.9 µg/l						Matongo et al., 2015
Lipid regulators								
Bezafibrate	Gauteng	0.05–0.4 µg/l						Archer et al., 2017

Pharmaceuticals and personal care products	Area	Concentration in various water matrices						References
		Surface Water		Groundwater		Drinking Water		
		Range	Mean	Range	Mean	Range	Mean	
Antivirals								
Tenofovir	Gauteng Free State	0.16–0.19 µg/l	0.25 µg/l					Wood et al., 2015 Wood et al., 2015
Lamivudine	Gauteng Gauteng	0.09–0.24 µg/l <LOD–8.912 ng/l	2.443 ng/l					Wood et al., 2015 Mhuka et al., 2015
Zalcitabine	Free State Gauteng		0.07 µg/l 0.03 µg/l			0.008 µg/l		Wood et al., 2015 Wood et al., 2015
Stavudine	Gauteng	0.41–0.78 µg/l						Wood et al., 2015
Zidovudine	Gauteng	0.22–0.62 µg/l				0.07 µg/l		Wood et al., 2015
Nevirapine	Gauteng Gauteng Gauteng	0.24–1.48 µg/l < LOQ–7.332 ng/l	0.41 µg/l					Gerber, 2019 Wood et al., 2015 Mhuka et al., 2020
Didanosine	Free State		0.05 µg/l					Wood et al., 2015
Lopinavir	Gauteng Gauteng	0.28–0.31 µg/l	24.35 µg/l					Gerber, 2019 Wood et al., 2015
Ritonavir	Gauteng Gauteng		1.69 µg/l 25.54 ng/l					Gerber, 2019 Wood et al., 2015
Efavirenz	Gauteng		15.04 µg/l					Gerber, 2019
Famciclovir	Gauteng	<LOD–8.69 ng/l	2.51 ng/l					Mhuka et al., 2020
Penciclovir	Gauteng	<LOD–18.66 ng/l	3.338 ng/l					Mhuka et al., 2020
Human indicators/Psychomotor stimulant								
Caffeine	KwaZulu-Natal	0.1–3.3 µg/l						Matongo et al., 2015
	Gauteng	0.6–6.6 µg/l						Archer et al., 2017
	North West	82.41 ng/l				6.4 ng/l		Wanda et al., 2017
	Gauteng		2.23 ng/l					Wanda et al., 2017
	Mpumalanga		81.24 ng/l					Wanda et al., 2017
	Gauteng	4.098–2 785 µg/l	1 424 ng/l					Mhuka et al., 2020.

Antibiotics

Various researchers have detected several antibiotics such as ampicillin, chloramphenicol, erythromycin, fluoroquinolones, nalidixic acid, streptomycin, sulfamethoxazole, tetracycline, trimethoprim, tylosin, clarithromycin, ciprofloxacin, ofloxacin, norfloxacin, sulfadiazine and doxycycline at various concentrations in water environments (Kanama et al., 2018; Agunbiade and Moodley, 2014; Agunbiade and Moodley, 2016; Ademoyegun, 2017; Mhuka et al., 2020; Matongo et al., 2015; Hendricks and Pool, 2012). Concentrations of antibiotics such as ampicillin, chloramphenicol, erythromycin, fluoroquinolones, nalidixic acid, streptomycin, tetracycline and tylosin were reported ranging from 2.5 to 14.5 µg/l, 0.5 to 10.7 µg/l, 0.6 to 22.6 µg/l, 0.7 to 6.9 µg/l, 1.7 to 30.8 µg/l, 0.8 to 8.4 µg/l, 0.6 to 5.7 µg/l, and 0.2 to 22.0 µg/l, respectively while sulfamethoxazole was reported at an average concentration of 3.68 µg/l in a study conducted in the Umgeni River water system, KwaZulu-Natal, targeting pharmaceuticals as emerging organic contaminants (Agunbiade and Moodley, 2014).

A study by Matongo et al. (2015) in the Msunduzi River, KwaZulu-Natal, reported the concentrations of erythromycin ranging from 0.1 to 0.2 µg/l, sulfamethoxazole ranging from 1.2 to 5.3 µg/l and trimethoprim with mean concentration of 0.3 µg/l. A follow-up study conducted in Msunduzi River, KwaZulu-Natal, reported occurrences of ampicillin, fluoroquinolones and nalidixic acid at concentrations ranging from 3.2 to 5.5 µg/l, 2.4 to 14.3 µg/l and 12.4 to 23.5 µg/l, respectively (Agunbiade and Moodley, 2016). A study done in the Apies River in the Gauteng province, detected high concentrations of various antibiotics such as erythromycin (6.59 ng/l), clarithromycin (5.480 ng/l), ofloxacin (4.65 ng/l), trimethoprim (114.8 ng/l), sulfamethoxazole (237.4 ng/l) and sulfadiazine (1.77 ng/l). Furthermore, ciprofloxacin and norfloxacin were below limit of detection (<LOD) in the upper stream of the Apies River (Mhuka et al., 2020).

Beta-blockers

Among the beta-blockers, atenolol was reported by Agunbiade and Moodley (2014) in their study conducted in the Umgeni River water system, KwaZulu-Natal, at concentrations ranging from 1.0 to 39.1 µg/l. In a study conducted in surface water around the Gauteng province, atenolol was detected at concentrations ranging from 0.1 to 0.5 µg/l (Archer et al., 2017). Mhuka et al. (2020), in their study conducted in the Apies River in the Gauteng province, detected metoprolol at a high concentration of 0.22 ng/l.

Antiepileptics

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

Mhuka et al. (2020) reported the concentrations of carbamazepine in the upper stream of the Apies River in Gauteng, ranging from 8.7 to 176 ng/l. In another study targeting the emerging micro-pollutants in water systems in Gauteng, Mpumalanga and North West provinces, South Africa, the mean concentration of carbamazepine in Mpumalanga surface water was reported as 29 ng/l, while in the Roodeplaat dam in Gauteng the mean concentration was 1.75 ng/l. Furthermore, a carbamazepine mean concentration of 52.35 ng/l was reported in Hartbeespoort Dam, Magalies River in the Northwest province (Wanda et al., 2017).

Antipsychotic and lipid regulators

Matongo et al. (2020) conducted a study in the Msunduzi River, KwaZulu-Natal, and detected clozapine among the antipsychotics at concentrations ranging from 2.2 to 8.9 µg/l. In another study conducted with the aim of determining pharmaceuticals and personal care products as endocrine disrupting contaminants in South African surface waters, bezafibrate was one of the lipid regulators detected at concentrations ranging from 0.05 to 0.4 µg/l in surface water of Gauteng the province (Archer et al., 2017).

Human indicators or psychomotor stimulants

Psychomotor stimulants such as caffeine was reported in surface water at concentrations ranging from 0.1 to 3.3 µg/l in a study conducted to determine pharmaceutical residues in the Msunduzi River, KwaZulu-Natal (Matongo et al., 2015). Archer et al. (2017) confirmed the prevalence of caffeine in surface water around Gauteng at concentrations ranging from 0.6 to 6.6 µg/l. In a study aimed at the occurrence of emerging micro-pollutants in water systems in the Gauteng, Mpumalanga and North West provinces in South Africa, caffeine was detected in surface water from the Mpumalanga province and the Roodeplaat dam in

Gauteng at a mean concentration of 82.41 ng/l and 2.23 ng/l, respectively. The same study also reported a mean concentration in surface water of 1-Krokodil River in the North West province as 81.24 ng/l (Wanda et al., 2017). Mhuka et al. (2020) detected caffeine in the upper stream of the Apies River, Gauteng province, at concentrations ranging from 4.09 to 2 785 µg/l.

Antivirals

A group of antivirals have been detected in various South African aquatic environments. Some antivirals detected in South African aquatic systems include ribavirin, tenofovir, lamivudine, zalcitabine, stavudine, zidovudine, nevirapine, didanosine, lopinavir, ritonavir, efavirenz, famciclovir and penciclovir (Mhuka et al., 2020; Oskunmakinde et al., 2013; Wood et al., 2015; Gerber, 2019). In a study conducted on endocrine disrupting effects of HIV antiretrovirals in the South African aquatic environment, nevirapine, lopinavir, ritonavir and efavirenz were detected in the upper stream of the Olifantsfontein River at mean concentrations of 0.41 µg/l, 24.35 µg/l, 1.69 µg/l and 15.04 µg/l, respectively (Gerber, 2019). Mhuka et al. (2020) detected various antivirals such as famciclovir, lamivudine, nevirapine, penciclovir and ritonavir at high concentrations of 8.69 ng/l, 8.912 ng/l, 7.332 ng/l and 58.84 ng/l, correspondingly, in the upper stream samples of the Apies River.

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

Antiseptics

In the study conducted to determine triclosan and ketoprofen in river water and wastewater by SPE and high performance liquid chromatography (HPLC), a concentration of triclosan

among the antiseptics in surface water was detected and reported ranging from 0.4 to 0.9 µg/l around Gauteng (Madikizela et al., 2014).

Illegal dumping of unused or expired medicinal drugs and release of effluents into nearby streams may be the possible sources of these contaminants in surface water sources. Runoff from nearby agricultural activities may also be attributed as the source of these compounds in water sources.

2.3.5.2 Pharmaceuticals and personal care products in wastewater influents and effluents

Non-steroidal anti-inflammatory drugs

The occurrence of pharmaceuticals and personal care products has also been detected in South African wastewater influents and effluents as summarised in Table 2.6. In a study conducted in the North West province, South Africa, the concentrations of NSAIDs such as acetaminophen (21.27–119.50 µg/l), diclofenac (0.12–10.34 µg/l), ibuprofen (0.33–53.40 µg/l) and ketoprofen (<LOQ–0.65 µg/l) were detected in influent samples. Furthermore, in effluent samples, their respective concentrations ranged from <LOQ to 11.39 µg/l, 0.07 to 0.75 µg/l, <LOQ to 13.66 µg/l and <LOQ to 0.24 µg/l (Kanama et al., 2018). In another study conducted by Archer et al. (2017), NSAIDs were prevalent in wastewater influent and effluent in various concentrations (Archer et al., 2017). Acetaminophen was detected at concentrations ranging from 136.9 to 343.6 µg/l in influent and 0.04 to 0.2 µg/l in effluent. The study also reported diclofenac in influent and effluent at concentrations ranging from 2.7 to 5.6 µg/l and 2.2 to 2.5 µg/l, respectively. Ibuprofen was detected in influent ranging from 9.1 to 15.8 µg/l and in effluent ranging from 0.3 to 1.2 µg/l. Furthermore, the same study detected ketoprofen in influent and effluent at concentrations ranging from 0.4 to 5.6 µg/l and 0.2 to 0.7 µg/l, respectively.

In Msunduzi River, KwaZulu-Natal, the mean concentrations of diclofenac, ibuprofen and ketoprofen in influent and effluent were as 222.7 µg/l and 123.7 µg/l, 1.2 µg/l and 1.1 µg/l, and 3.2 µg/l and 0.4 µg/l, respectively (Agunbiade et al., 2016). Mhuka et al. (2020) also detected various NSAIDs such as diclofenac, fenoprofen, ibuprofen, ketoprofen, mefenamic acid and naproxen in influent at high concentrations of 246.3 ng/l, <LOD, 76 377 ng/l, 23.10 ng/l, 91.15 ng/l and 546.1 ng/l, whereas in effluent they were detected at maximum concentrations of 243.6 ng/l, 207.6 ng/l, 7 652 ng/l, 49.48 ng/l, 55.05 ng/l and 349.6 ng/l, respectively. Furthermore, in a study by Ademoyegun (2017) in selected WWTPs in the Eastern Cape, aspirin, ibuprofen, diclofenac, paracetamol and codeine were detected in influent at concentrations ranging from 1.45 to 4.00 µg/l, 0.39 to 17.5 µg/l, 0.04 to 5.46 µg/l,

0.77 to 35.01 µg/l, and high concentrations of codeine at 0.35 µg/l, whereas in effluent they ranged from 0.16 to 0.99 µg/l, 0.10 to 5.27 µg/l, 0.03 to 2.19 µg/l and 0.21 to 10.54 µg/l, respectively, and high concentration of codeine was 0.17 µg/l. In eThekweni, KwaZulu-Natal province, Späth et al. (2021) reported the average concentrations of diclofenac, paracetamol and tramadol in influent as 2 300 ng/l, 140 000 ng/l and 330 ng/l, respectively, while their respective mean concentrations in effluent were as 2 100 ng/l, 4 600 ng/l and 400 ng/l.

Antibiotics

Ademoyegun (2017) detected trimethoprim, chloramphenicol and doxycycline in influent samples at high concentrations of 0.63 µg/l, 1.74 µg/l and 0.19 µg/l, while in effluent samples their respective concentrations were as 0.41 µg/l, 1.22 µg/l and 0.07 µg/l. Another study was conducted in the North West province, which reported respective concentrations of tetracycline, ciprofloxacin and norfloxacin in influent, ranging from 1.09 to 45.38 µg/l, 0.08 to 1.40 µg/l and 0.03 to 0.35 µg/l, while in effluent their respective mean concentrations ranged from 0.52 to 1.43 µg/l, 0.12 to 2.00 µg/l and 0.10 to 1.53 µg/l (Kanama et al., 2018). Matongo et al. (2015), in their study conducted in KwaZulu-Natal, reported the mean concentrations of erythromycin as 0.6 µg/l and 0.2 µg/l in both influent and effluent, respectively. The same study also detected sulfamethoxazole in influent at a mean concentration of 34.5 µg/l. Another study in the Western Cape detected fluoroquinolones and sulfamethoxazole in influent and effluent at concentrations ranging from 0.09 to 0.1 µg/l and 0.07 to 0.09 µg/l, respectively (Hendricks and Pool, 2012). Ampicillin, fluoroquinolones and nalidixic acid were reported at average concentrations of 6.6 µg/l and 8.9 µg/l, 27.1 µg/l and 20.5 µg/l, and 29.9 µg/l and 25.2 µg/l in influent and effluent, respectively, in a study conducted in WWTPs around KwaZulu-Natal (Agunbiade and Moodley, 2016).

Mhuka et al. (2020) detected and quantified erythromycin, clarithromycin, ciprofloxacin, norfloxacin, ofloxacin, trimethoprim, sulfamethoxazole and sulfadiazine in influent at high concentrations of <LOD, 10.06 ng/l, 77.04 ng/l, 31.7 ng/l, 67.5 ng/l, 577.6 ng/l, 2 405 ng/l and 0.42 ng/l, respectively. The same study also reported respective maximum concentrations of erythromycin, clarithromycin, ciprofloxacin, norfloxacin, ofloxacin, trimethoprim and sulfamethoxazole as 11.89 ng/l, 75.44 ng/l, 5.59 ng/l, 9.83 ng/l, 86.51 ng/l, 136.6 ng/l and 504.4 ng/l in effluent, while sulfadiazine was not detected. A study by Späth et al. (2021) in eThekweni, KwaZulu-Natal, reported average concentrations of ciprofloxacin, clindamycin, levofloxacin, sulfamethoxazole and trimethoprim in influent as 1 300 ng/l, 270 ng/l, 25 ng/l, 12 000 ng/l and 1 400 ng/l, respectively, while in effluent their respective mean concentrations were 1 600 ng/l, 270 ng/l, 22 ng/l, 2 500 ng/l and 290 ng/l.

Beta-blockers

Among the beta-blockers, atenolol was detected in both influent and effluent samples at concentrations ranging from 1.08 to 8.34 $\mu\text{g}/\ell$ and 0.33 to 3.22 $\mu\text{g}/\ell$ in a study conducted in WWTPs receiving inflows from health facilities in the North West province (Kanama et al., 2018). In the Umgeni River water system, KwaZulu-Natal, a study was conducted to detect pharmaceuticals as emerging organic contaminants and reported atenolol as one of the beta-blockers at concentrations ranging from 1.0 to 39.1 $\mu\text{g}/\ell$ (Agunbiade and Moodley, 2014). In another study, atenolol was reported in influent samples at concentrations ranging from 1.6 to 2.5 $\mu\text{g}/\ell$, and in effluent samples as 0.4 to 0.7 $\mu\text{g}/\ell$ around Gauteng (Archer et al., 2017). Osunmakinde et al. (2013) conducted a study in Gauteng and reported mean concentrations of pindolol in influent and effluent as 0.03 $\mu\text{g}/\ell$ and 0.00003 $\mu\text{g}/\ell$, respectively. Mhuka et al. (2020), in their study on the occurrence of pharmaceuticals and personal care products in wastewater and receiving waters, detected metoprolol at a high concentration of 0.09 ng/ ℓ in influent and in effluent at a high concentration of 2.22 ng/ ℓ .

Antiepileptics

Among the antiepileptics, carbamazepine was reported at mean concentrations of 2.2 $\mu\text{g}/\ell$ and 0.9 $\mu\text{g}/\ell$ in both influent and effluent in a study conducted in KwaZulu-Natal (Matongo et al., 2015). Furthermore, Archer et al. (2017) observed carbamazepine in influent at concentrations ranging from 0.3 to 0.6 $\mu\text{g}/\ell$, and in effluent around Gauteng at a mean concentration of 0.4 $\mu\text{g}/\ell$. In another study conducted around Mpumalanga province, a mean concentration of carbamazepine in wastewater effluent was reported at 58 ng/ ℓ (Wanda et al., 2017). Mhuka et al. (2020) conducted a study targeting pharmaceuticals and personal care products in wastewater and receiving waters and detected a high concentration of carbamazepine as 115.7 ng/ ℓ in influent and 416.3 ng/ ℓ in an effluent sample. Ademoyegun's (2017) study in the Eastern Cape, detected a high concentration of diazepam (0.90 $\mu\text{g}/\ell$) and carbamazepine (2.61 $\mu\text{g}/\ell$) in influent, while in effluent their respective high concentration was 0.69 $\mu\text{g}/\ell$ and 1.33 $\mu\text{g}/\ell$. A study in eThekweni, KwaZulu-Natal province, reported the average concentrations of carbamazepine and lamotrigine in influent as 480 ng/ ℓ and 240 ng/ ℓ , respectively. In effluent, their respective mean concentrations were reported as 480 ng/ ℓ and 0 ng/ ℓ (Dalvi et al., 2009).

Antipsychotic and lipid regulators

Among the antipsychotics, Matongo et al. (2015) reported mean concentrations of clozapine in influent and effluent as 8.6 $\mu\text{g}/\ell$ and 9.6 $\mu\text{g}/\ell$, respectively in their study conducted in KwaZulu-Natal province. Moreover, in a study conducted around Gauteng, bezafibrate as

one of the lipid regulator was detected in influent at concentrations ranging from 0.05 to 0.4 µg/l and in effluent at concentrations ranging from 0.3 to 0.7 µg/l (Archer et al., 2017).

Human indicators or psychomotor stimulants

In a study conducted in KwaZulu-Natal, caffeine was one of the human indicators detected in influent and effluent at mean concentrations of 4.5 µg/l and 0.6 µg/l, respectively (Matongo et al., 2015). It was also detected in influent and effluent around Gauteng at concentrations ranging from 5.1 to 1 214.4 µg/l and 0.5 to 3.8 µg/l, respectively (Archer et al., 2017). In another study conducted in Mpumalanga, caffeine was detected in influent and effluent at mean concentrations of 9.1 ng/l and 11.0 ng/l, respectively (Wanda et al., 2017). Mhuka et al. (2020) conducted a study on the occurrence of pharmaceuticals and personal care products in wastewater and receiving waters and indicated that influent samples were having concentrations of caffeine ranging from 1 170 to 60 136 ng/l, while in influent samples caffeine ranged from 85.76 to 4 878 ng/l. Späth et al. (2021) in eThekweni, KwaZulu-Natal province, reported the average concentrations of caffeine in influent and effluent as 22 000 ng/l and 7 500 ng/l, respectively. Caffeine was also reported at concentrations ranging from 4.69 to 69.49 µg/l in influent and 0.98 to 12.77 µg/l in effluent samples in a study conducted in the Eastern Cape (Ademoyegun, 2017).

Antivirals

In eThekweni, KwaZulu-Natal, average concentrations of abacavir, atazanavir, darunavir, lamivudine, nevirapine, raltegravir and acyclovir were reported in wastewater influent as 100 ng/l, 3 100 ng/l, 14 000 ng/l, 74 000 ng/l, 350 ng/l, 4 100 ng/l and 3 000 ng/l, respectively. The study also reported mean concentrations of the same compounds in effluent as 540 ng/l, 3 000 ng/l, 10 000 ng/l, 130 000 ng/l, 350 ng/l, 3 500 ng/l and 1 900 ng/l, respectively (Spath et al., 2021). Osunmakinde et al. (2013), in their study conducted in Gauteng, detected antivirals such as ribavirin in influent and effluent at mean concentrations of 0.02 µg/l and 0.00004 µg/l, respectively. They also detected famciclovir in influent at average concentrations of 0.02 µg/l and 0.00006 µg/l in effluent. Wood et al. (2015) conducted a study targeting antiretroviral compounds used for HIV treatment in South African surface water and detected lopinavir in effluent at an average concentration of 0.13 µg/l. A study conducted to determine the occurrence of pharmaceuticals and personal care products in wastewater and receiving waters, detected concentrations of famciclovir, lamivudine, nevirapine, penciclovir, and ritonavir in influent as 17.67 ng/l, 1 001 ng/l, 26.34 ng/l, 22.94 ng/l, and 393.90 ng/l, while in effluent samples, they were detected as 7.17 ng/l, 323.40 ng/l, 80.53 ng/l, 104.8 ng/l and 675.90 ng/l, respectively (Mhuka et al., 2020). Späth et al. (2021), in their study in eThekweni, reported average concentrations of acyclovir as 3 000 ng/l and 1 900 ng/l in both influent and effluent, respectively.

Table 2.6 Occurrence of pharmaceuticals and personal care products in South African wastewater influent and effluents

Pharmaceuticals and personal care products	Area	WWTP Influent		WWTP Effluent		References
		Range	Mean	Range	Mean	
Non-steroidal anti-inflammatory drugs (NSAIDs)						
Acetaminophen	North West	21.27–119.50 µg/l	49.79 µg/l	<LOQ–11.39 µg/l	6.1 µg/l	Kanama et al., 2018
	Gauteng	136.9–343.6 µg/l		0.04–0.2 µg/l		Archer et al., 2017
Aspirin	Eastern Cape	1.45–4.00 µg/l	2.46 µg/l	0.16–0.99 µg/l	0.51 µg/l	Ademoyegun, 2017
	North West	0.12–10.34 µg/l	2.38 µg/l	0.07–0.75 µg/l	0.3 µg/l	Kanama et al., 2018
	Gauteng	2.7–5.6 µg/l		2.2–2.5 µg/l		Archer et al., 2017
Diclofenac	KwaZulu-Natal		222.7 µg/l		123.7 µg/l	Agunbiade and Moodley, 2016
	Gauteng	12.16–246.3 ng/l	147.5 ng/l	5.56–243.6 ng/l	74.44 ng/l	Mhuka et al., 2020
	Eastern Cape	0.04–5.46 µg/l	2.41 µg/l	0.03–2.19 µg/l	0.84 µg/l	Ademoyegun, 2017
	KwaZulu-Natal		2 300 ng/l		2 100 ng/l	Spath et al., 2021
Ibuprofen	North West	0.33–53.40 µg/l	16.44 µg/l	<LOQ–13.66 µg/l	5.25 µg/l	Kanama et al., 2018
	Gauteng	9.1–15.8 µg/l		0.3–1.2 µg/l		Archer et al., 2017
	KwaZulu-Natal		1.2 µg/l		1.1 µg/l	Agunbiade and Moodley, 2016
	Gauteng	568.7–76377 ng/l	15831 ng/l	<LOD–7652 ng/l	2504 ng/l	Mhuka et al., 2020
	Eastern Cape	0.39–17.50 µg/l	6.82 µg/l	0.10–5.27 µg/l	1.56 µg/l	Ademoyegun, 2017
Ketoprofen	North West	<LOQ–0.65 µg/l	0.39 µg/l	<LOQ–0.24 µg/l		Kanama et al., 2018
	Gauteng	0.4–5.6 µg/l		0.2–0.7 µg/l		Archer et al., 2017
	KwaZulu-Natal		3.2 µg/l		0.4 µg/l	Agunbiade and Moodley, 2016
	Gauteng	<LOD–23.10 ng/l		<LOD–49.48 ng/l	13.38 ng/l	Mhuka et al., 2020
Naproxen	Gauteng	2.9–5.5 µg/l		1.8–2.9 µg/l		Archer et al., 2017
	Gauteng	16.85–546.1 ng/l	64.07 ng/l	13.09–349.6 ng/l	122.3 ng/l	Mhuka et al., 2020
Fenoprofen	Gauteng	<LOD	<LOD	<LOD–207.6 ng/l	46.8 ng/l	Mhuka et al., 2020
Mefenamic acid	Gauteng	11.30–91.15 ng/l	31.95 ng/l	4.789–55.05 ng/l	19.99 ng/l	Mhuka et al., 2020
	KwaZulu-Natal		330 ng/l		400 ng/l	Spath et al., 2021
Paracetamol	Eastern Cape	0.77–35.01 µg/l	13.64 µg/l	0.21–10.54 µg/l	3.11 µg/l	Ademoyegun, 2017
	KwaZulu-Natal		140 000 ng/l		4 600 ng/l	Spath et al., 2021
Codeine	Eastern Cape	LOQ–0.35 µg/l	0.18 µg/l	LOQ–0.17 µg/l	0.09 µg/l	Ademoyegun, 2017
Antibiotics						
Ampicillin	KwaZulu Natal		6.6 µg/l		8.9 µg/l	Agunbiade and Moodley, 2016
Chloramphenicol	Eastern Cape	0.07–1.74 µg/l	0.34 µg/l	0.02–1.22 µg/l	0.27 µg/l	Ademoyegun, 2017
Erythromycin	KwaZulu-Natal		0.6 µg/l		0.2 µg/l	Matongo et al., 2015
	Gauteng	<LOD	<LOD	<LOD–11.89 ng/l	4.01 ng/l	Mhuka et al., 2020
Fluoroquinolones	KwaZulu-Natal		27.1 µg/l		20.5 µg/l	Agunbiade and Moodley, 2016
	Western Cape		0.09–0.1 µg/l		0.07–0.09 µg/l	Hendricks and Pool, 2012
Nalidixic acid	KwaZulu-Natal		29.9 µg/l		25.2 µg/l	Agunbiade and Moodley, 2016
Levofloxacin	KwaZulu-Natal		25 ng/l		22 ng/l	Spath et al., 2021
Nalidixic acid	KwaZulu-Natal		34.5 µg/l			Matongo et al., 2015
	Western Cape	0.1–0.2 µg/l		0.08–0.1 µg/l		Hendricks and Pool, 2012

Pharmaceuticals and personal care products	Area	WWTP Influent		WWTP Effluent		References
		Range	Mean	Range	Mean	
	Gauteng	52.92–2405 ng/l		34.93–504.4 ng/l		Mhuka et al., 2020
Tetracycline	North West	1.09–45.38 µg/l	11.04 µg/l	0.52–1.43 µg/l	0.95 µg/l	Kanama et al., 2018
Trimethoprim	Gauteng	16.61–577.6 ng/l	108.7 ng/l	<LOD–136.6 ng/l	50.4 ng/l	Mhuka et al., 2020
	Eastern Cape	0.05–0.63 µg/l	0.17 µg/l	0.03–0.41 µg/l	0.16 µg/l	Ademoyegun, 2017
	KwaZulu-Natal		1 400 ng/l		290 ng/l	Spath et al., 2021
Clarithromycin	Gauteng	<LOD–10.06 ng/l	0.45 ng/l	<LOD–75.44 ng/l	9.84 ng/l	Mhuka et al., 2020
Clindamycin	KwaZulu-Natal		270 ng/l		270 ng/l	Spath et al., 2021
Ciprofloxacin	North West	0.12–2.00 µg/l	0.99 µg/l	0.08–1.40 µg/l	0.51 µg/l	Kanama et al., 2018
	Gauteng	<LOQ–77.04 ng/l	35.32 ng/l	<LOD–5.59 ng/l	1.03 ng/l	Mhuka et al., 2020
	KwaZulu-Natal		1 300 ng/l		1 600 ng/l	Spath et al., 2021
Ofloxacin	Gauteng	24.66–67.50 ng/l	36.39 ng/l	11.54–86.51 ng/l	42.05 ng/l	Mhuka et al., 2020
Norfloxacin	North West	0.10–1.53 µg/l	0.42 µg/l	0.03–0.35 µg/l	0.12 µg/l	Kanama et al., 2018
	Gauteng	<LOD–31.70 ng/l	3.12 ng/l	<LOD–9.83 ng/l	0.61 ng/l	Kanama et al., 2018
Sulfadiazine	Gauteng	<LOD–0.42 ng/l	0.05 ng/l			Kanama et al., 2018
Doxycycline	Eastern Cape	ND–0.19 µg/l		ND–0.07 µg/l		Ademoyegun, 2017
Sulfamethoxazole	KwaZulu-Natal		12 000 ng/l		2 500 ng/l	Spath et al., 2021
Antiseptics						
Triclosan	Gauteng	2.1–9.0 µg/l		1.3–6.4 µg/l		Madikizela et al., 2014
	Eastern Cape	2.45–18.73 µg/l	10.23 µg/l	0.10–11.05 µg/l	10.23 µg/l	Ademoyegun, 2017
Triclocarban	North West	0.23–1.75 µg/l	0.76 µg/l	0.01–0.46 µg/l	0.11 µg/l	Kanama et al., 2018
N,N-Diethyltoluamide (DEET)	Eastern Cape		9.63 µg/l		3.43 µg/l	Ademoyegun, 2017
Tonalide	Gauteng	0.21–80.16 ng/l	71.3 ng/l	<LOD–28.57 ng/l	7.247 ng/l	Mhuka et al., 2020
Beta-blockers						
Atenolol	North West	1.08–8.34 µg/l	4.41 µg/l	0.33–3.22 µg/l	1.19 µg/l	Kanama et al., 2018
	Gauteng	1.6–2.5 µg/l		0.4–0.7 µg/l		Archer et al., 2017
Metoprolol	Gauteng	<LOD–0.09 ng/l		<LOD–2.22 ng/l	0.6 ng/l	Mhuka et al., 2020
Pindolol	Gauteng		0.03 µg/l		0.00003 µg/l	Osunmakinde et al., 2013
Anti-epileptics						
Carbamazepine	KwaZulu-Natal		2.2 µg/l		0.9 µg/l	Matongo et al., 2015
	Gauteng	0.3–0.6 µg/l			0.4 µg/l	Archer et al., 2017
	Mpumalanga				58 ng/l	Wanda et al., 2017
	Gauteng	<LOQ–115.7 ng/l	30.89 ng/l	<LOQ–416.3 ng/l	193.6 ng/l	Mhuka et al., 2020
	Eastern Cape	0.05–2.61 µg/l	0.5 µg/l	0.03–1.33 µg/l	0.5 µg/l	Ademoyegun, 2017
	KwaZulu-Natal		480 ng/l		480 ng/l	Spath et al., 2021
Lamotrigine	KwaZulu-Natal		240 ng/l		0 ng/l	Spath et al., 2021
Diazepam	Eastern Cape	0.20–0.90 µg/l	0.29 µg/l	0.06–0.69 µg/l	0.29 µg/l	Ademoyegun, 2017
Anti-psychotic						
Clozapine	KwaZulu-Natal		8.6 µg/l		9.6 µg/l	Matongo et al., 2015

Pharmaceuticals and personal care products	Area	WWTP Influent		WWTP Effluent		References
		Range	Mean	Range	Mean	
Lipid regulators						
Bezafibrate	Gauteng	1.4–3.0 µg/l		0.3–0.7 µg/l		Archer et al., 2017
Antivirals						
Abacavir	KwaZulu-Natal		100 ng/l		540 ng/l	Spath et al., 202
Atazanavir	KwaZulu-Natal		3 100 ng/l		3 000 ng/l	Spath et al., 2021
Acyclovir	KwaZulu-Natal		3 000 ng/l		1 900 ng/l	Spath et al., 2021
Ribavirin	Gauteng		0.02 µg/l		0.00004 µg/l	Osunmakinde et al., 2013
Lamivudine	Gauteng	<LOD–1 001 ng/l	267.5 ng/l	<LOD–323.40 ng/l	28.07 ng/l	Mhuka et al., 2020
	KwaZulu-Natal		350 ng/l		350 ng/l	Spath et al., 202
Zidovudine	Gauteng			0.45–0.97 µg/l		Wood et al., 2015.
Nevirapine	Gauteng	<LOQ–26.34 ng/l	9.383 ng/l	<LOQ–80.53 ng/l	9.931 ng/l	Mhuka et al., 2020
	KwaZulu-Natal		74 000 ng/l		130 000 ng/l	Spath et al., 2021
Lopinavir	Gauteng				0.13 µg/l	Wood et al., 2015
Ritonavir	Gauteng	4.08–393.90 ng/l	72.77 ng/l	14.43–675.90 ng/l		Gerber, 2019
Famciclovir	Gauteng		0.02 µg/l		0.00006 µg/l	Osunmakinde et al., 2013
	Gauteng	<LOD–17.67 ng/l	0.86 ng/l	<LOD–7.17 ng/l	1.21 ng/l	Mhuka et al., 2020
Penciclovir	Gauteng	<LOD–22.94 ng/l	4.24 ng/l	16.31–104.8 ng/l	56.05 ng/l	Mhuka et al., 2020
Raltegravir	KwaZulu-Natal		4 100 ng/l		3 500 ng/l	Spath et al., 2021
Human indicators/psychomotor stimulant						
Caffeine	KwaZulu-Natal		4.5 µg/l		0.6 µg/l	Matongo et al., 2015
	Gauteng	5.1–1214.4 µg/l		0.5–3.8 µg/l		Archer et al., 2017
	Mpumalanga		9.1 ng/l		11 ng/l	Wanda et al., 2017
	KwaZulu-Natal		22 000 ng/l		7 500 ng/l	Spath et al., 2021
	Gauteng	1170–60 136 ng/l	28 171 ng/l	85.76–4 878 ng/l	1 533 ng/l	Mhuka et al., 2020.
	Eastern Cape	4.69–69.49 µg/l	10.79 µg/l	0.98–12.77 µg/l	10.79 µg/l	Ademoyegun, 2017

Antiseptics

Kanama et al. (2018) conducted a study in the North West province and detected triclocarban in wastewater influent and effluent at concentrations ranging from 0.23 to 1.75 µg/l and 0.01 to 0.46 µg/l, respectively. Triclosan was reported at concentrations ranging from 2.45 to 18.73 µg/l in wastewater influent samples and 0.10 to 11.05 µg/l in wastewater effluent in a study conducted in selected WWTPs in the Eastern Cape (Ademoyegun, 2017). Another study conducted in WWTPs around Gauteng detected the concentration of triclosan among the antiseptics in both influent and effluent at concentrations ranging from 2.1 to 9.0 µg/l and 1.3 to 6.4 µg/l (Madikizela et al., 2014).

Fragrance

Mhuka et al. (2020) conducted a study to quantify pharmaceuticals and personal care products in wastewater and receiving waters and detected tonalide among the personal care products in influent at concentrations ranging from 0.21 to 80.16 ng/l, with a mean concentration of 71.3 ng/l. The study also detected tonalide at concentrations ranging from <LOD to 28.57 ng/l, with a mean concentration of 7.247 ng/l in effluent.

Insect repellents

In a study aimed at evaluating some pharmaceuticals and personal care products and pesticide residues in selected wastewater treatment plants and receiving watersheds in the Eastern Cape, South Africa, a mean concentration of DEET in both influent and effluent were detected as 9.63 µg/l and 3.43 µg/l, respectively (Ademoyegun, 2017).

2.3.5.3 Herbicides in surface water, groundwater and drinking water

Agriculture is well developed in South Africa and contributes approximately 12.5% to the gross domestic product. South Africa is one of the countries with utmost use of pesticides in sub-Saharan Africa with approximately eight thousands (8 000) listed pesticide formulations (Dalvi et al., 2009). The use of pesticides in agricultural activities have caused serious environmental pollution and several studies have highlighted the prevalent of pesticides in South African surface water and groundwater (Dabrowski et al., 2002; London et al., 2000; Sereda and Meinhardt, 2005) as shown in Table 2.7.

A study conducted by Curchod et al. (2020) in rivers around the Western Cape, reported the concentrations of S-metolachlor, simazine, terbutylazine, atraton, prometryn, terbutryn, atrazine, diuron, propyzamide, haloxyfop, MCPA and oxyfluorfen ranging from 1.6 to 15.6 ng/l, 6.8 to 67.4 ng/l, 71.8 to 717.0 ng/l, 5.7 to 56.9 ng/l, 0.8 to 8.0 ng/l, 4.3 to

43.2 ng/l, 2.3 to 23.2 ng/l, 5.9 to 59.0 ng/l, 6.3 to 63.2 ng/l, 0.1 to 1.2 ng/l, 13.4 to 133.4 ng/l and 0.2 to 2.1 ng/l, respectively.

Horn et al. (2019) conducted a study in surface water of South Africa and detected 2,4-D in River (No. A1) and Dam (No. A2) from Farm A in the Free State, at mean concentrations of 0.93 µg/l and 0.72 µg/l, respectively, after spraying. In Farm B, located at the border between North West and the Free State, 2,4-D was also detected at mean concentrations of 1.02 µg/l and 0.96 µg/l after spraying and at the end of the season, respectively. The same study also detected 2,4-D in Dam (No. B3) located at the border separating the North West and Free State, before spraying, after spraying and at the end of the season at mean concentrations of 0.74 µg/l, 0.9 µg/l and 0.92 µg/l, respectively.

A study conducted in Cape Town in some selected marine environments, reported mean concentrations of various herbicides such as alachlor, metolachlor, butachlor, simazine and atrazine in Seawater (No. 1) as <LOQ, 0.3 ng/l, 0.5 ng/l, 1.4 ng/l and 1.9 ng/l, respectively. In Seawater (No. 2), their respective mean concentrations were as 3.4 ng/l, 2.3 ng/l, 1.6 ng/l, 4.2 ng/l and 1.6 ng/l (Ojemaye, 2020).

Mugudamani et al. (2023) conducted a study in the Mangaung Metropolitan Municipality (MMM) targeting herbicides in various water sources. In rivers, mean concentrations of atrazine, metolachlor, simazine and terbuthylazine were recorded as 0.03 mg/l, 0.01 mg/l, 1.82 mg/l and 0.03 mg/l, respectively. In dams/reservoirs, the authors reported atrazine, metolachlor, simazine and terbuthylazine at mean concentrations of 0.02 mg/l, 0.01 mg/l, 0.12 mg/l and 0.03 mg/l, respectively. Moreover, treated drinking water were found to have mean concentrations of 0.02 mg/l, 0.01 mg/l, 0.03 mg/l and 0.02 mg/l for atrazine, metolachlor, simazine and terbuthylazine, respectively.

Table 2.7 Occurrence of herbicides in South African surface water, groundwater and drinking water

Herbicides	Area	Concentration in various water matrices						References
		Surface Water		Groundwater		Drinking Water		
		Range	Mean	Range	Mean	Range	Mean	
2,4-D	Free State		0.93 µg/l					Horn et al., 2019
	Free State		0.72 µg/l					Horn et al., 2019
	North West/Free State		1.02 µg/l					Horn et al., 2019
	North West/Free State		0.96 µg/l					Horn et al., 2019
	North West/Free State		0.74 µg/l					Horn et al., 2019
	North West/Free State		0.90 µg/l					Horn et al., 2019
	North West/Free State		0.92 µg/l					Horn et al., 2019
Alachlor	Cape Town		<LOQ					Ojemaye, 2020
	Cape Town		3.4 ng/l					Ojemaye, 2020
Atraton	Western Cape	5.7–56.9 ng/l						Curchod et al., 2020
Atrazine	Western Cape	2.3–23.2 ng/l						Curchod et al., 2020
	Cape Town		1.9 ng/l			0.02 mg/l		Ojemaye, 2020
	Mangaung		0.03 mg/l					Mugudamani et al., 2023
	Mangaung		0.02 mg/l					Mugudamani et al., 2023
	Cape Town		1.6 ng/l					Ojemaye, 2020
Butachlor	Cape Town		0.5 ng/l					Ojemaye, 2020
	Cape Town		1.6 ng/l					Ojemaye, 2020
Diuron	Western Cape	5.9–59.0 ng/l						Curchod et al., 2020.
Haloxypop	Western Cape	0.1–1.2 ng/l						Curchod et al., 2020
MCPA	Western Cape	13.4–133.4 ng/l						Curchod et al., 2020
Oxyfluorfen	Western Cape	0.2–2.1 ng/l						Curchod et al., 2020
Prometryn	Western Cape	0.8–8.0 ng/l						Curchod et al., 2020
Propyzamide	Western Cape	6.3–63.2 ng/l						Curchod et al., 2020
S-metolachlor	Western Cape	1.6–15.6 ng/l						Curchod et al., 2020
	Mangaung		0.01 mg/l			0.02 mg/l		Mugudamani et al., 2023
	Mangaung		0.02 mg/l					Mugudamani et al., 2023
	Cape Town		0.3 ng/l					Ojemaye, 2020
	Cape Town		2.3 ng/l					Ojemaye, 2020
Simazine	Western Cape	6.8–67.4 ng/l						Curchod et al., 2020
	Mangaung		1.82 mg/l			0.03 mg/l		Mugudamani et al., 2023
	Mangaung		0.12 mg/l					Mugudamani et al., 2023
	Cape Town		1.4 ng/l					Ojemaye, 2020
	Cape Town		4.2 ng/l					Ojemaye, 2020
Terbuthylazine	Western Cape	71.8–717.0 ng/l						Curchod et al., 2020
Terbuthylazine	Mangaung		0.06 mg/l			0.02 mg/l		Mugudamani et al., 2023
Terbuthylazine	Mangaung		0.03 mg/l					Mugudamani et al., 2023
Terbutryn	Western Cape	4.3–43.2 ng/l						Curchod et al., 2020

2.3.5.4 Herbicides in wastewater influents and effluents

Späth et al. (2021) conducted a study in eThekweni and reported average concentrations of tebuthiuron and terbuthylazine in influent as 96 ng/l and 41 ng/l, respectively. In effluent, their respective mean concentrations were reported as 110 ng/l and 53 ng/l. A study conducted to analyse pesticides in water, soil, sediments and sludge in KwaZulu-Natal reported simazine and atrazine during the cold season at average concentrations of 9.7 µg/l and 7.8 µg/l in influent around the Darvill site, respectively. In effluents, these compounds were reported as 28 µg/l and 9.0 µg/l, respectively. The study also detected simazine, atrazine, ametryn and terbuthylazine in influent around Amanzimtoti at average concentrations of 8.2 µg/l, 2.5 µg/l, 6.2 µg/l and 8.0 µg/l, respectively. In effluent, their respective average concentrations were reported as 17 µg/l, 49 µg/l, 17 µg/l and 2.9 µg/l, respectively (Kunene, 2019).

2.3.5.5 Steroid hormones in surface water, groundwater and drinking water

From the literature review, steroid hormone compounds that are mostly detected in surface water, groundwater and drinking water around South Africa, included compounds such as estrone, 17-beta-estradiol, 17-alpha-ethinyl-estradiol and progesterone. A study was conducted targeting estrogenic activity, chemical levels and health risk assessment of municipal distribution point water from Pretoria and Cape Town, and detected estrone (E1) in drinking water at concentrations ranging from 0.002 to 0.004 µg/l in Pretoria and 0.0004 to 0.001 µg/l in Cape Town (Van Zijl et al., 2018).

Mhuka et al. (2020), in their study aimed at the occurrence of pharmaceuticals and personal care products in wastewater and receiving waters, detected compounds such as estradiol, estriol, estrone and testosterone at high concentrations of 644.0 ng/l, 244.5 ng/l, 63.04 ng/l and <LOD, respectively, in the upper stream of the Apies River. Van Wyk et al. (2014) reported estradiol (E2) in surface water in Mpumalanga at concentrations ranging from 0.001 to 0.03 µg/l. In a study conducted around Gauteng and the Western Cape, estradiol (E2) was detected at concentrations ranging from 0.04 to 0.37 µg/l in Gauteng, while in the Western Cape it ranged from 0.05 to 0.37 µg/l (De Jager et al., 2013). Furthermore, laboratory and field studies targeting pesticides as endocrine disruptors in South Africa reported 17-alpha-ethinyl-estradiol (EE2) in surface water around Mpumalanga at concentrations ranging from 0.001 to 0.01 µg/l (Van Wyk et al., 2014). Another study also reported an average concentration of ethinyl-estradiol (0.00002 µg/l) in drinking water around Pretoria (Van Zijl et al., 2018).

2.3.5.6 Steroid hormones in wastewater influents and effluents

Detection of steroid hormones has been reported in different regions of the country. A study was conducted in North West and reported the concentration of estrone (E1) ranging from 0.013 to 0.053 $\mu\text{g}/\text{l}$, estradiol (E2) ranging from 0.008 to 0.035 $\mu\text{g}/\text{l}$, ethinyl-estradiol (EE2) ranging from 2.654 to 9.833 $\mu\text{g}/\text{l}$ and estriol (E3) ranging from 0.134 to 1.480 $\mu\text{g}/\text{l}$ in influent samples. The same study also reported the concentration of estrone (E1) ranging from 0.007 to 0.041 $\mu\text{g}/\text{l}$, estradiol (E2) ranging from 0.008 to 0.0191 $\mu\text{g}/\text{l}$, ethinyl-estradiol (EE2) ranging from 0.448 to 4.608 $\mu\text{g}/\text{l}$ and estriol (E3) ranging from 0.111 to 0.539 $\mu\text{g}/\text{l}$ (Kanama et al., 2018).

Manickum and John (2014), in their study conducted in the WWTPs in Pietermaritzburg, reported estrone (E1) at a high concentration of 0.35 $\mu\text{g}/\text{l}$ in influent and 0.08 $\mu\text{g}/\text{l}$ in effluent. The same study also detected estradiol (E2) ranging from 0.02 to 0.20 $\mu\text{g}/\text{l}$ in influent and 0.004 to 0.11 $\mu\text{g}/\text{l}$ in effluent. Furthermore, they detected ethinyl-estradiol (EE2) in both influent and effluent at concentrations ranging from 0.01 to 0.095 $\mu\text{g}/\text{l}$ and 0.001 to 0.008 $\mu\text{g}/\text{l}$, respectively. Progesterone and testosterone were reported in influent at concentrations ranging from 0.16 to 0.90 $\mu\text{g}/\text{l}$ and 0.12 to 0.64 $\mu\text{g}/\text{l}$, respectively. Furthermore, their respective mean concentration in effluent was as 0.03 $\mu\text{g}/\text{l}$ and 0.03 $\mu\text{g}/\text{l}$.

Another study conducted to determine the occurrence of pharmaceuticals and personal care products in wastewater and receiving waters, detected estradiol, estriol, estrone and testosterone in influent at high concentrations of 2 206 ng/l, 1 313 ng/l, 35.96 ng/l and 44.09 ng/l, while in effluent they were detected as 7 133 ng/l, 779.1 ng/l, 60.83 ng/l and 5.83 ng/l, respectively (Mhuka et al., 2020).

2.3.6 Analytical procedure for detection of emerging contaminants

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

2.3.6.1 Sample preparation and extraction process

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

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

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

The most commonly used method for extraction of samples from the water environment is the solid-phase extraction (SPE) method. In SPE, a micro and lyophilisation method of extraction may also be utilised. Sample extraction and clean-up can be conducted simultaneously with the SPE technique. Cartridges packed with sorbents such as C-18, ion-exchange phases, polymeric phases and nonpolar phases are mostly used in SPE. For the off-line SPE, polymeric, octadecylsilica, or hydrophilic-lipophilic balanced with either disks or cartridges at low pH is used (Petrovic et al., 2003). In pre-concentration of polar and

nonpolar compounds hydrophilic–lipophilic balanced cartridges are the most preferred. For direct extraction and analysis an online automated SPE, which is done by coupling an automated SPE directly to liquid chromatography–mass spectrometry (LC–MS or LC–MS2) (Swartz et al., 2018).

2.3.6.2 Chromatography analysis

A highly sensitive and selective analytical method such as gas chromatography (GC) and liquid chromatography (LC) combined with mass spectrometry (MS) are crucial in the analysis of various emerging contaminants (Galindo-Marinda et al., 2019). Liquid chromatography combined with tandem mass spectrometry (LC–tandem–MS) is one of the most widely used techniques for the analysis of various groups of emerging contaminants occurring in an aqueous environment (Hernes et al., 2018). LC–tandem–MS can minimise the time of preparing samples and permits for the detection of polar and non-volatile compounds (Galindo-Marinda et al., 2019). It can achieve a little higher limit of detection (LOD) than GC–MS and allows for identification of highly polar organic pollutants in the environment at ng/l levels. For sample preparation and preconcentration methods, it can be coupled with on-line devices such as SPE methods (Swartz et al., 2018). The use of chromatographic systems at a very high pressure, such as ultra-HPLC, is used to speed up analysis and reduce solvent intake (Robles-Molina et al., 2013). The combination of high pressure and 1.7 µm-particle-size columns save time and solvent without compromising sensitivity or peak resolution (Chauveau-Duriot et al., 2010).

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

2.3.6.3 Detection systems

GC or HPLC are the most widely used analytical instruments for the detection of emerging contaminants. Single quadrupole MS, tandem MS (MS2), triple quadrupole (QqQ) MS, ion-

trap MS (IT–MS), and time-of-flight MS (QTOF–MS) are some of the detection systems used in different ionisation modes, for example atmospheric chemical pressure ionisation and electrospray ionisation (Swartz et al., 2018). Hybrid instruments, QqToF, QqLIT and orbitrap have become more commonly used mass analysers of emerging contaminants in an aqueous environment because of their effectiveness to achieve precise mass measurements and acquire crucial qualitative full-scan spectra data (Galindo-Marinda et al., 2019; Pitarch et al., 2016).

2.3.6.4 Ionisation sources

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

2.3.7 Other analytical techniques

2.3.7.1 Capillary electrophoresis technique

The capillary electrophoresis technique is a method mostly used for the analysis of pharmaceuticals and personal care products in an aqueous solution. Separation takes place in fused silica capillaries, and in order to achieve separation, a high voltage is often applied through buffer field capillaries. It has high effective and analysing speed, less use of reagent, less sample intake, and it is quick to develop. Furthermore, it is less selective compared to HPLC. In most cases, it is used as a complementary or alternative technique because its separation selectivity can be similar to that of HPLC. When combined with the MS capillary electrophoresis technique, it has the highest potential (Swartz et al., 2018).

2.3.7.2 Bio-analytical techniques

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

2.3.8 Removal mechanisms and advance treatment of emerging contaminants in water sources

2.3.8.1 Removal mechanism

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

2.3.8.2 Biodegradation

Biodegradation is one of the most important mechanisms used to eliminate emerging pollutants. Its aim is to decrease the organic matter concentrations in WWTPs by converting the decomposable materials into an acceptable end product. Furthermore, it aims at eliminating nutrients such as phosphorus and nitrogen. In a biological process, nitrifications and de-nitrifications are the leading processes that occur. Nitrification is the process whereby ammonia is converted into nitrate. When nitrosomonas bacteria oxidise ammonia to nitrite ($\text{NO}_2\text{-N}$) and nitrobacter bacteria oxidise nitrite to nitrate ($\text{NO}_3\text{-N}$), this biological process happens. Factors such as dissolved oxygen, pH, temperature, metals, acids, and free ammonia effect the pace of nitrification. Although nitrification may be influenced by such factors, it needs a long retention period, a low food-to-microorganism ratio, and a long mean cell residence time or age of the sludge (Langford and Lester, 2003).

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

2.3.8.3 Sorption

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

2.3.8.4 Photolysis

The photolysis process is accountable for the total or incomplete elimination of some emerging contaminants (Jonna, 2011). Certain contaminants of emerging concern may be certainly degraded, slowly degraded, whereas other chemical compounds are unaffected by

the process of photolysis (Gomez et al., 2008; Yamamoto et al., 2009). The removal rate of emerging contaminants under the photolysis process is influenced by factors such as pH, level of oxygen, compound structural properties, and amount of organic matter (Neamtu and Frimmel, 2006). Furthermore, the structure of the sewage treatment works may influence removal of some emerging contaminants during photolysis, for example big aeration tanks or polishing lagoons permit occurrence of some photolysis (Janna, 2011).

2.3.8.5 Volatilisation

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

2.3.9 Advance treatment of emerging contaminants in water sources

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

2.3.9.1 Pressure-driven membrane filtration

Pressure-driven membrane filtration is a tertiary treatment process for eliminating contaminants of emerging concern (Schaar et al., 2010) by forcing water through semi-permeable membranes against a concentration gradient (Cochran, 2018). Pollutants are physically eliminated from the membranes by pore size limits or electrostatic repulsion and its elimination proficiency is uppermost in reverse osmosis, trailed by nanofiltration, ultrafiltration, and microfiltration (Liu et al., 2009). Microfiltration and ultrafiltration offer pre-treatment for nanofiltration and reverse osmosis (Oulton and Cwierny, 2010). The usage of

reverse osmosis and nanofiltration is well known in the elimination of micropollutants for high-quality drinking water or industrially processed water. These tertiary treatment methods have the ability to eliminate a high quantity of emerging pollutants, and consequently, they are progressively applied in newer advanced wastewater treatment systems (Cochran, 2018).

2.3.9.2 Direct oxidation

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

2.3.9.3 Sand filtration

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

2.3.9.4 Activated carbon

Activated carbon is combined with the treatment procedure either through granular or powdered activated carbon. For the elimination of emerging contaminants in tertiary treatments, granular activated carbon is contained in a column, whereas powdered activated carbon is added and recirculated internally. These forms of activated carbons are regarded

as an alternative methods to tertiary treatment chemical methods due to their abilities to eliminated high quantities of emerging contaminants (Karelid et al., 2017). Biological activated carbon can be applied for tertiary treatment in addition to granular activated carbon and powdered activated carbon as it has a biofilm on the material surface that both biodegrades and sorbs pollutants (Oulton and Cwiertny, 2010). To promote the elimination of emerging pollutants in tertiary treatments, adsorption onto activated carbon is frequently applied (Karelid et al., 2017). Generally, the combination of activated carbon adsorption and chemical processes have effective elimination rates of emerging pollutants, although the elimination effectiveness is reliant on the adsorption capacity of the activated carbon (Esplugas et al., 2007). This factor restricts the effectiveness of activated carbon as the capacity of adsorption is understood to decline over time (Cochran, 2018; Liu et al., 2009).

2.3.10 Environmental health impacts of emerging contaminants

The review has shown that water sources in South Africa and other parts of the world contain traces of pesticides (herbicides), pharmaceuticals, steroid hormones and personal care products. The presence of these emerging contaminants may endanger aquatic life and water, affecting consumers' health. However, Ebele et al. (2017) indicated that the finding of analytes in an aqueous environment not necessarily imply that they are of concern or may cause health risks unless there is evidence. There is evidence showing that exposure to pesticides may cause dermatological, gastrointestinal, neurological, carcinogenic, respiratory, reproductive, and endocrine effects (Sathiakumar et al., 2011; Nicolopoulou-Stamati et al., 2016). Furthermore, studies have shown that exposure to pharmaceuticals may lead to endocrine disorders, reduced reproductive rates, reduced life expectancy (Pei et al., 2022), disruption of red and white blood cells, and insomnia (Wanda et al., 2017). Some pharmaceuticals were reported to be the cause of vulture population decline in Pakistan (Oaks et al., 2004). Personal care products may cause reduced T4 hormone levels in female rats, reduced sperm counts in male fish, reduced hatchability and time of hatching of fertilised eggs in fish (Archer et al., 2017). Steroids and their metabolites may pose high risks to aquatic organisms at very low environmental concentrations (Ademoyegun et al., 2017). They have the ability to mimic or hinder hormones, altering normal bodily functions (Gogoi et al., 2018), consequently causing serious medical implications such as cancer, reproductive impairment, cognitive deficits and obesity (La-Merrill et al., 2020). Furthermore, the presence of some steroid hormones can impact the sustainability of wild fish populations even at low concentrations (Kidd et al., 2007).

2.3.11 Mitigation of risks associated with emerging contaminants

There is a need to implement mitigation strategies to control the influx of emerging contaminants into the environment and minimise the risk associated with their exposure. Regulating the release of emerging contaminants into the environment is one of the best strategies to manage their influx and toxic effects. This is achievable by proper monitoring and regulating point sources such as industries, hospitals, and water treatment facilities together with the maintenance and enforcement of standard procedures for every source in effluent streams. Point source separation can be part of a sustainable solution for industries, hospitals, and water treatment facilities (Mutyar and Mittal, 2014). Medicines that are environmentally benign, have low noxiousness, do not bio-accumulate, and have a short environmental persistence, may help to reduce the amount of pharmaceuticals that end up in the environment (Gunnarsson et al., 2009). Classification and labelling methods may also play a crucial role in reducing emerging contaminant risks. This strategy entails identifying and labelling all active medicinal compounds with information on their environmental implications in order to educate the general public. The information is made available to people through websites and information booklets (Boxall, 2012). Although inappropriate medical drug disposal has a minimal impact on total environmental pollution, taking back unused or expired medication may help to mitigate their quantities in landfill sites and aqueous environments and their possible health risks (Daughton and Ruhoy, 2009). According to Boxall (2012), the effectiveness of this strategy rests on teaching people the possible environmental implications of unused or expired medicinal drugs.

Furthermore, improvements in agricultural practices may protect water bodies and also contribute to the reduction of risks associated with the presence of emerging contaminants in the environment. Changes in treatment timings and intensities, as well as manure application rates and timings, may help to reduce discharges of emerging contaminants into the environment. Furthermore, developing a standard operating process for applying manure to unstable slopes and defining buffer zones could help to reduce risks (Pope et al., 2009). Injection application is better than broadcast application as it can minimise overland run-off of pharmaceuticals and personal care products (Topp et al., 2008). The application of sewage sludge in dry seasons may reduce the possibility of some chemical compounds to be introduced in surface water (Boxall, 2012). Improving the management of pesticides may limit introduction of pesticides into groundwater or surface water. This can be done by reducing the amount of products available for loss, reducing storage and handling losses, reducing the potential for transport and providing a mechanism for deposition (Aydinalp et al., 2004).

2.4 Conclusion

It is clear that the occurrence of emerging contaminants in aqueous sources is a topic of concern in all continents. Although there is evidence that their introduction into water sources is contributed mostly by WWTP effluent, on-site wastewater disposal systems, roadways runoff, runoff from agricultural activities, recreational activities, deposition from the atmosphere, sewerage connection leaks, landfill and septic tank leachates, no permanent clarifications have been suggested to solve the challenges concomitant to organic chemical pollution in several parts of the world. The quantity of these emerging contaminants is still estimated to upsurge in water sources due to increase in inhabitants, which is a community health concern as their exposure may have negative effects on the water creatures and human health. Most of the contaminants detected in the majority of studies reviewed were targeted compounds. Studies on qualitative screening of emerging contaminants in water sources are still lacking in many countries around the world.

2.5 Recommendation

From the findings of this study, the following is recommended:

- Qualitative studies should be prioritised in pollution monitoring and risk assessment studies of emerging pollutants as the numbers of these compounds are always increasing. This will help to identify unknown or unexpected contaminants in water sources and WWTPs.
- More studies should be conducted on contamination of groundwater, particularly in regions where groundwater is still regarded as a source of drinking water.
- More studies that deal with ecological risk assessment of emerging contaminants in water sources are needed in South Africa and Africa as a whole, because the use of chemicals is rising, together with lack of proper disposal methods.
- Studies focusing on developing water quality guidelines for emerging contaminants in water sources should be undertaken.
- Tracing of steroid hormones and pesticides in surface water and treated drinking water should be prioritised in future studies.

Chapter 3

DESCRIPTION OF THE STUDY AREA: BLOEMFONTEIN

This chapter profiles the status quo of the study area which is located in Bloemfontein. It gives an overview of the study location, environmental attributes such as climate, geology, soil, topography, land use and water resources. Furthermore, the socio-economic status such as population, municipal economy, the health care system, housing and development, water supply and sanitation as well as waste management are discussed. The study area was carefully chosen for the study because there is paucity of information on environmental health risk assessment of emerging contaminants in water sources, which is a distress as these contaminants may affect aquatic life and public health.

3.1 Study location

The study was conducted around Bloemfontein. Bloemfontein is the sixth largest city in South Africa and it serves as the administrative headquarters of the Free State province (MMM Integrated Development Plan [IDP], 2022). The city of Bloemfontein is geographically located in central South Africa on the southern edge of the Highveld on 29°5'13.9" S and 26°9'17.6" E at an elevation of 1 392 m (Figure 3.1). It covers an area of approximately 236.2 km². Bloemfontein is the major city under the MMM, which has an area measured at 9 886 km². The MMM is accessible via national roads such as the N1 that links Bloemfontein to Gauteng in the north and the Western Cape to the southwest, the N6 that links Bloemfontein to the Eastern Cape and the N8 that links the city to Lesotho in the east and the Northern Cape to the west (Esterhuizen, 2014). The MMM also covers areas such as Botshabelo and Thaba 'Nchu. As these townships are located around the city of Bloemfontein, they were also considered in this study. Botshabelo is located 45 km east of Bloemfontein on 29°16'2.5"S and 26°43'55.7"E at an elevation of 1 609 m above sea level. It is one of the largest townships in the Free State province. Thaba Nchu, which exhibits a large area of rural settlements, is situated 70.9 km from Bloemfontein on 29°12'33.6"S and 26°50'20.3"E (MMM IDP, 2022).

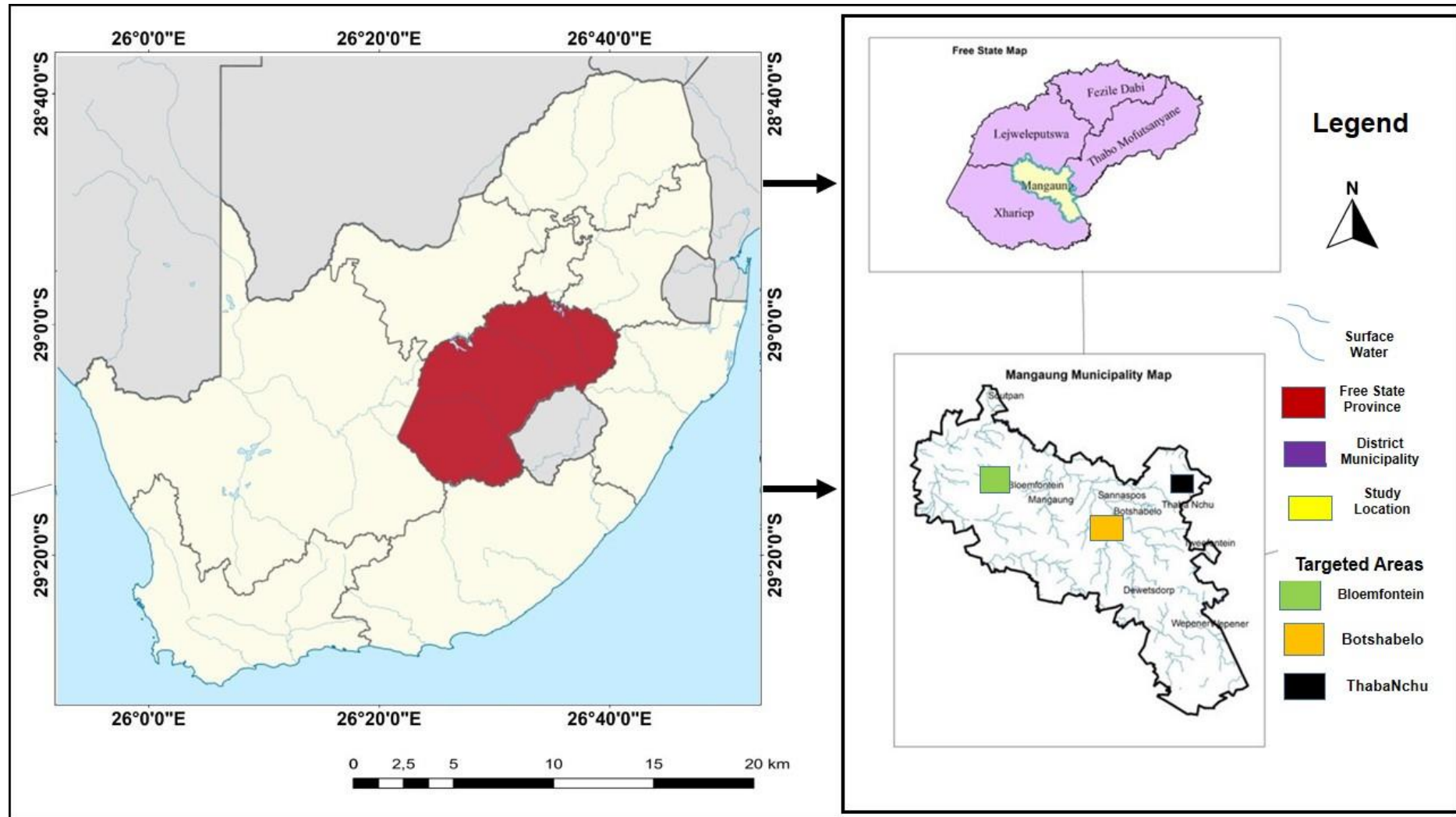


Figure 3.1 Geographical location of the study area

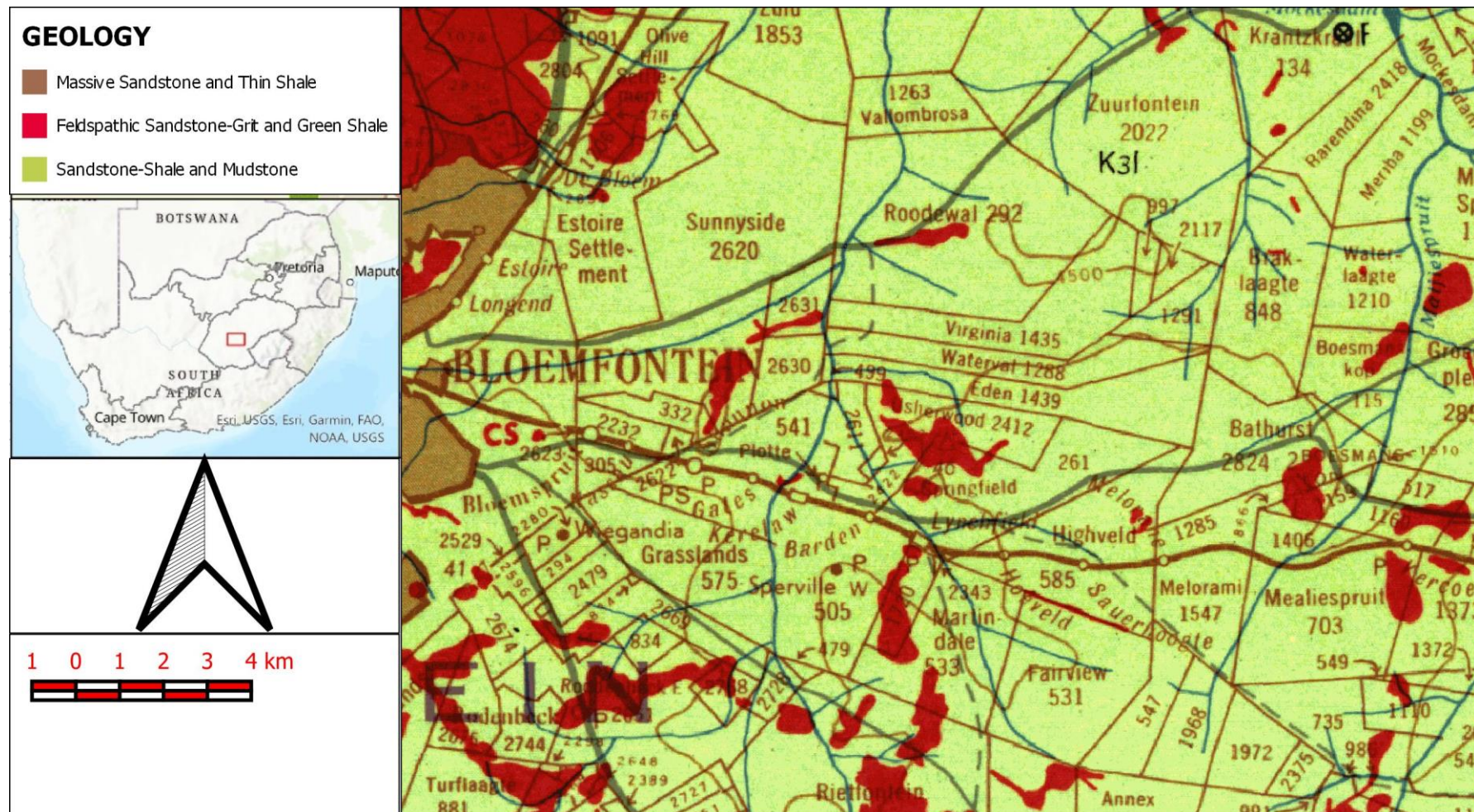
3.2 Environmental attributes

3.2.1 Climate

Bloemfontein has a semi-arid climate with cold summers and cold dry winters often with frost. The temperatures range between 15°C and 31°C in summer, whereas in winter the temperatures range between -2°C and 17°C (Esterhuizen, 2014). The summer season starts from October to February and the winter from May to August (Makhadi et al., 2020). The study area is located in the Highveld summer rainfall region with the mean annual rainfall ranging between 600 mm and 750 mm. The rainy season generally occurs between October and March (Slabbert, 2007). Thunderstorms and soft rains occur in approximately equal quantities. Thunderstorms are characterised by rain and hailstorms, which promote runoff in this region over short periods of time. Frost occurs throughout the metropolitan area most notably in the higher-lying areas from May to early September (MMM IDP, 2022).

3.2.2 Geology and soil

The regional geology of the MMM, which is a host of the city of Bloemfontein, falls under the Ecca and Beaufort Groups of the Karoo Supergroup. These groups are dominated by sedimentary rocks mostly siliciclastic rocks formed by quartz and feldspars (Makhadi et al., 2020). These include rocks such as sandstone, shale and mudstone (Usher et al., 2007; Slabbert, 2007). As shown in Figure 3.2, the geology around Bloemfontein includes sandstone, shale and mudstone of the lower stage of the Beaufort Group, while the Thaba 'Nchu area consists of purple and green shale and sandstone deposited during the upper stage. An intensive array of dolerite dykes and sills can be found in Thaba 'Nchu and areas northwest of Bloemfontein (Esterhuizen, 2014; Van Wyk, 2019). Generally, dolerite weathers easily, forming clayey or vertic soils such as that of Arcadia and Rustenburg in the study area. Mudstone is overlain by the typical red-brown, sandy loam to sandy clay loam soils of the Glenrosa and Mispah soil forms. The fine-grained sedimentary rocks such as shale, mudrock and siltstone weather to clay minerals that have a tendency to swell and shrink. The mudstones from the Beaufort Group cover most of the eastern parts of the MMM area, from Bloemfontein eastwards to Thaba Nchu. The soils of the MMM area are generally shallow, with the deepest soils found in the south of the municipal area (MMM IDP, 2022).



3.2.3 Topography

The MMM is characterised by the Highveld eco-region. In this eco-region, the plains generally characterise the area with low and moderate relief. The area also has significant lowlands having low and high relief, open hills with low relief and closed hills with moderate relief (Slabbert, 2007). Generally, the MMM is largely a vast, flat and open plain that is interspersed with low hills. The altitudes range between 1 200 and 2 120 mean above sea level. The city of Bloemfontein is located at an altitude of 1 390 mean above sea level. The Thaba Nchu mountain, located in the east of the metropolitan area, is the highest point in the MMM (IDP, 2022).

3.2.4 Land use

The city of Bloemfontein is under administrative boundaries of the MMM. The MMM is characterised by three different land use types, including formalised stands in urban areas, smallholdings and farms. The city of Bloemfontein has become a mixed land use area. It is characterised by commercial and residential areas within proximity to each other. Bloemfontein is a rapidly growing city, with the increase in new residential, commercial and mixed land use areas (Bashingi et al., 2018). The bulk of the land to the west, southeast and east of Bloemfontein has a high agricultural potential. The agricultural land to the east of Bloemfontein is communally owned and farmed, with the balance being privately owned farms. Agriculture in the area is one of the key economic activities with both commercial, small-scale and subsistence farming being practiced. In the MMM, 22.96% of land is under commercial agriculture of which 1.4% is under pivot irrigation and 0.02% is cultivated orchards. While agricultural activities in the province are diverse, major crops such as maize, soybeans, wheat, sorghum, sunflowers, potatoes, groundnuts and wool are grown, while horticultural products such as cherries (90% of which are grown in the Free State), are also key to the sector. Other activities include livestock, dairy farming, game farming, aquaculture and fruit and vegetable production as well as agro-processing. Commercial agriculture in the Free State and in the MMM is highly dependent on irrigation. Large areas of the municipality have a grazing capacity of 11–17 ha per animal unit (MMM IDP, 2022). Considering that agriculture in the area depends more on irrigation, it may put more pressure on the already strained water resources. Moreover, an intense agriculture in this area may lead to the introduction of organic contaminants to the nearby streams and possibly groundwater.

3.2.5 Water resources

The MMM is located in one of South Africa's pivotal water management areas called the Upper Orange management area. The MMM area of jurisdiction is located in the Modder and Caledon River catchments. Furthermore, smaller sections of the MMM extend to the Vet and Riet River catchments. The northern parts of the MMM, which covers Bloemfontein, Botshabelo and Thaba Nchu, are located in the Modder River catchment. These areas rely on surface water and groundwater as the source of potable water in the urban areas and for agricultural purposes, while a number of pans also occur in the north-western part of the MMM area (MMM IDP, 2022).

3.2.5.1 Surface water

The Modder River is a relatively small river which drains an area of 7 960 km² in the central region of the Free State province and has a mean annual runoff of 184×10⁶ m³. The total catchment wherein the Modder River falls comprises an area of about 17 360 km². The Modder River has a number of tributaries and these are the Klein Modder River, Sepane, Koring, Kgabanyane, Koranna, Renoster, Doring, Riet and Kaalspruit. Water from the Modder River is stored in the Rustfontein, Mockes, Mazelspoort and Krugersdrift dams (Slabbert, 2007). Rustfontein Dam is an important source of supply to the Bloemfontein area, while the Mockes Dam is a balancing dam further downstream to regulate the flow through the Maselspoort Dam where water is abstracted for urban consumption. The Krugersdrift Dam is situated further downstream on the Modder River northwest of Bloemfontein and supplies water to the Modder River Government Water Scheme. Currently, only about 25% of the potable water supply of Bloemfontein is provided by the Modder River. The surface water of the MMM area is extensively developed and the utilisation of surface water resources exceeds the local yields (MMM IDP, 2022; Slabbert, 2007).

3.2.5.2 Groundwater

Groundwater is currently not extensively utilised as a water resource to supply potable water to the Bloemfontein area. Some individuals in the urban areas of the MMM use groundwater for irrigation purposes, while farms in the area depend on groundwater resources (MMM IDP, 2022). The regional aquifer underlying the area is classified as fracture in the western portion and intergranular in the central and eastern portion of the MMM boundary. The majority of the study area is underlain by an intergranular aquifer, which indicates that groundwater flows in openings and void space between grains or weathered rock, expecting yields of 0.1–0.5 l/s. The western portion hosts a fractured aquifer, which indicates that

groundwater is located with fractures in a hard rock formation, expected yields of 0.5–2.0 l/s (Oke and Alowo, 2021; Van Wyk, 2019; Vermeulen, 2012).

3.2.5.3 Treated drinking water

The MMM is the water services authority, while it is also one of the water services providers. The MMM treats potable water at its Maselspoort water treatment plant and also purchases approximately two-thirds of its potable water from Vaal Central Water (formerly Bloem Water). It provides potable water to 214 445 households. Vaal Central Water is the main supplier of bulk potable water to the urban centres of the Modder–Riet sub-catchment, supplying about 100 million m³ per annum of treated water to about 580 000 people. The Maselspoort Scheme on the Modder River supplies approximately 25% of the water needs. Water supply to the MMM is severely stressed. The total current capacity of the reservoirs serving the metropolitan area is 0.425 million m³. The capacity of Vaal Central Water's bulk reservoirs is 0.278 million m³. The Thaba Nchu and Botshabelo reservoirs have a capacity of 0.156 million m³ and 0.052 million m³, respectively (MMM IDP, 2022).

3.2.5.4 Wastewater treatment

The MMM provides sanitation services to Bloemfontein, Thaba Nchu and Botshabelo. Eight WWTPs service the three urban areas. The Botshabelo WWTP discharges its effluent in the Klein Modder River. The Bloemspruit WWTP discharges its effluent in the Vaal River, Harts River and Skoonspruit. Although several WWTPs are currently being upgraded or are planned to be upgraded to improve performance, the operation of WWTPs remains problematic. Some of these problems include the exceeding legal limits for key water quality parameters, exceeding design capacities, and not meeting the legal requirements for staffing and staff competencies (MMM IDP, 2022). Considering that all WWTPs in these areas receive domestic, hospital and industrial wastewater, there is a high chances of detecting traces of emerging contaminants in rivers, dams and treated drinking water. This is because WWTPs are not designed to eliminate these contaminants and their wastewater effluents are therefore discharged into nearby streams.

3.3 Socio-economic status

3.3.1 Population

The MMM has a population of 878 834 people. This population represents 28% of the Free State province population. Over half of the population (546 568) of the MMM is concentrated

in Bloemfontein (63%), followed by Botshabelo (24%), Thaba Nchu (9%) and other areas (4%) (Statistics South Africa [Stats SA], 2019). The MMM population is made up of 85% African, 11% White and 4% Coloureds (Figure 3.3). Among these racial groups, 51.07% of the population are females, while 48.9% of the population are males, as shown in Figure 3.4 (Nkadile, 2022; Stats SA, 2019).

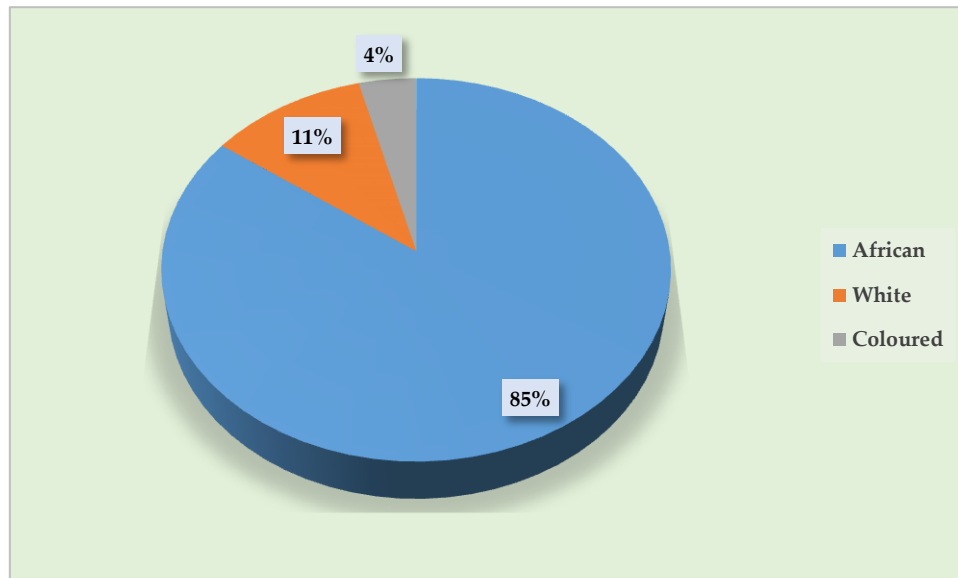


Figure 3.3 Racial composition of Mangaung Metropolitan Municipality

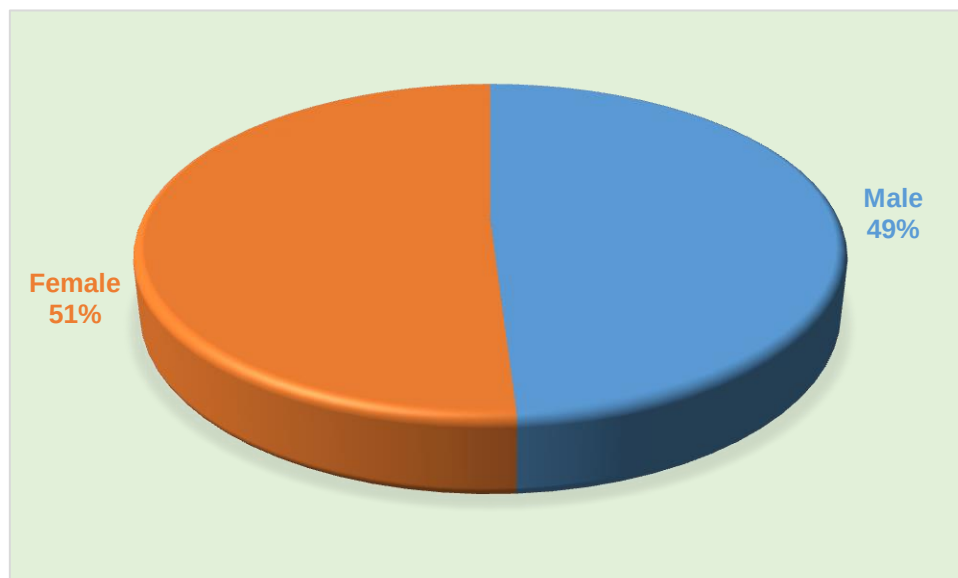


Figure 3.4 Gender distribution in Mangaung Metropolitan Municipality

The contribution to the population of Mangaung can be divided into various age groups such as 25–44 years (31.8%), 0–14 years (25.6%), 45–64 years (18.1%), 15–24 years (17.1%) as

well as 65 years and above (7.4%) as presented in Figure 3.5. These comprises children, university students, workers, business owners and retired people (MMM IDP, 2022). The rising population in Bloemfontein can be attributed to the continuous migration of people from the surrounding areas to the city in order to work, study, run businesses or other services that are not available in villages and townships. Consequently, this exert pressure on water resources. Population growth generate large quantities of wastewater, rise in medicinal drugs and domestic waste, which if not properly managed, may introduce emerging contaminants in water sources.

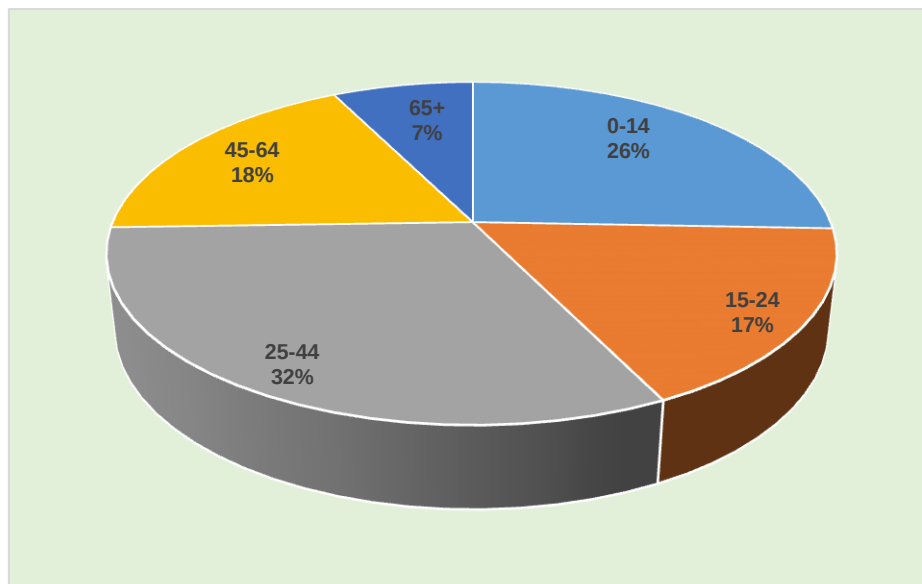


Figure 3.5 Age distribution in Mangaung Metropolitan Municipality

3.3.2 Municipal economy

The MMM is the biggest gross domestic product contributor in the Free State province and is regarded as one of the most diverse economies with Bloemfontein as the economic hub. The economy of Bloemfontein is driven by government services (42%), trade (22%), finance (18%), transport (15%), agriculture (2%) and mining (1%), as shown in Figure 3.6. Over half (55.5%) of the households in the MMM are dependent on salaries. Approximately 20% of the households get their income from grants, 8.3% from remittances, 4.2% from pensions and the remaining 12% from other sources such as rental, business, sales of farming products and other services (Esterhuizen, 2014; MMM IDP, 2022; Nkadile, 2022). Domestic and industrial wastewater generated in this area may contain traces of emerging contaminants that may lead to emerging contaminant pollution in local water resources as a result of mismanagement, clogged sewage overflow, poor removal in WWTPs and stormwater runoff. Runoff from agricultural activities, industrial areas, settlements, paved areas and roads may also introduce various emerging contaminants in surface water.

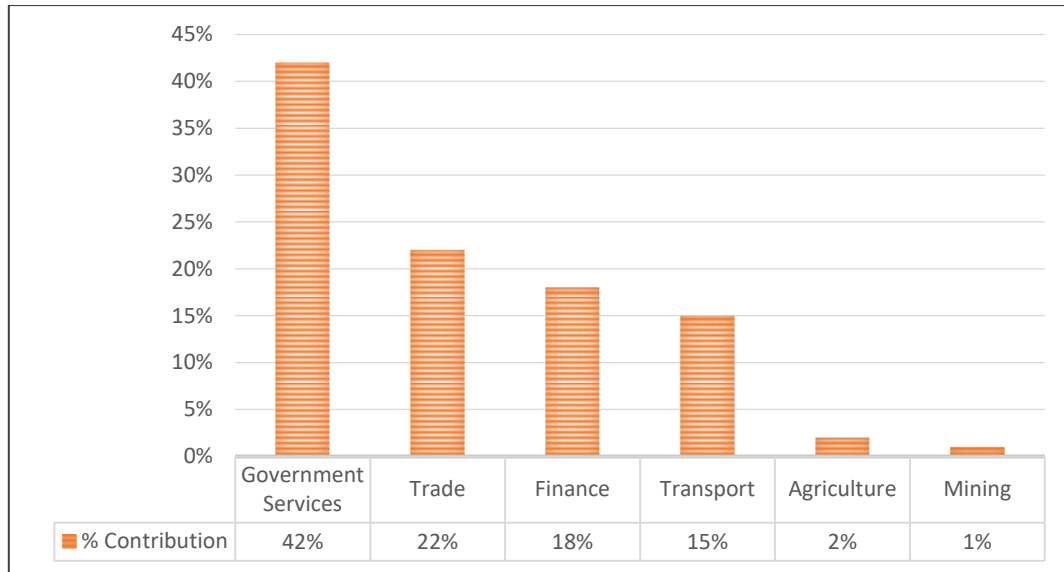


Figure 3.6 *Economic drivers of Mangaung Metropolitan Municipality.*

3.3.3 Health care system

The MMM has four health subdistricts, namely Bloemfontein, Botshabelo, Naledi and Thaba Nchu, with a total of 313 clinics and 122 mobile clinics. Most clinics are located in Bloemfontein, Botshabelo and Thaba Nchu, but the smaller towns have one to three clinics each. “There are 36 state-owned hospitals and 26 private hospitals, all hospitals are located in Bloemfontein besides three that are in Thaba Nchu and Botshabelo” (Cooperative Governance and Traditional Affairs, 2016). Hospital wastewater and waste generated are considered as a source of emerging contaminants, namely personal care products, steroid hormones and pharmaceuticals. Improper management of these waste may introduce organic compounds in water sources. In Bloemfontein, wastewater from hospitals are released into traditional WWTPs together with industrial and households wastewater. These WWTPs are not designed to eliminate emerging contaminants and as a result they end up in nearby rivers.

3.3.4 Housing and development

The majority of the people who live in the MMM live in urban areas in formal dwelling structures. Some also live in formal structures on freehold farms and smallholdings or on communally managed land. Informal settlements are also found in the urban, rural and communal areas. The MMM has approximately 238 000 households, with an average household size of 3.1 persons per household. Approximately 178 000 (75%) of households are located in formal settlements of the MMM, while approximately 33 100 (14%) live in informal settlements. The remaining 11% live on farms and smallholdings. There are

currently approximately 45 informal settlement areas in the MMM, and the demand for housing far outweighs the available resources. Bloemfontein has well developed modern urban areas, as well as economical and sub-economical residential developments. This is supplemented by well-functioning business sectors and well-developed industrial zones. The basic infrastructure facilities found in the study area include roads, railway lines, airport, housing, potable water supply, electricity, telecommunication and sanitation (Nkadile, 2022; MMM IDP, 2022). Although Bloemfontein is a well-developed city, the development of informal settlements may intensify illegal dumping of domestic wastes (containing unused or expired medicinal drugs) which may lead to contamination of water sources by emerging contaminants.

3.3.5 Water supply and sanitation

A total of 221 127 households in the MMM area have access to water by means of a regional or local water scheme, while others use boreholes and water tanks as sources of water. The city is serviced by eight dams with a storage capacity of approximately 300 million cubic metres. Two of the dams, namely Mockes Dam and Maselspoort Dam, are managed by the municipality. Only 52% of the households have piped water inside their yards. While 39% of households receive piped water inside the dwelling, 4% receive piped water on a community stand and 2% from a community tap. A total of 185 268 households have flush toilet facilities that are connected to the WWTPs, while the remaining households use pit toilets with ventilation, pit toilets without ventilation, bucket toilets, and flush toilets with septic tanks (MMM IDP, 2022). Pit toilets and septic tanks leakages may lead to the groundwater contamination by emerging contaminants (medicinal drugs consumed by patients) mostly during the rainy season where the water table is likely to rise. The MMM has twelve WWTPs, which may also introduce traces of emerging contaminants in surface water sources as their effluents are discharged in rivers.

3.3.6 Waste management

Waste generation in the MMM is increasing in direct proportion to population growth, improvements in the quality of life and changes in lifestyle. Sources such as domestic dwellings, commercial nodes, government institutions and offices, mining, industry, agricultural farms, medicinal facilities, and events contribute to waste generation. The waste collection service covers between 80 and 90% of all the households, collecting 96% of all waste generated. Waste is supposed to be collected once a week by the sub-directorate waste management of the MMM. However, in some areas due to a number of challenges, including vehicle and human resources shortages, at times it is collected once in two weeks.

The MMM has three large solid waste sites, the largest is the South Park landfill site of 73.7 ha located south of the city of Bloemfontein. The Northridge landfill site is the second largest site with 36.4 ha is in the northern parts of Bloemfontein, and the third being the Botshabelo landfill site with 24 ha (Makhadi et al., 2020).

The management of health care risk waste and hazardous waste in the MMM area of jurisdiction remains a provincial competence. No landfill sites operated by the MMM are authorised to receive health care risk waste and hazardous waste (MMM IDP, 2022). Although there are proper waste management strategies in the municipality, illegal dumping of waste across the municipality is notable. Delays in waste collections may lead to illegal dumping of waste in the area which may introduce emerging contaminants in water sources through runoff, or leachate, especially during rainy seasons.

Chapter 4

METHODOLOGY

This chapter discusses the methods used to achieve the objectives of the study. The chapter starts by describing the collection of samples in water sources around Bloemfontein together with sample handling procedures for rivers and dams, treated drinking water and WWTPs. The laboratory work followed in this project, namely reagents and materials, sample preparation and extraction; sample analysis as well as method verification and quality control are described. The method used to determine the efficiency of WWTPs in removing emerging contaminants is also described. Furthermore, the methods adopted to determine the sources and risks of emerging contaminants are presented.

4.1 Sample collection and handling

Water samples were collected from treated drinking water, WWTPs, dams and rivers around Bloemfontein. The samples were collected during all four seasons of the year, starting from September 2022 to July 2023. In 2022, samples were collected during the spring season, while in 2023, samples were collected during summer, autumn and winter. During the sampling campaign five rivers, five dams, three WWTPs and two water treatment plants were targeted. The targeted rivers were Klein Modder River, Koringspruit, Renosterspruit, Modder River (Lekatlong) and Bloemspruit, while Rustfontein, Mockes, Maselspoort, Krugersdrift and Seroalo were the targeted dams. Three WWTPs, namely Bloemfontein North East, Bloemspruit and Botshabelo, were considered in this study. Furthermore, two treated drinking water samples from two water treatment plants around Bloemfontein were sampled. When collecting surface water samples, accessibility was considered and only WWTPs that gave permission of entry were chosen in this study. In each season, samples ($n=18$) were collected as rivers ($n=5$), dams ($n=5$), wastewater influent ($n=3$), wastewater effluent ($n=3$) and treated drinking water ($n=2$). In total, seventy-two ($n=72$) grab water samples were collected in the four seasons. The chosen sampling points are presented in Figure 4.1 and Table 4.1.

All water samples were collected in 750 ml cleaned bottles (Appendix A) randomly using the grab sampling method throughout the project. At the site of sampling, the 750 ml cleaned bottles were labelled for identification convenience at the laboratory and data management. In order to collect enough water, river samples were collected by submerging the bottles in

water against the flow direction. Samples from surface water (dams) were obtained by submerging the bottle below the water surface. To collect water samples from treated drinking water, the tap was allowed to flow for a little time before collection of the sample. To collect wastewater influent and effluent, a clean bucket with a long rope was used to draw enough water, which was then transferred to the labelled sample bottles. During the sampling campaign, all the collected samples were kept in a cooler filled with ice blocks (Appendix A). After the sampling campaign, the samples were conveyed to the University of the Free State Biotechnology Research Laboratory for analysis. The samples were kept at 4 °C until analysis.

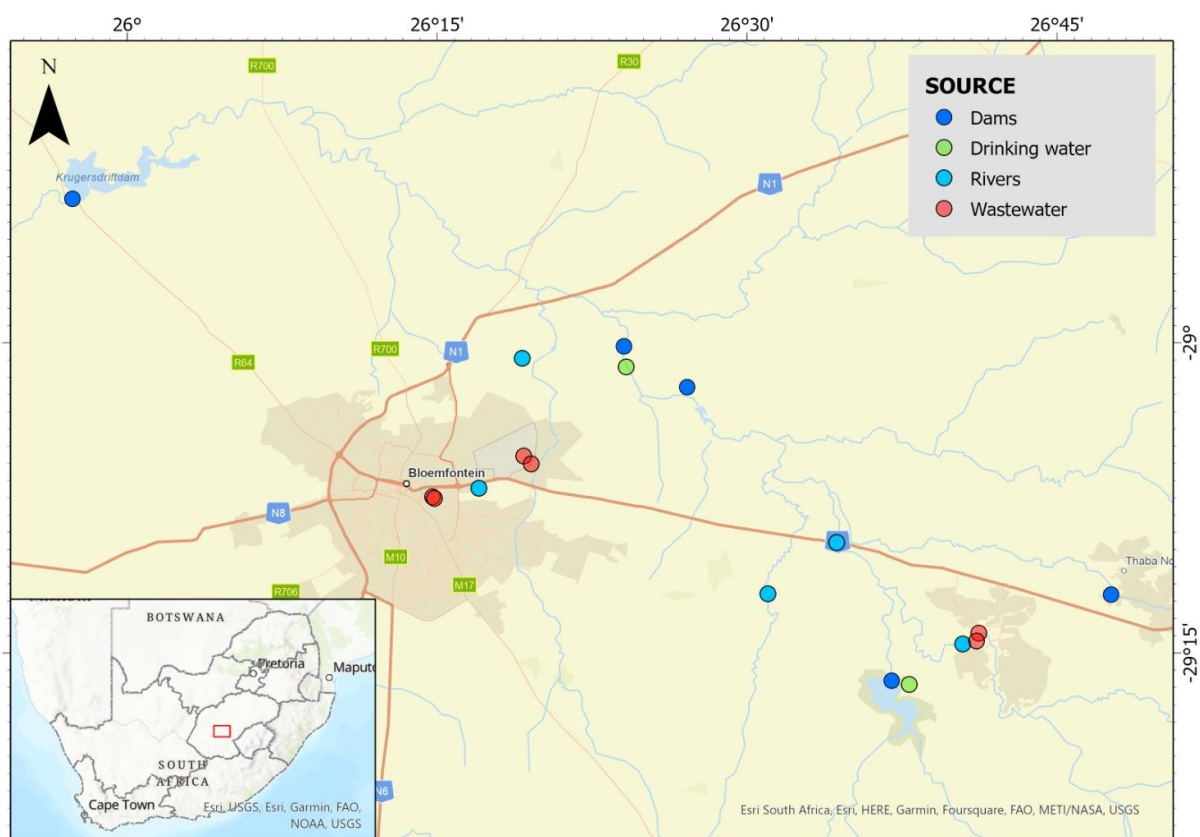


Figure 4.1 Sampling points within the study area

Table 4.1 Sampling sites at various water sources around the study area

Collection of samples during spring, summer, autumn and winter season						
Item	Sample ID	Collected samples (n=72)	Latitude	Longitude	Elevation	Site description
Surface water (Dam)						
1	SWMSO1	1 per season	29° 01' 4.9" S	26° 24' 2.7" E	1 344 m	Collectd at Maselspoort Dam
2	SWMD02	1 per season	29° 02' 8.4" S	26° 27' 5.8" E	1 354 m	Collected at Mockes Dam
3	SWKD08	1 per season	28° 53' 03" S	25° 57' 21" E	1 226 m	Collected at the Krugersdrift Dam
4	SWSD09	1 per season	29° 12' 10" S	26° 47' 38" E	1 460 m	Collected at the Seralo Dam
5	SWRUSD10	1 per season	29° 16' 20" S	26° 37' 00" E	1 370 m	Collected at Rustfontein Dam
Surface water (River)						
6	SWRS03	1 per season	29° 06' 9.6" S	26° 19' 7.2" E	1 379 m	Collected at Renosterspruit
7	SWBS04	1 per season	29° 07' 2.4" S	26° 17' 1.5" E	1 390 m	Collected at Bloemspruit
8	SWKOR05	1 per season	29° 12' 8.3" S	26° 31' 0.4" E	1 334 m	Collected at Koringspruit
9	SWMOR06	1 per Clseason	29° 09' 39.3" S	26° 34' 20.3" E	1 327 m	Collected at Modder River (Lekatlong)
10	SWKLM07	1 per season	29° 14' 34.3" S	26° 40' 26.2" E	1 373 m	Collected at Kleinmodder River
Wastewater treatment plants						
11	WWTP01I	1 per season	29° 05' 29" S	26° 19' 12" E	1 386 m	Influent from Bloemfontein North East WWTP
12	WWTP01E	1 per season	29° 05' 51" S	26° 19' 33" E	1 384 m	Effluent from Bloemfontein North East WWTP
13	WWTP02I	1 per season	29° 14' 2.8" S	26° 41' 12.9" E	1 380 m	Influent from Botshabelo WWTP
14	WWTP02E	1 per season	29° 14' 25.4" S	26° 41' 6.2" E	1 376 m	Effluent from Botshabelo WWTP
15	WWTP03I	1 per season	29° 07' 27.4" S	26° 14' 46.7" E	1 558 m	Influent from Bloemspruit WWTP
16	WWTP03E	1 per season	29° 07' 31.8" S	26° 14' 51.8" E	1 364 m	Effluent from Bloemspruit WWTP
Treated water						
17	TWWRUS01	1 per season	29° 16' 31" S	26° 37' 51" E	1 366 m	Treated water from Rustfontein water treatment plant
18	TWWMSP02	1 per season	29° 01' 10.3" S	26° 24' 9.2" E	1 339 m	Maselspoort water treated plant

4.1.1 Collection of river samples

4.1.1.1 Renosterspruit

Renosterspruit is located at 29° 06' 9.6" S and 26° 19' 7.2" E as shown in Figure 4.1. The Renosterspruit flows past Bloemfontein and drains into the Modder River. A grab sample was collected from the Renosterspruit (Appendix A). For identification and laboratory analysis it was named as SWRS03 (Table 4.1). It was accessed via the N8. Approximately 700 m away from the river, intense agricultural activities were noticed. These included animal and plant productions activities. Furthermore, a few farm houses with septic tanks were noticed during the site visit.

4.1.1.2 Bloemspruit

Bloemspruit is a tributary of the Renosterspruit. It runs through the city. Most wastewater from residential and industrial areas end up in this river. It also receives effluents from the Bloemspruit WWTP. This can be confirmed as the water collected was smelling and having high turbidity. The sample collected at Bloemspruit (Appendix A) was located at 29° 07' 2.4" S and 26° 17' 1.5" E (Figure 4.1). Only one sample was collected and labelled as SWBS04 as shown in Table 4.1. It was close to the residential and some industrial areas.

4.1.1.3 Koringspruit

Koringspruit is an intermittent stream located at 29° 12' 8.3" S and 26° 31' 0.4" E as shown in Figure 4.1. The collected sample from Koringspruit (Appendix A) was labelled as SWKOR05 (Table 4.1). Close to the sampling point there was some houses with pit latrine toilets and septic tanks. Small-scale agricultural activities with animal productions were noticed during the site visit. The houses nearby withdrew water from the River. Furthermore, a small bridge was seen near the site, while at a distance there was a railway line and an old mechanical workshop.

4.1.1.4 Modder River (Lekatlong)

Geographically, the water sample was collected at 29° 09' 39.3" S and 26° 34' 20.3" E at an elevation of 1327 m, as presented in Figure 4.1. The river passes under the national N8 road and a railway line. As shown in Table 4.1, the collected sample was labelled as SWMOR06. During the sampling campaign, community members were seen drawing water from the river and domestic animals were also seen drinking water from this river (Appendix A).

4.1.1.5 Klein Modder River

The Klein Modder River passes through the Botshabelo residential area. Some of the houses around the river could be seen with government pit latrine toilets. There was a bridge passing over the river which drains its stormwater into it. Illegal dumping of waste was also witnessed during site visit. Close to the river (Appendix A), domestic animals such as goats and cows were seen drinking water. Effluent from Botshabelo WWTPs is discharged in this river. The sample in Klein Modder River was collected at 29°14' 34.3" S and 26° 40' 26.2" E as shown in Figure 4.1. The collected sample was labelled as SWKLM07 for easy identification in the laboratory (Table 4.1).

4.1.2 Collections of dam samples

4.1.2.1 Maselspoort Dam

Maselspoort Dam is a popular resort complex and fishing spot. The Maselspoort Dam is situated 23 km from Bloemfontein at 29° 01' 4.9" S and 26° 24' 2.7" E in the Modder River catchment (Figure 4.1). The dam serves as a water source for the Maselspoort water treatment plant. One sample was taken from the Maselspoort Dam (Appendix A). The sample's identification was SWMS01, as presented in Table 4.1. Around the dam, there was a resort as well as a few family units with septic tanks and pit latrine toilets. Septic tanks and latrine toilets may possibly leak certain emerging toxins, particularly during heavy rains. Furthermore, a large well-maintained open turf surrounds the dam.

4.1.2.2 Mockes Dam

The Mockes Dam serves primarily as a balancing dam to guarantee a steady flow of water to the Maselspoort weir purification works (Appendix A). The dam has a full supply level of 1 303.6 m, with a dead storage level of 1 301.9 m, and the bottom of the reservoir is at 1 299.5 m. It serves as a domestic water supply and is located east of Bloemfontein. One sample from the Mockes Dam was taken and labelled as SWMD02 (Table 4.1). The sample point was located at 29° 02' 8.4" S and 26° 27' 5.8" E (Figure 4.1). There was some dense vegetation around and a bridge constructed on the other side of the dam. The dam serves as a resort and conference venue. As a result, it is surrounded by a well-equipped resort. Moreover, some farm houses are located about 500 m from the dam.

4.1.2.3 Krugersdrift Dam

It is situated at the Modder River catchment 35 km northwest of Bloemfontein. The dam has a full supply level of 1 248.1 m. The dead storage level and the bottom of the reservoir is at

1 229.9 m. The dam has a capacity of 73.2 million m³. It also supports downstream irrigation. The sample labelled SWKD08 (Table 4.1) was taken at the Krugersdrift Dam at 29° 53' 03" S and 26° 57' 21" E (Figure 4.1). It is a well-liked bird-watching location. There are several farming and fishing operations close to the dam (Appendix A).

4.1.2.4 Seroalo Dam

It is an artificial pond or lake. The Seroalo Dam is located in Thaba Nchu (Appendix A). The dam is located 700 m to 1 km away from the Seloshesha villages and 3 km away from the industrial area. The sample was extracted at 29°12' 10" S and 26° 47' 38" E (Figure 4.1). The estimated terrain elevation above sea level was 1 463 m. The collected sample was labelled as SWSD09 as presented in Table 4.1. Two raw sewage drainage systems were running into the dam at the time of the visit. Domesticated animals, including cows and donkeys, were drinking water from the dam. Additionally, household garbage were thrown close to the dam, which could lead to water pollution.

4.1.2.5 Rustfontein Dam

The Rustfontein Dam was also considered as a water source (Appendix A) and it is located 10 km east of Botshabelo. The Rustfontein Dam is a gravity type dam located in the Modder River and is the major storage reservoir in the Modder River catchment. Water from the Rustfontein Dam is treated by Vaal Central Water, which supplies communities such as Botshabelo and Thaba Nchu. The sample was identified as SWRUD10 (Table 4.1) and extracted at 29° 16' 20" S and 26° 37' 0" E (Figure 4.1). The surrounding countryside, with its tree-studded koppies and grassy hillsides, provides an attractive backdrop to this dam that water sport enthusiasts have chosen as their playground.

4.1.3 Collection of treated drinking water

4.1.3.1 Rustfontein water treatment plant

The Rustfontein Dam receives water from the Novo Transfer Scheme and provides treated water to the Rustfontein water treatment plant and release water to the MMM to augment the Mockes Dam. The dam has a capacity of 70 million m³ and with a storage capacity of 15.26 million m³. The water supply area includes the towns of Botshabelo and Thaba Nchu. Treated water is also currently supplied to the greater Bloemfontein due to the high water demand in the city. One sample was collected from the Rustfontein water treatment plant. This sample was labelled as TWWRUS01 (Table 4.1). The treatment method in this plant comprises abstraction, macro/micro sieving, coagulation, flocculation, sedimentation,

filtration and disinfection. They utilise polydiallyldimethylammonium chloride (polydadmac) as a coagulant in water purification.

4.1.3.2 Maselspoort water treatment plant

The Maselspoort water treatment plant receives bulk water from the Modder River which is augmented by continuous effluent from the Thaba Nchu and Botshabelo WWTPs. The water from Maselspoort treatment plant supply the city of Bloemfontein. The collected sample from the Maselspoort water treatment plant was labelled TWWMSP02 (Table 4.1). The treatment method used in Maselspoort water treatment plant consists of abstraction, macro/micro sieving, coagulation, flocculation, sedimentation, filtration and disinfection. They also utilise polydiallyldimethylammonium chloride (polydadmac) as a coagulant in water purification.

4.1.4 Collection of wastewater influent and effluent samples

4.1.4.1 Bloemfontein north-east wastewater treatment plant influent and effluent

It is the largest of its kind in the MMM. The Bloemfontein north-east WWTP receives domestic, industrial and hospital wastewater (Appendix A). In this WWTP, one sample was taken from the influent at 29° 05' 29" S and 26°19' 12" E (Figure 4.1). The collected sample was labelled as WWTP01I (Table 4.1). Another sample was collected from the effluent located at 29° 05' 51" S and 26°19' 33" E and was labelled as WWTP01E (Table 4.1). The WWTP was not built with the intention of removing emerging contaminants received from domestic, industrial and hospital wastewater. It uses primary treatment which involves removal of suspended solids by flotation, settling and screening mechanisms and secondary treatment for removal of the remaining organic matter via trickling filters utilising bacteria-coated stones and bacteria-activated sludge. The effluent from this treatment plant is discharged into Bloemspruit.

4.1.4.2 Botshabelo wastewater treatment plant influent and effluent

The Botshabelo WWTP receives domestic, industrial and hospital wastewater. The flow rate of wastewater was minimal, which may be attributed to low population and the fact that some houses uses pit latrine toilets. One sample was collected from both influent and effluent (Appendix A). The influent sample located at 29°14' 2.8" S and 26°41' 12.9" E (Figure 4.1) was tagged as WWTP02I, whereas the effluent located at 29°14' 25.4" and S 26° 41' 6.2" E was tagged as WWTP02E (Table 4.1). The available treatment process consisted of primary treatment, which included removal of suspended solids by flotation, settling, and screening mechanisms, and secondary treatment for removal of remaining organic matter via trickling

filters utilising bacteria-coated stones and bacterial-activated sludge. Its effluent is discharged into the Klein Modder River. The surrounding community used the effluent for their small-scales agricultural activities.

4.1.4.3 Bloemspruit wastewater treatment plant influent and effluent

The existing Bloemspruit WWTP currently services the greater Bloemfontein area and is hydraulically overloaded. The Bloemspruit WWTPs receives all domestic, industrial and hospital effluent from Bloemfontein city (Appendix A). One sample was collected from both influent and effluent. The influent sample located at 29° 07' 27" S 26°14' 46.7" E was tagged as WWTP03I, whereas the effluent located at 29° 07' 31.8" S 26° 14' 51.8" E (Figure 4.1) was tagged as WWTP03E (Table 4.1). The available treatment process consists of primary treatment, which includes removal of suspended solids by flotation, settling and screening mechanisms, and secondary treatment for removal of remaining organic matter via trickling filters utilising bacteria-coated stones and bacterial-activated sludge. Its effluent is discharged into Bloemspruit. The effluent from this treatment plant is used by the local golf park for irrigation.

4.2 Laboratory analysis

4.2.1 Reagents and materials

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

4.2.2 Sample preparation and extraction

The samples received were filtered through glass fibre filters to eliminate small particles. The ultra-pure water (99%) spiked with emerging contaminant chemical standards was used to improve SPE parameters. For sample recovery, a solid-phase extraction (SPE) cartridge

were used. The SPE cartridges were equilibrated with 6 mL methanol and Milli-Q water before extraction. Afterwards, the samples were loaded at a flow rate of approximately 6 mL/min. The sample cartridges were cleaned with 6 mL purified water and dried for 20 minutes under vacuum. A 2 mL methanol was used to slowly elute the bound sample from the dried cartridges, followed by 2 mL ethyl acetate. The eluant was vacuum dried until almost dry, using a Thermo Scientific Savant Speedvac SC 210A concentrator (Waltham, Massachusetts, United States). The extract were reconstituted in 1 mL purified water and 0.1% formic acid.

4.2.3 Sample analysis

4.2.3.1 Unknown analytes

A multiple reaction monitoring–information dependent acquisition–enhanced production ion workflow (MRM–IDA–EPI) was used on the instrument to perform the qualitative non-target screening. In this workflow, the instrument spends one cycle in triple quadrupole mode performing a multiple reaction monitoring scan type. When a multiple reaction monitoring signal exceeds a predefined threshold, the ion trap in the third quadrupole is activated and the next cycle is spent collecting fragment masses from the precursor. This is repeated over and over for the duration of sample acquisition. The enriched fragment spectra are then compared to the database for precursor identification. Only identifications with a fit or reverse fit over 65% is considered during manual curation of the data. The multiple reaction monitoring chromatograms of various analytes in water samples around Bloemfontein are presented in Appendix B. The chromatograms include the name of the analyte, multiple reaction monitoring transition that triggered the fragmentation spectra, the fit and reverse fit percentage that was used for the selection, as well as the acquired spectra versus the library spectra (MS/MS) which is a custom created library that identification was based on.

4.2.3.2 Selection of target analytes

The selected compounds were under pharmaceuticals and personal care products; pesticides and steroid hormones. Under pharmaceuticals and personal care products, the analgesic/anti-inflammatory drugs acetaminophen, ibuprofen, the antiepileptic carbamazepine and the disinfectant triclosan were selected. The selected pesticides were the herbicides atrazine, simazine, metolachlor and terbuthylazine. These emerging contaminants were targeted because of their level of occurrence in selected water sources, high usage, their known fate and behaviour in the environment such as water solubility or persistency and their environmental and health risks (Medkova et al., 2023; Nannou et al.,

2015; Pei et al. 2022). They were also chosen based on the availability of commercial analytical standards (Čelić et al., 2020). Under steroid hormones, progesterone, testosterone, estradiol and 17-alpha-ethinyl-estradiol were targeted in this study. As the targeted steroid and hormonal compounds were not detected in the screening of results, the motivation for their selection was based on the fact that they are endocrine disruptor compounds, as well as for their frequent existence in water sources (Yazdan et al., 2022) and partial elimination in WWTPs (Völker et al., 2019).

4.2.3.3 Analysis of targeted compounds

The analysis was performed on a HPLC linked to hybrid triple quadrupole ion trap mass spectrometer (AB SCIEX 4000, Framingham, MA, USA). Analyst 1.5 (AB SCIEX) software was used for all data acquisition and processing. Positive and negative ionisation modes were used to analyse the samples. In the positive ionisation mode, 20 µl of each extracted sample was separated on a C18 (150 mm × 4.6 mm, Gemini NX, Phenomenex) column at a flow rate of 300 µl/min using a five-minutes gradient from 5% solvent A (H₂O/0.1% formic acid) to 95% solvent B (MeOH/0.1% formic acid) with a total run time of nine minutes to allow for column re-equilibration. Eluting analytes were electrospray ionised in the TurboV ion source with a heater temperature of 500 °C to evaporate excess solvent, 40 psi nebuliser gas, 40 psi heater gas and a curtain gas of 15 psi. In negative ionisation mode, 20 µl of each extracted sample was separated on a C18 (150 m × 4.6 mm, Gemini NX, Phenomenex) column at a flow rate of 300 µl/min using a two-minutes gradient from 5% solvent A (H₂O/0.1% NH₃OH) to 95% solvent B (MeOH/0.1% NH₃OH) with a total run time of ten minutes to allow for column re-equilibration. Eluting analytes were electrospray ionised in the TurboV ion source with a heater temperature of 500 °C to evaporate excess solvent, 40 psi nebuliser gas, 40 psi heater gas, and a curtain gas of 15 psi. In positive ionisation mode, the ion spray voltage was set at 5 500 V, while in a negative ionisation mode, it was set at -4 500 V.

Analysis of target analytes such as acetaminophen, ibuprofen, carbamazepine, triclosan, atrazine, metolachlor, simazine, terbuthylazine, 17-alpha-ethinyl-estradiol, estradiol, progesterone and testosterone were carried out using multiple reaction monitoring transitions per analyte. Multiple reaction monitoring provides increased selectivity and reduces the likelihood of spectral interferences. The quantifier was the peak area on the chromatogram generated by the first and most sensitive transition, while the qualifier was the peak area generated by the second transition. The qualifier served as an additional level of confirmation for the presence of analytes, and the retention time for these two transitions must be the same. The details of the multiple reaction monitoring transitions for each

compound are listed in Appendix B. The first transition values (m/z) were used in this study as bolded in Appendix B.

4.2.3.4 Method verification and quality control

For validation of the performance of instruments, selectivity, linearity and limit of quantification were taken into account in this study. For selectivity, samples were submitted in batches with solvent blank runs between each sample analysed and quality control samples of known concentrations interspersed. The selectivity was evaluated by comparison between the retention time of the extracted blank sample and the retention time of each spiked standard or internal standard (IS) in the extracted samples. If any interferences were observed, the signal of their peak area should be less than 20% of the peak area of limit of quantification (LOQ) and less than 5% of the average peak area of IS in blank samples. The calibration values showed a concentration range of 5×10^{-5} to 1×10^{-1} mg/l. There was no interference effect from the endogenous matrix at the retention time of all analytes and IS. To evaluate linearity, a four-point calibration curve was generated for each analyte with concentrations ranging from 0.001 ppm to 1 ppm. The linear fit yielded a correlation coefficient (r) value exceeding 0.98. For each compound, the instrument limit of quantification was determined and it ranged from 0.0001 mg/l to 0.1 mg/l (Table 4.2). Laboratory blanks were used as quality control parameters to ensure that there was no external contamination, and all equipment were thoroughly cleaned.

Table 4.2 Measurement of linearity and limit of quantification.

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

4.3 Removal efficiency of emerging contaminants in wastewater treatment plants

The removal efficiency (%) expresses the decrease in a compound's concentration during treatment and is based on comparison of the average influent and effluent concentrations (Nannou et al., 2022). Kanama et al. (2018) stated that the elimination rate of pollutants in wastewater can be used to assess the performance of WWTPs. Solubility, volatility, adsorption to solids and other factors in WWTPs contribute to the removal and persistence of steroid hormones, pharmaceuticals, herbicides and personal care products. The removal efficiencies of all the targeted emerging contaminants detected in three WWTPs were assessed using Equation 1:

$$RF (\%) = \frac{\text{Influent concentration} - \text{Effluent concentration}}{\text{Influent concentration}} \times 100 \quad (1)$$

In this study, when the removal efficiency was 100%, it was considered as complete removal: 70–79% shows efficient removal, 50–69% moderate removal and poor removal for 0–49%. Moreover, any negative value (–%) was considered as negative removal.

4.4 Multivariate statistical analysis

The descriptive statistics of the data collected were performed on the Microsoft Excel software and presented in a simple descriptive statistics (minimum, maximum, mean and standard deviation). The interrelationships and the potential sources of emerging contaminants in water sources were determined by exploring different statistical methods such as Pearson's correlation coefficients, principal component analysis (PCA) and hierarchical cluster analysis, using MatLab R2019b software.

4.5 Environmental risk assessment of emerging contaminants

4.5.1 Individual risk assessment

The environmental risk assessment for individual analytes was assessed by the risk quotient (RQ) method. This method was centred on both acute and chronic toxicity studies that measures the risks on the most sensitive species within the environments (Archer et al., 2017). The RQ value was determined by paralleling the measured environmental concentration (MEC) and the predicted no effect concentration (PNEC) using Equation 2:

$$RQ = \frac{MEC}{PNEC} \quad (2)$$

The PNEC was obtained by dividing the value of acute (short-term) or chronic (long-term) toxicity by an assessment factor. During the process of determining the predicted no-effect concentration of particular emerging contaminants in water sources, the toxicity results were adjusted by an assessment factor as presented in Equation 3. Acute toxicity was considered as the median lethal concentration (LC_{50}) or mean effective concentration (EC_{50}), in which case the assessment factor is 1 000. Chronic toxicity was given by no observable effect concentration (NOEC), in which case the assessment factor can be 100, 50, 10 for algae, daphnids and fish, respectively (Nannou et al., 2022; Vasilachi et al., 2021). After correction of the toxicity data by an assessment factor, the RQ was obtained by comparing the PNEC with the MEC of the targeted emerging contaminant (Archer et al., 2017).

$$PNEC = \frac{EC_{50}}{AF} \text{ or } PNEC = \frac{NOEC}{AF} \quad (3)$$

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

4.5.2 Mixture risk assessment

The study adopted concentration addition method to assess mixture toxicity of emerging contaminants towards algae, daphnids and fish. Concentration addition in this study was approximated by sums of RQ values (RQmix) and sums of toxic units (TUs_{sum}) as proposed by various researchers (Backhaus and Faust, 2012; Backhaus and Karlsson, 2014; Backhaus et al., 2013; Białk-Bielińska et al., 2022; Kienzler et al., 2019; Maasz et al., 2019). The risk quotient mixture (RQmix) method uses the sum of RQs as an alternate for concentration addition-based predictions. The concentration addition assumes that the components of mixture have the same molecular site of action and can be regarded as dilutions of one another. In this method, the RQs for individual substances obtained using Equation 2 were used to determine the environmental risk mixture (RQmix). The environmental risk mixture for emerging contaminants were summed up using Equation 4:

$$RQ_{mix} = \sum_{i=1}^n RQ_i \quad (4)$$

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

Additionally, the mixture risks of emerging contaminants were also evaluated by the sum of toxic units (TUs) applied for each trophic level as shown in Equation 5. The TUsum was the sum of toxic units. In this approach, the toxic unit (TU) was defined as the ratio between the MEC and a respective measured or predicted EC₅₀ for algae, daphnids and fish.

$$TU_{sum} = \max(TU_{sum_{algae}}, TU_{sum_{daphnids}}, TU_{sum_{fish}}) \times AF$$

$$TU_{sum} = \max\left(\sum_{i=1}^n \frac{MEC}{EC50_{algae}}, \sum_{i=1}^n \frac{MEC}{EC50_{daphnids}}, \sum_{i=1}^n \frac{MEC}{EC50_{fish}}\right) \times AF \quad (5)$$

The RQ of the mixture was defined as the highest TUsum between the three trophic levels such as algae, daphnids and fish (Backhaus and Faust, 2012; Backhaus and Karlsson, 2014; Finckh et al., 2022; Kienzler et al., 2019). The TUsum above 1 (TUsum>1) shows ecosystem at risk, while TUsum below 1 (TUsum<1) indicates sufficient safety for the ecosystem.

4.5.3 Human health risk assessment

Health risk assessment on the inhabitants of the city of Bloemfontein was carried out using the USEPA method (USEPA, 2004, 2021; see also Kamunda et al., 2018; Mugudamani et al., 2022). The assessment included exposure to pesticides such as terbutylazine, simazine, metolachlor and atrazine throughout the life of both children and adults. In this study, it was assumed that ingestion route remains a foremost risk among the various ways of exposure. The average daily dose (ADD) associated with the ingestion of these herbicides in water sources were calculated using Equation 6:

$$ADD_{ing} = \frac{C \times IngR \times EF \times ED \times CF}{BW \times AT} \quad (6)$$

The ADDing denoted the average daily dose (mg/l per day) of selected herbicide through water ingestion for both children and adults. The concentration (mg/l) of herbicides in water sources is represented by C. In this study, IngR represent the ingestion rate (l/day), which is 2 for adults and 1.5 for children (USEPA, 2016). The EF connotes exposure frequency (days/year) which is 350 for the entire population (Mugudamani et al., 2022; USEPA, 2004). The ED is the exposure duration of 30 years for adults and 6 years for children (Mugudamani et al., 2022; USEPA, 2004). The conversion factor (l/cm³) is represented by CF which is 0.003 for both adults and children (Kamunda et al., 2018; Mugudamani et al., 2022; USEPA, 2002). The body weight (BW) of the exposed individual in this study is 70 kg and 28 kg for adults and children, respectively (Mugudamani et al., 2022). The average time (AT) for cancer risk is 365 × 70 days for the entire population, while for non-cancer risk it is 365 × 30 days for adults and 365 × 6 days for children (Mugudamani et al., 2022; USEPA, 2004).

4.5.4 Non-carcinogenic risk assessment

The probability of the population to suffer non-carcinogenic risks from ingestion of water polluted by herbicides was assessed by the hazard quotient (HQ). The hazard quotient is the ratio of the ADD of a selected herbicide to its reference dose (RfD) for the same exposure pathway (ingestion in this study) calculated by Equation 7. Equation 8 is then used to calculate the hazard index, which is the sum of the hazard quotients of various exposure pathways (Kamunda et al., 2018; Mugudamani et al., 2022, USEPA, 2004; 2021).

$$HQ = \frac{ADD}{RfD} \quad (7)$$

$$HI = \sum HQ \quad (8)$$

The reference doses for atrazine, metolachlor and simazine were 0.0035 mg/kg per day, 0.15 mg/kg per day and 0.005 mg/kg per day, respectively (USEPA, 2021). The terbutylazine reference dose was not available. In order to characterise the non-carcinogenic risks, a hazard quotient of less than one was considered as a very low risk; between one and four was considered as a probable risk and when greater than four was considered as a high risk (Mugudamani et al., 2022; USEPA, 2004; 2021).

4.5.5 Carcinogenic risk assessment

Moreover, the probability of an individual to develop cancer risks from exposure to herbicides in water sources through the ingestion pathway was assessed using Equation 9. The ADD in Equation 6 were used to assess cancer risks of selected herbicides by multiplying the ADD by an equivalent slope factor (SF).

$$CR = ADD \times SF \quad (9)$$

The corresponding slope factors for atrazine, metolachlor and simazine were 0.23 mg/kg per day, 0.0092 mg/kg per day and 0.12 mg/kg per day, respectively (USEPA, 2004, 2021). In this study, the carcinogenic risks were rated as very low ($<10^{-6}$), low (10^{-6} – 10^{-5}) medium (10^{-5} – 10^{-4}), high risk (10^{-4} – 10^{-3}) and very high ($>10^{-3}$) (Mugudamani et al., 2022; USEPA, 2004; 2021).

Chapter 5

INVESTIGATION AND MONITORING OF EMERGING CONTAMINANTS IN WATER SOURCES

This chapter focuses on the investigation and monitoring of emerging contaminants in various water sources around Bloemfontein. It presents the results obtained from qualitative screening of emerging contaminants in rivers, dams or reservoirs, treated drinking water, and wastewater influent and effluents. The selection of target analytes and their quantification in various water sources are presented and discussed. The chapter also delves into the elimination efficiency of selected emerging contaminants in WWTPs.

5.1 Introduction

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

Emerging contaminants are man-made tenacious organic substances that are not typically examined in the environment but have the possibility to cause effects on the environment and population health (Vasilachi et al., 2021). Emerging contaminants comprise an extensive collection of anthropogenic compounds, such as pesticides, cosmetics, personal and

domestic care products, pharmaceuticals, hormones, and brominated flame retardants, which are used universally and are essential for contemporary civilisation (Odendaal et al., 2015; Thomaidis et al., 2012). These numerous chemical compounds found in the water sources are derived from everyday man-made activities such as domestic, health care, aquaculture, agricultural and industrial processes (Ramrez-Malule et al., 2020). Several direct and indirect conduits for the introduction of emerging contaminants into the aqueous environment are available (Yazdan et al., 2022), such as run-off or leakage (Ngqwala and Muchesa, 2020). They may occur in wastewater influent due to excretion, bathing, or direct disposal, as well as wastewater effluent discharge that is one of the major conduits for emerging contaminants into rivers, dams and marine waters (Mhuka et al., 2020). Scientific instrumentation advancements, particularly chromatography and mass spectrometry-based techniques, have significantly expanded the range of detectable compounds in water environments (Nannou et al., 2022).

These analytical techniques enable the investigation and monitoring of compounds that were previously undetectable in the water environment at extremely low concentrations (Odendaal et al., 2015). In spite of the fact that these compounds are detected at low level, their global occurrence in water sources has stretch to a level that may be hazardous to the environment and health of communities (Nannou et al., 2022). The issue of emerging pollutants is a constant challenge (Vasilachi et al., 2021), because their numbers are increasing all the time (Patel et al., 2019). According to Galindo-Miranda et al. (2019), the conversion or end products of these compounds are frequently more noxious than the original compounds. Given their incessant introduction into the water resources and the effect on aquatic life and population health, qualitative screening and quantification of these compounds is required, particularly in water-stressed countries such as South Africa (Galindo-Miranda et al., 2019). However, most studies on emerging contaminants in South Africa only monitor known or targeted compounds in aqueous environments (Agunbiade and Moodley, 2016; Archer et al., 2017; Madikizela and Chimuka, 2017; Matongo et al., 2015; Mhuka et al., 2020; Sorensen et al., 2015; Wanda et al., 2017; Wilkinson et al., 2022; Wood et al., 2015). Furthermore, there have been only a few reports in the country focusing on qualitative non-target screening of extensive array of emerging contaminants in urban and natural water sources (Abafe et al., 2023; Odendaal, et al., 2015; Rimalyi et al., 2019).

The majority of these quantitative and qualitative studies were conducted in specific provinces such as Gauteng and KwaZulu-Natal, with data in other provinces, including the Free State province, being scarce. Chemical monitoring based on target compounds, according to Abafe et al. (2023) and Brack et al. (2019), fails to account for the majority of

unforeseen and unknown chemicals that may cause adverse health risks to aquatic and human life. Target investigation was applied in the detection of well-known compounds carefully chosen before quantification, and of which their reference standard is available (Brumovský et al., 2017; Čelić et al., 2021). To overcome this shortcomings, qualitative screening was also very crucial (Aalizadeh et al., 2016; Čelić et al., 2021) as it permits researchers to detect a comprehensive type of analytes present in water sources (Hollender et al., 2017; Montes et al., 2022) and such information can be used for target analysis in pollution monitoring studies (Brack et al., 2019).

Therefore, this chapter aimed at investigating and monitoring emerging contaminant pollution in rivers, dams, treated drinking water and WWTPs around Bloemfontein. This aim was achieved by incorporating qualitative and quantitative analysis techniques in order to visualise the true pollution status of water sources around the area. The study's findings may greatly provide and increase the list of analytes that may be considered in the future for monitoring and risk assessment in the Free State province and throughout the country. Furthermore, it may help water managers and policymakers to assess water quality and manage pollution more effectively.

5.2 Non-target screening of emerging contaminants in water sources

A qualitative screening of emerging contaminants in rivers, dams, treated drinking water and WWTPs was performed. This study was critical in the city of Bloemfontein as it provides information on a variety of unknown emerging contaminants that may also contribute to negative environmental health risks. Barack et al. (2019) echoed these sentiments, stating that qualitative non-target screening aids in the identification of the majority of unforeseen and unknown chemicals that may also lead to adverse health risks in the environment. The initial screening results in this study revealed 32 analytes under pharmaceutical and pesticide groups as presented in Table 5.1. From these groups, 14 classes of emerging contaminants including stimulants, NSAIDs, illicit drugs, lipid regulators, antiepileptics, antibiotics, antidepressants, antidiabetics, betablockers, antivirals, diuretics, herbicides, fungicides and insecticides were detected (Figure 5.1).

Eleven classes were grouped under pharmaceutical and among them, stimulants were detected the most, while the remaining three classes of pesticides were dominated by herbicides. A high number of these analytes was observed in river samples and least in treated drinking water. Their trend were as rivers > effluent > influent > dams > treated drinking water (Figure 5.2). Among the analytes found in water sources around Bloemfontein, three stimulants and two herbicides were found to be of environmental concern, namely

terbutylazine, ephedrine, nicotine, metformin and sebutylazine, as they were detected the most. Most notably was the detection of terbutylazine in all samples collected in dams, effluents and treated drinking water. The detection of more analytes in effluent than influent samples in this study as presented in Table 5.1 and Table 5.2 is worth mentioning. This situation, however, was also observed in other studies (Köck-Schulmeyer et al., 2013; Ofrydopoulou et al., 2021).

Table 5.1 Qualitative non-target screening and occurrence (%) of emerging contaminants in water sources around Bloemfontein

Analyte	Dams		Rivers		Influent		Effluent		Treated drinking water	
	N=5	DF (%)	N=5	DF (%)	N=3	DF (%)	N=3	DF (%)	N=2	DF (%)
Pharmaceuticals										
NSAID	Diphenhydramine	–	–	4	80	–	–	–	–	–
	Orphenadrine	1	20	3	60	–	–	–	–	–
	Cyclicine	–	–	1	20	1	33	–	–	–
Antibiotic	Paracetamol	–	–	1	20	3	100	–	–	–
	Sulfamethoxazol	–	–	1	20	–	–	–	–	–
Antiepileptics	Carbamazepine	1	20	–	–	–	–	–	–	–
Antidiabetic	Metformin	4	80	2	40	2	66	1	33	–
Antidepressant	Sertaline	–	–	–	–	1	33	–	–	–
Lipid regulator	Bezafibrate	–	–	2	40	1	33	1	33	–
	Atorvastatin	–	–	–	–	–	–	1	33	–
Betablocker	Cimetidine	–	–	–	–	–	–	1	33	–
Antiviral	Lamivudine	–	–	1	20	–	–	–	–	–
Illicit drug	THC-COOH	–	–	1	20	1	33	1	33	–
	Ecgoninemethylester	–	–	–	–	–	–	2	66	–
	Methamphetamine	–	–	3	60	2	66	2	66	–
Simulant	Nicotine	5	100	2	40	–	–	1	33	1
	Amphetamine	–	–	–	–	2	66	2	66	–
	Ephedrine	–	–	–	–	2	66	3	100	–
Diuretic	Theophylline	1	20	1	20	2	66	1	33	–
	Hordenine	–	–	1	20	1	33	–	–	–
	Hydrochlorothiazide	–	–	–	–	2	66	1	33	–
Herbicide	Sebutylazine	4	80	2	40	1	33	1	33	1
	Atrazine	4	80	1	20	1	33	–	–	2
	Terbutylazine	5	100	3	60	1	33	3	100	2
Fungicide	Metolachlor	2	40	2	40	–	–	1	33	1
	Simazine	–	–	2	40	–	–	1	33	–
	Tebuthiuron	–	–	–	–	–	–	–	–	1
Insecticide	Carbendazim	–	–	1	20	1	33	2	66	–
	Diazinon	–	–	1	20	–	–	–	–	–
	Carbaril	–	–	–	–	–	–	1	33	–
	Imidacloprid	–	–	–	–	–	–	1	33	–
	Propoxur	–	–	–	–	–	–	1	33	–

Notation: N = Number of samples; DF = Detection frequency; THC-COOH = 11-nor-9-carboxy-Δ⁹-tetrahydrocannabinol

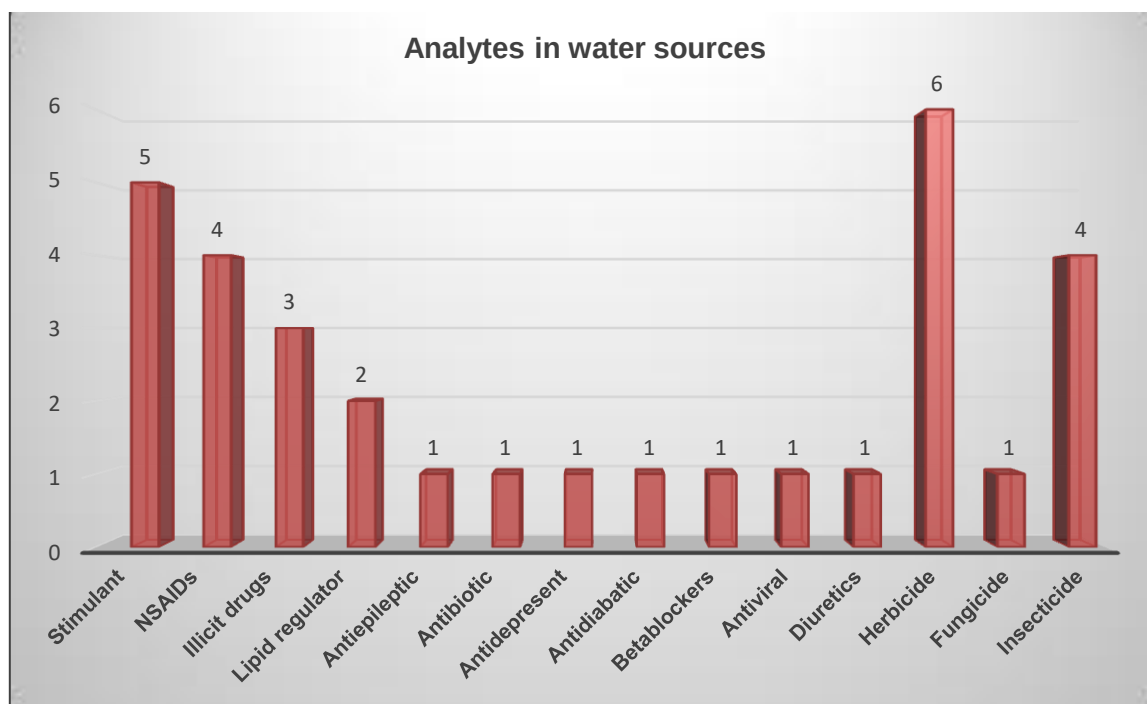


Figure 5.1 Screening of emerging contaminants in water sources around Bloemfontein

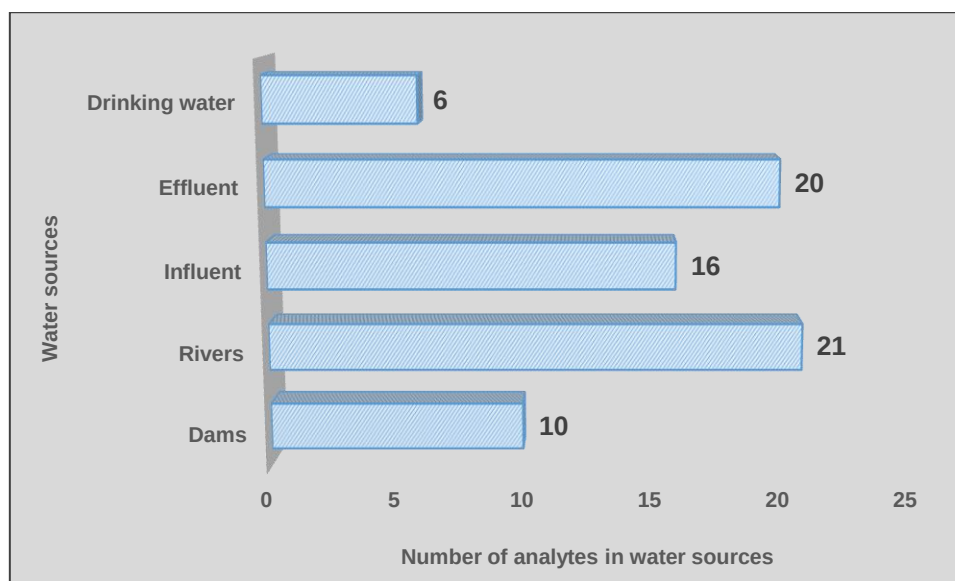


Figure 5.2 Detection of analytes per water source in Bloemfontein

5.2.1 Screening of emerging contaminants in rivers

As shown in Table 5.1, two groups of emerging contaminants, namely pharmaceuticals and pesticides, were detected. These outcomes are comparable to the findings of Hollender et al. (2017), who reported pharmaceuticals and pesticides as the two groups regularly detected in the Rhine River. Under pharmaceuticals, NSAIDs, stimulants, illicit drugs,

diabetics, lipid regulators, antibiotics and antivirals were detected, while under pesticides, herbicides, fungicides and insecticides were detected. Other classes of emerging contaminants were not found. From these two groups of emerging contaminants, NSAIDs, stimulants and herbicides were the utmost detected classes of analytes. A similar screening study for emerging contaminants in rivers in the Gauteng province of South Africa found NSAIDs to be one of the most detected classes of emerging contaminants (Rimayi et al., 2019).

In this study, NSAIDs such as diphenhydramine was found in 80% of the river samples. Other analytes found in 60% of the river samples included an NSAID (orphenadrine); herbicide (terbuthylazine); stimulant (ephedrine) and an illicit drug (methamphetamine). Previous researches on emerging contaminants in aqueous environments also found terbuthylazine in the Western Cape province of South Africa (Curchod et al., 2020), ephedrine in South African surface waters (Archer et al., 2017), diphenhydramine and methamphetamine in rivers in the Gauteng province of South Africa (Rimayi et al., 2019). Although nicotine, paracetamol and sulfamethoxazole were least detected in this study, their occurrence were also detected in many rivers of the world such as Pienaars River, South Africa; Madejera River, Tunisia; Yamuna River, India, Torrens River, Australia, Piracicaba River, Brazil and Trinity River, United States (Wilkinson et al., 2022).

The high detection of diphenhydramine could be attributed to the fact that it is an over-the-counter medication used to treat a variety of symptoms, including insomnia, fever, insect bites and eczema. Herbicides are effective at controlling invasive plants in agricultural lands. Orphenadrine is a prescription medication that may help to alleviate the symptoms of Parkinson's disease, such as trembling. Methamphetamine is an illegal stimulant that can be smoked or injected into veins to keep people awake and is therefore popular at parties. Ephedrine is primarily prescribed to treat asthma and nasal congestion. As a result, the presence of these compounds in more river samples suggests that community members use herbicides, medicinal drugs and possibly abuse drugs. Agricultural activities are a most important economic contributor in the Free State province, therefore the detection of herbicides in rivers as a result of runoff from agricultural fields was expected. Additionally, because WWTPs are the carriers of the majority of emerging contaminants (Nannou et al., 2022; Wang et al., 2022), wastewater effluents discharged from these plants into streams may introduce emerging contaminants such as pharmaceuticals and pesticides. Some of the rivers run through townships and cities; hence, community members' direct urination, runoff from clogged sewage systems or improper waste disposal may have introduced the detected drugs into the rivers.

5.2.2 Screening of emerging contaminants in dams and reservoirs

Emerging contaminants in dam samples showed different trends from those detected in river samples. As presented in Table 5.1, among the pharmaceuticals only stimulants, antidiabetics, NSAIDs and antiepileptic drugs were detected, while herbicides were the only class of pesticides detected in dam samples. From these classes of emerging contaminants, the stimulant nicotine and the herbicide terbuthylazine were the most detected contaminants as they were detected in 100% of the collected dam samples. Herbicides (atrazine and sebuthylazine) and the antidiabetic (metformin) were also found in 80% of the collected samples. In the Hartbeespoort Dam, South Africa, triazine herbicides such as atrazine were also detected (Rimayi et al., 2018), which correspond to the outcomes of this study. Moreover, atrazine, terbuthylazine and sebuthylazine were also found in surface water in Cape Town, South Africa (Ojemaye, 2020), surface water in Hungary (Székács et al., 2015), and the South Fork of the Zumbro River watershed in the United States (Fairbairn et al., 2014). Another study found antidiabetic metformin in surface water around South Africa's Gauteng province (Rimayi et al., 2019). Various researchers have discovered stimulants such as nicotine in South African surface water (Matongo et al., 2015; Rimayi et al., 2019; Wood et al., 2015).

The use of herbicides to control aquatic weeds in dams may have contributed to their concentrations in this study. Herbicides, according to Pandey et al. (2019), can be useful in controlling invasive plants in water. The detected herbicides could also be a result of runoff from a nearby agricultural fields. The application of herbicides to manage or kill weeds in a well maintained large open turf witnessed near some of the dams that serve as conference centres may be a source of herbicides. Rimayi et al. (2018) mentioned that most of triazine herbicides such as atrazine and terbuthylazine are used or applied to kill unwanted grasses or weeds. Furthermore, nicotine is a stimulant and anxiolytic that can be used recreationally, whereas metformin is used to treat high blood sugar levels. During the sampling campaign, it was discovered that the majority of the dams served as conference and resort centres with lodging houses that use septic tanks. As a result, septic tanks may introduce pollutants such as nicotine and metformin, particularly during the rainy season when the water table rises. Visitors' improper disposal of medicinal drugs and unwanted cigarettes may also contribute to traces of these contaminants. Moreover, effluents from WWTPs are mostly released in nearby streams. Therefore, rivers that release their water in these dams may present traces of these compounds in dams.

5.2.3 Screening of emerging contaminants in wastewater treatment plants

In influents samples, pharmaceuticals such as stimulants, NSAIDs, illicit drugs, diuretics, antidiabetics, antidepressants and lipid regulators were detected. Pesticides, herbicides and fungicides were identified in influent samples as presented in Table 5.1. It was only paracetamol that was detected in 100% of the collected influent samples. Paracetamol is a pain reliever and fever reducer that is widely available in supermarkets. The detection of paracetamol in all collected samples may be attributed to the fact that the selected WWTPs are located in the city where the use of drugs is expected to be high. According to Al Kaf et al. (2017), detection of medicinal drugs is expected to be high in urban areas as the use of drugs is high, which support the current findings. The detection of paracetamol in wastewater influents was also reported by other researchers in Oslo, Norway (Thomas et al., 2007); Eastern Cape, South Africa (Ademoyegun, 2017); North West province (Kanama et al., 2018); eThekweni, South Africa (Späth et al., 2021) and in Vidyanarayanapuram, India (Shipingana et al., 2022). Most of the WWTPs in this region receives wastewater from domestic, industrial and hospital wastewater. Human excretion and flushing of expired or unused medicinal drugs may have contributed to the high detection of these compounds in wastewater influents around the city of Bloemfontein. This also demonstrated high reliance of these drugs within the study area. Furthermore, wastewater from factories and hospitals may also be attributed as a source of these compounds.

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

plants are unable to remove some of the emerging contaminants and need improvement. This was also supported by Morin-Crini et al. (2022), who stated that tertiary treatment systems should be added in WWTPs in order to eliminate and limit emerging contaminant pollution.

In South Africa, wastewater effluent is typically discharged into nearby streams, introducing pollutants into the aqueous environment. As a result, prioritising these chemicals in pollution monitoring studies is critical. Not only will this protect aquatic life, but will also preserve or sustain South Africa's water resources. Moreover, wastewater effluent in this study were found to have more analytes than influent samples as presented in Table 5.2. The occurrence of high concentrations of some emerging contaminants in effluents than influent was also reported by other authors (Köck-Schulmeyer et al., 2013; Ofrydopoulou et al., 2021). According to Kortesmäki et al. (2020), non-removal and the present of higher concentration of some analytes in effluent than influent may be attributed to factors such as wastewater composition, structure of analyte and conversion of the conjugated metabolites to the parent compound by enzymatic processes in the WWTPs. Their high detection in effluent than influent may also be influenced by factors such as working faults of the WWTPs and the current electricity load shedding problems in the country.

Table 5.2 Composition of influent and effluent samples

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

*THC = 11-nor-9-carboxy- Δ^9 -tetrahydrocannabinol

5.2.4 Screening of emerging contaminants in treated drinking water

In treated drinking water, one class of pharmaceuticals (stimulants) and one class of pesticides (herbicides) were detected as presented in Table 5.1. Herbicides atrazine and terbutylazine were detected in 100% of the collected treated drinking water samples. Analytes such as tebuthiuron, metolachlor, sebuthylazine and nicotine were detected in less than 60% of the collected samples. The outcomes of this study are comparable to the findings of the screening study of emerging contaminants in South African drinking water (Odendaal et al., 2015). These researchers detected terbutylazine in 100% of the samples collected, which is similar to the findings of this study. Similarly, Caldas et al. (2019) reported that atrazine was the most detected in their monitoring study of pesticides in drinking water in southern Brazil. Furthermore, in a nationwide survey of emerging pollutants in Brazilian waters, atrazine was detected in 75% of the collected treated drinking water samples (Machado et al., 2016), which was less than the findings of the current study.

The application of herbicides to eliminate weeds in dams operating as a source of water in water treatment plants may be the source of these herbicides. Rivers that recharge these dams may be contaminated by herbicides as they mostly receive wastewater effluents. High detections of atrazine in water sources may also be linked to their nature of being persistent. Almqvist et al. (2018) stated that herbicides such as atrazine are persistent in soil and their transport to water, making it the most frequently identified pesticide in water sources. Additionally, the occurrence of pesticides in treated drinking water confirms the incapability of the methods employed in selected water treatment plants, which include abstraction, macro/micro sieving, coagulation, flocculation, sedimentation, filtration and disinfection in removing these contaminants. Long-term exposure to these herbicides may have negative consequences for water users in the city of Bloemfontein. These pesticides should be prioritised in the treatment processes in order to find the best methods for their removal. In addition, pollution monitoring and toxicity studies should prioritise them and determine whether their concentrations have any negative effects on water consumers.

5.3 Selection of target analytes

The selected compounds were organised under three groups of emerging contaminants, namely pharmaceuticals and personal care products, pesticides and steroid hormones. Under pharmaceuticals and personal care products, the analgesic/anti-inflammatory drugs acetaminophen, ibuprofen, the antiepileptic carbamazepine and the disinfectant triclosan were selected. The selected pesticides were the herbicides atrazine, simazine, metolachlor

and terbuthylazine. These emerging contaminants were targeted because of their level of occurrence in selected water sources, high usage, their known fate and behaviour in the environment such as water solubility or persistency, and their environmental health risks (Medkova et al., 2023; Nannou et al., 2015; Pei et al., 2022). Under steroid hormones, progesterone, androgens testosterone, estrogens, estradiol and 17-alpha-ethinyl-estradiol were also targeted in this study. As the targeted steroid and hormonal compounds were not detected in the screening of results, the motivation for their selection was based on the fact that they are endocrine disruptor compounds, their frequent existence in water sources (Yazdan et al., 2022) and partial elimination in WWTPs (Völker et al., 2019). Moreover, the targeted compounds in this study were also chosen based on the availability of commercial analytical standards (Čelić et al., 2020).

5.4 Quantitative analysis of emerging contaminants in water sources

A total of 72 samples were collected during the spring ($n=18$), summer ($n=18$), autumn ($n=18$) and winter ($n=18$) seasons from rivers ($n=5$), dams and reservoirs ($n=5$), treated drinking water ($n=2$), wastewater influent ($n=3$) and wastewater effluent ($n=3$). During the laboratory analysis, 12 organic contaminants were targeted. These emerging contaminants were pharmaceuticals (acetaminophen, ibuprofen and carbamazepine), personal care products (triclosan), herbicides (atrazine, simazine, terbuthylazine and metolachlor) and steroid hormones (17-alpha-ethinyl-estradiol, estradiol, progesterone and testosterone). The descriptive statistics of these 12 selected contaminants in various water sources are presented in Table 5.3. They were summarised as detection frequency, minimum, maximum, mean concentrations and standard deviations ($\pm$ SD). The mean concentrations and standard deviations of contaminants detected only in one sample were not calculated. Their results in water sources around Bloemfontein are presented and discussed based on their source of occurrence.

5.4.1 Occurrence of emerging contaminants in rivers

Among the pharmaceuticals and personal care products, acetaminophen, carbamazepine, ibuprofen and triclosan were the only contaminants targeted in rivers around Bloemfontein. As presented in Table 5.3, their respective average concentrations during the spring season were 0.12 mg/l, 0.57 mg/l, 2.22 mg/l and <LOQ. In the summer season their respective mean concentrations were <LOQ, 0.7 mg/l, 1.16 mg/l and <LOQ. In the autumn season their respective mean concentrations were <LOQ, 0.25 mg/l, 0.92 mg/l and <LOQ. Moreover, the winter season showed average concentrations of <LOQ, 0.31 mg/l, 2.20 mg/l

and <LOQ, respectively. Among these contaminants, ibuprofen had the highest average concentrations followed by carbamazepine in all seasons. Their average concentrations ranged as ibuprofen > carbamazepine > acetaminophen > triclosan. Seasonally, the spring season recorded the highest mean concentrations of pharmaceuticals and personal care products and they ranged as spring > winter > summer > autumn (Figure 5.3). The concentrations of ibuprofen in this study were higher than the one reported in the Mississippi River in the United States (Zhang et al., 2006), the Hanoi in Vietnam (Tran et al., 2014), Chongqing in China (Yan et al., 2015), the Msunduzi River in KwaZulu-Natal, South Africa (Agunbiade and Moodley, 2016) and the Apies River in Mpmualanga, South Africa (Mhuka et al., 2020). Moreover, similar cases of the occurrence of carbamazepine in rivers was also reported by other researchers (Archer et al., 2017; Glassmeyer et al., 2017; Hossain et al., 2018; Vumazonke et al., 2020; Wanda et al., 2017; Wilkinson et al., 2022). Ibuprofen is used to treat pain and fever, which are common illnesses in many communities (Ekinci et al., 2020). Given that ibuprofen is used to treat a variety of diseases and is available without a prescription, it was not surprising that it was the leading pollutant in rivers. The presence of carbamazepine as a prescription drug may have been influenced by the presence of patients suffering from seizures and bipolar disorders in those areas (Nannou et al., 2022). The majority of the rivers in this study run through townships, the city centre and agricultural farms. Illegal waste dumping near rivers was also observed in the majority of townships. Waste dumped near rivers that run through these settlements may contain unwanted or expired medicinal drugs such as ibuprofen and carbamazepine, introducing these contaminants into the rivers. Some of the emerging contaminants may be spread into water bodies by WWTPs that discharge their effluents into nearby streams. Furthermore, farm houses equipped with septic tanks and latrine toilets may have an impact on the concentration of these pharmaceutical compounds in nearby rivers.

Pesticides were another group of contaminants detected in rivers. As presented in Table 5.3, atrazine, metolachlor, simazine and terbuthylazine were the types of herbicides targeted. The respective average concentrations of these herbicides were 0.03 mg/l, 0.01 mg/l, 1.82 mg/l and 0.06 mg/l in the spring season. In the summer season, their respective mean concentrations were 0.05 mg/l, 0.06 mg/l, 1.04 mg/l and 0.08 mg/l. The autumn season recorded mean concentrations of 0.69 mg/l, 0.02 mg/l, 0.69 mg/l and 0.01 mg/l, respectively. Additionally, in winter season the average concentrations of these contaminants were 0.08 mg/l, 0.12 mg/l, 0.37 mg/l and 0.05 mg/l, correspondingly. Overall, in rivers, the herbicide simazine had the highest average concentrations, followed by atrazine. Their overall average concentrations ranged as simazine > atrazine > metolachlor > terbuthylazine. Seasonally, their highest sum concentrations were recorded during the

spring season and their trend was spring > autumn > summer > winter (Figure 5.3). Other scholars also detected atrazine in Kabwe, Zambia (Sorensen et al., 2014), metolachlor in the Samambaia River basin in Brazil (Correia et al., 2020), and terbuthylazine in the Western Cape, South Africa (Curchod et al., 2020). The occurrence of herbicides in rivers was not surprising in this area, particularly atrazine, simazine and terbuthylazine, which were the leading herbicides in river samples. Trazine herbicides are regarded as effective and low-cost substances that are largely applied in crop production (Wang et al., 2022). The agriculture is the mainstay of the Free State province's economy which is the host of the city of Bloemfontein. It is recognised as the producer of a lot of maize, soy beans, wheat, sorghum, sunflower, potatoes, groundnuts and wool. All of these practices compel the application of weed control herbicides before, during and after farming. Moreover, the city of Bloemfontein is characterised by well-developed roads, public parks, industrial areas and golf clubs. With all these significant areas, significant amounts of herbicides are applied to control weeds on pavings, in parks, golf courts, roadsides, buildings and industrial areas. Runoff from agricultural fields, roads, public squares, golf courses and industrial areas may increase the level of herbicides in nearby streams.

Furthermore, steroid hormones were also detected in rivers around Bloemfontein. As presented in Table 5.3, 17-alpha-ethinyl-estradiol, estradiol, progesterone and testosterone were the only steroid hormones targeted. Their respective average concentrations in the spring season were 12.18 mg/l, 0.07 mg/l, <LOQ, and <LOQ. In summer, they showed average concentrations of 7.79 mg/l, <LOQ, <LOQ, <LOQ and <LOQ, respectively. Their respective average concentrations in the autumn season were 31.55 mg/l, <LOQ, <LOQ and <LOQ. Additionally, these contaminants' average concentrations in the winter season were 12.34 mg/l, <LOQ, <LOQ and <LOQ, respectively. The concentrations of 17-alpha-ethinyl-estradiol were the highest in all seasons. Its most notable concentration was recorded in the autumn season. Their overall average concentrations ranged as 17-alpha-ethinyl-estradiol > estradiol = progesterone = testosterone. They recorded the highest average concentration in the autumn seasons and their trend was autumn > winter > spring > winter (Figure 5.3). The occurrences of 17-alpha-ethinyl-estradiol in rivers were also reported in rivers around the world: in Ningbo, China (Lin et al., 2020), Atibaia River, Brazil (Montagner et al., 2013), Lagos, Nigeria (Olarinmoye et al., 2016), southern Brazil (Pivetta and Gastaldini, 2019) and the Liao river basin in northern China (Tan et al., 2018). The presence of steroid hormones in rivers may have been influenced by wastewater effluents that are discharged in nearby streams. Wastewater treatment plants in this area receive influent from domestic, industrial and hospital wastewater, thus becoming major sources of these compounds (Forghani et al., 2018). In relation to that, one of the WWTPs within the

study area was out of order. Hence, wastewater influents from industrial activities, for example, from pharmaceutical, manufacturing, domestic and hospital activities, were received and discharged into nearby streams without any treatment. These situations may have influenced the high concentrations of this compound in river samples that are the highest to be ever detected in rivers. Additionally, rivers that pass through townships and city centres are likely to be contaminated by these compounds as a result of illegal dumping of household wastes (e.g., medicinal drugs) near them. According to Forghani et al. (2018), estradiol is a natural estrogenic hormone released by humans and livestock. Animals that drink the water from these rivers, as well as people who visit, may end up introducing these hormones into the river water through open urination and defecation. Moreover, runoff from animal husbandry activities near some rivers may also introduce these hormones. In summation, the concentrations of these emerging contaminants were highest in the autumn season specifying the autumn season as the largest contributor to river pollution in the area. It was mostly contributed by 17-alpha-ethinyl-estradiol, simazine and ibuprofen, which make them contaminants of concern in water sources around Bloemfontein.

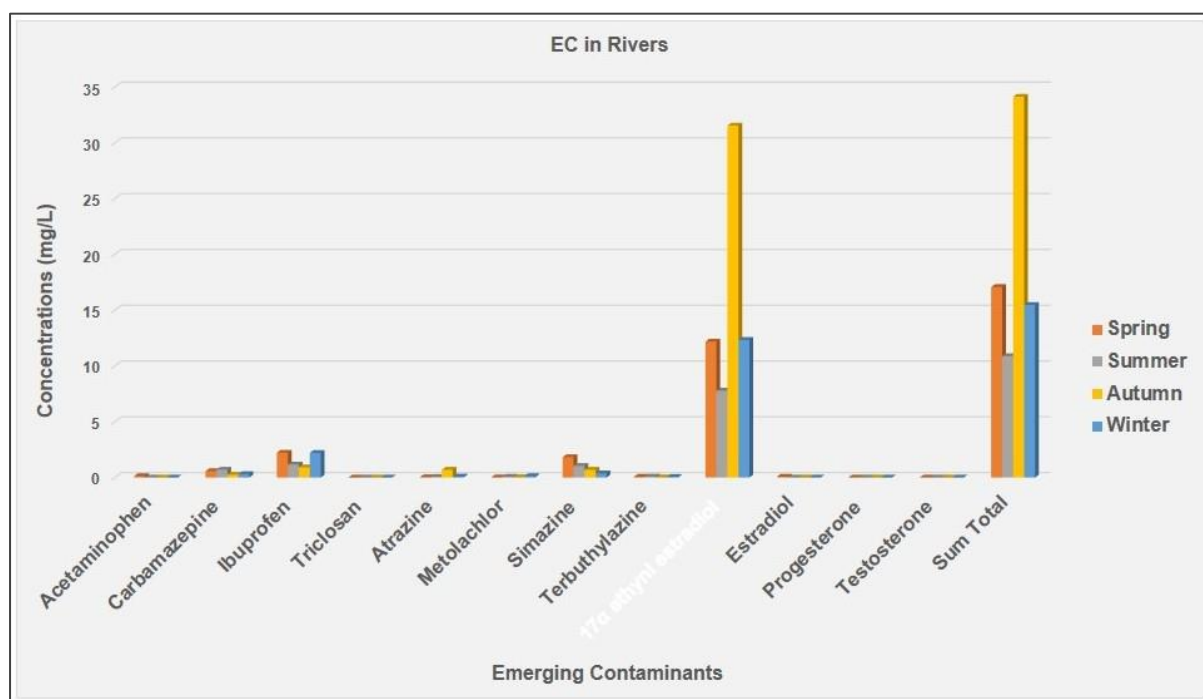


Figure 5.3 Seasonal concentrations of emerging contaminants in rivers

Table 5.3 Occurrence of emerging contaminants in rivers

Compound	Concentration (mg/ℓ)											
	Spring (n=5)			Summer (n=5)			Autumn (n=5)			Winter (n=5)		
	DF	Minimum–Maximum	Mean ±SD	DF	Minimum–Maximum	Mean ±SD	DF	Minimum–Maximum	Mean ±SD	DF	Minimum–Maximum	Mean ±SD
Pharmaceuticals and personal care products												
Acetaminophen	2	<LOQ–0.15	0.12±0.05	0	<LOQ	–	0	<LOQ	–	1	<LOQ–0.03	–
Carbamazepine	4	<LOQ–0.68	0.57±0.08	4	0.40–1.43	0.7±0.49	4	<LOQ–0.32	0.25±0.07	4	<LOQ–0.36	0.31±0.04
Ibuprofen	4	<LOQ–3.44	2.22±1.13	4	0.38–2.11	1.16±0.76	3	<LOQ–2.26	0.92±1.16	4	<LOQ–0.60	2.20±1.40
Triclosan	1	<LOQ–0.09	–	0	<LOQ	–	0	<LOQ	–	0	<LOQ	–
Pesticides (herbicides)												
Atrazine	5	0.002–0.06	0.03±0.03	5	0.03–0.11	0.05±0.03	5	0.0014–0.03	0.69±0.01	5	0.002–0.32	0.08±0.13
Metolachlor	5	0.003–0.03	0.01±0.01	5	0.02–0.12	0.06±0.04	5	0.0007–0.03	0.02±0.01	4	<LOQ–0.004	0.12±0.05
Simazine	4	<LOQ–5.67	1.82±2.66	4	0.10–3.22	1.04±1.48	2	<LOQ–0.91	0.69±0.30	2	<LOQ–0.61	0.37±0.35
Terbuthylazine	5	0.007–0.21	0.06±0.09	5	0.03–0.14	0.08±0.05	5	0.0016–0.03	0.01±0.01	5	0.001–0.16	0.05±0.07
Endocrine disrupting compound (steroid hormones)												
17α ethinyl estradiol	5	0.09–25	12.18±8.86	5	1.08–14.5	7.79±5.34	4	<LOQ–53.80	31.55±18.79	5	0.28–23.5	12.34±9.20
Estradiol	2	<LOQ–0.08	0.07±0.01	0	<LOQ	–	0	<LOQ	–	0	<LOQ	–
Progesterone	0	<LOQ	–	0	<LOQ	–	0	<LOQ	–	0	<LOQ	–
Testosterone	0	<LOQ	–	0	<LOQ	–	0	<LOQ	–	0	<LOQ	–

Notation: LOQ = limit of quantification, DF = detection frequency, n = number of samples, ±SD = standard deviation, µg/ml = microgram per millilitre.

5.4.2 Occurrence of emerging contaminants in dams/reservoirs

The concentrations of pharmaceuticals and personal care products such as acetaminophen, carbamazepine, ibuprofen and triclosan in dams are presented in Table 5.4. The respective mean concentrations of these contaminants during the spring season were 0.07 mg/l, 0.29 mg/l, 0.3 mg/l and <LOQ. During the summer season, their recorded mean concentrations were <LOQ, 0.12 mg/l, <LOQ and <LOQ, respectively. Their recorded respective mean concentrations during the autumn season were <LOQ, 0.08 mg/l, 0.02 mg/l and <LOQ. Moreover, the winter season recorded mean concentrations of these contaminants as <LOQ, 0.06 mg/l, <LOQ and <LOQ. The pharmaceuticals and personal care products recorded the highest average concentration in the spring season and their trend was spring > summer > autumn > winter. The concentrations of carbamazepine were found to be the highest in all seasons. Their overall average concentrations ranged as carbamazepine > ibuprofen > acetaminophen > triclosan (Figure 5.4). The presence of carbamazepine as a leading contaminant in dam samples indicates that carbamazepine is a commonly used drug in and around Bloemfontein. An anticonvulsant such as carbamazepine is regarded as a prescription drug that works in the brain and nervous system to control seizures, pain and bipolar disorder (Kanama et al., 2018; Nannou et al., 2022). The concentrations of ibuprofen in dams can be explained by the fact that analgesics and non-steroid anti-inflammatory drugs are available without a prescription and are used to treat pain and inflammation, which are symptoms of a variety of diseases (Nannou et al., 2022). Ibuprofen is a medication used to manage and treat inflammatory diseases, rheumatoid arthritis, pain, fever and dysmenorrhea (Ekinci et al., 2020). Some of the dams in this study are close to settlements, open to the public and serve as resorts, conference centres and fishing spots. People who visit those resorts or live near these dams may have urinated near the dams or improperly disposed of these drugs. Illegal dumping of household waste containing unused or unfinished medication, as well as sewage runoff from nearby communities observed during a site visit, may have contributed to the concentration of these compounds. Furthermore, lodging houses and some farm houses with septic tanks and latrine toilets near some of the dams may leak these contaminants.

As presented in Table 5.4, the mean concentrations of targeted herbicides, such as atrazine, metolachlor, simazine and terbutylazine in dams, were recorded as 0.01 mg/l, 0.01 mg/l, 0.09 mg/l and 0.03 mg/l during the spring season, correspondingly. During the summer season, their respective mean concentrations were as 0.03 mg/l, 0.03 mg/l, 0.13 mg/l and 0.05 mg/l. During the autumn season their respective mean concentrations were recorded as 0.01 mg/l, 0.01 mg/l, 0.12 mg/l and 0.01 mg/l. Moreover, the winter season recorded

mean concentrations of 0.04 mg/l, 0.04 mg/l, 0.14 mg/l and 0.02 mg/l, correspondingly. The targeted pesticides recorded the highest average concentration in the summer season. Their sum seasonal concentrations were trending as summer > winter > autumn > spring. Among the detected herbicides, simazine had the highest average concentrations in all seasons. Their overall average concentrations ranged as simazine > terbuthylazine > atrazine > metolachlor (Figure 5.4). The presence of atrazine and terbuthylazine in dams were also reported in the Hartbeespoort Dam, South Africa (Rimayi et al., 2018). High concentrations of pesticides in dams may be attributed to the fact that they are located nearby agricultural fields (of which maize crops are common) which necessitate the application of these herbicides to kill weeds. Considerable amounts are also applied in forestry, industrial areas, public areas, parks, golf courts and sports grounds for weed control and maintenance. Runoff from these areas may introduce simazine, terbuthylazine, atrazine and metolachlor in dams. Pandey et al. (2019) also indicated that these herbicides can be applied in controlling invasive plants in water. Hence, their presence in dams could be credited to their application to control aquatic weeds such as algae and submerged weeds.

Table 5.4 also presents the concentrations of the targeted steroid hormones in dams such as 17-alpha-ethinyl-estradiol, estradiol, progesterone and testosterone. In all seasons only 17-alpha-ethinyl-estradiol was detected, while other contaminants concentrations were below the limit of quantification (<LOQ). Its mean concentrations were 3.67 mg/l, 1.83 mg/l, 6.90 mg/l and 2.78 mg/l during the spring, summer, autumn and winter seasons, respectively. The most notable concentration of steroid hormones was recorded in the autumn season. Their sum seasonal concentrations were trending as autumn > spring > winter > summer. Among the detected steroid hormones, 17-alpha-ethinyl-estradiol had the utmost concentration in all seasons. The overall average concentrations of steroid hormones ranged as 17-alpha-ethinyl-estradiol > estradiol = progesterone = testosterone. The occurrence of 17-alpha-ethinyl-estradiol in dams around Bloemfontein, which fall under the Modder River catchment, is higher than the ones reported in the Joao Goulart catchments in Brazil (Pivetta and Gastaldini, 2019) and in the Nigerian river catchment (Ogunbanwo et al., 2020). The 17-alpha-ethinyl-estradiol, a synthetic estrogenic compound, is commonly used as the active ingredient in many oral contraceptives and postmenopausal hormone therapy (Kanama et al., 2018). Many factors contributed to the detection of steroid hormones in dams, including illegal dumping of household waste containing unused or expired drugs near the dams and sewage runoff from nearby settlements, which was observed near one of the sampling points. Agricultural areas near some dams, particularly those with livestock production, may also serve as a secondary source of these compounds. Some steroid hormones may be leaked into fresh water from septic tanks in some farm houses and dams

with resorts. Furthermore, rivers that receive wastewater effluents and discharge their water to these dams may introduce steroid hormones into the dams. In summation, high levels of the emerging contaminants in dams was recorded in the autumn season (Figure 5.4). It was mostly contributed by 17-alpha-ethinyl-estradiol, simazine and carbamazepine, which make them contaminants of concern in this area.

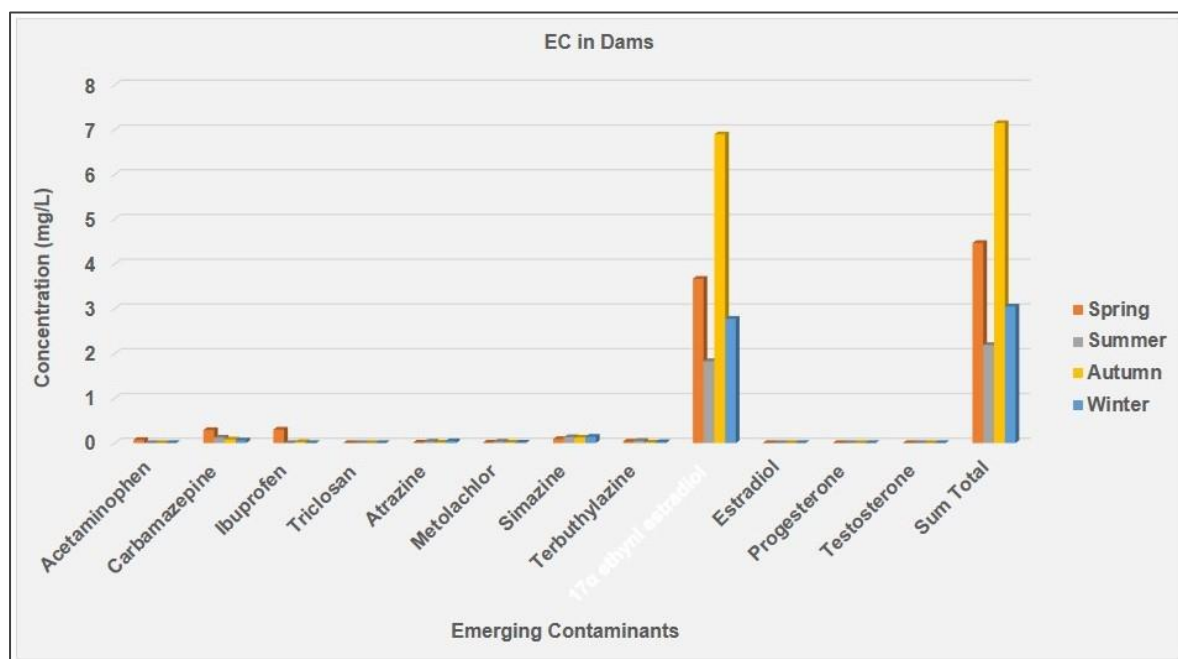


Figure 5.4 Seasonal concentrations of emerging contaminants in dams

Table 5.4 Occurrence of emerging contaminants in dams

Compound	Concentration (mg/l)											
	Spring (n=5)			Summer (n=5)			Autumn (n=5)			Winter (n=5)		
	DF	Minimum–Maximum	Mean ±SD	DF	Minimum–Maximum	Mean ±SD	DF	Minimum–Maximum	Mean ±SD	DF	Minimum–Maximum	Mean ±SD
Pharmaceuticals and personal care products												
Acetaminophen	2	<LOQ–0.12	0.07±0.07	0	<LOQ	–	1	<LOQ–0.09	–	0	<LOQ	–
Carbamazepine	5	0.01–0.63	0.29±0.24	5	0.01–0.21	0.12±0.08	5	0.03–0.19	0.08±0.06	4	<LOQ–0.08	0.06±0.02
Ibuprofen	3	<LOQ–0.81	0.3±0.44	0	<LOQ	–	2	<LOQ–0.03	0.02±0.01	1	<LOQ–0.10	–
Triclosan	0	<LOQ	–	0	<LOQ	–	0	<LOQ	–	0	<LOQ	–
Pesticides (herbicides)												
Atrazine	5	0.008–0.03	0.01±0.01	5	0.02–0.04	0.03±0.01	5	0.003–0.02	0.01±0.01	5	0.01–0.08	0.04±0.03
Metolachlor	5	0.002–0.03	0.01±0.01	5	0.01–0.04	0.03±0.01	5	0.01–0.02	0.01±0.01	5	0.003–0.02	0.01±0.01
Simazine	4	<LOQ–0.20	0.09±0.08	4	<LOQ–0.24	0.13±0.11	4	<LOQ–0.29	0.12±0.12	2	<LOQ–0.23	0.14±0.13
Terbutylazine	5	0.01–0.06	0.03±0.02	5	0.02–0.08	0.05±0.02	5	0.003–0.03	0.01±0.01	5	0.01–0.03	0.02±0.01
Endocrine disrupting compound (steroid hormones)												
17α ethinyl estradiol	5	0.28–6.13	3.67±2.15	5	0.25–3.40	1.83±1.13	5	1.30–14.80	6.90±5.08	5	0.39–4.62	2.78±1.97
Estradiol	0	<LOQ	–	0	<LOQ	–	0	<LOQ	–	0	<LOQ	–
Progesterone	0	<LOQ	–	0	<LOQ	–	0	<LOQ	–	0	<LOQ	–
Testosterone	0	<LOQ	–	0	<LOQ	–	0	<LOQ	–	0	<LOQ	–

Notation: LOQ = limit of quantification, DF = detection frequency, n = number of samples, ±SD = standard deviation, µg/ml = microgram per millilitre.

5.4.3 Occurrence of emerging contaminants in wastewater treatment plants

In order to investigate and monitor emerging contaminants in WWTPs, three WWTPs were selected. All of the targeted WWTPs receive domestic, industrial and hospital wastewater. The treatment processes used in all WWTPs selected in this study include primary, secondary and tertiary treatment as shown in Figure 5.5. The primary treatment entails the removal of suspended solids and floating debris. Additionally, clarified liquid stays above and is ready for processing, while suspended solids gradually sink due to gravity to form primary sludge. The biological remediation of soluble organic matter that has eluded primary treatment is the focus of the secondary treatment process. The dissolved organics are taken up by the bacteria, who then transform them into biomass and gases like carbon dioxide and nitrogen. The active process of activated sludge, which promotes microbial growth through mechanical mixing and aeration, is essential for secondary treatment. Before the discharge of effluent into nearby streams, the wastewater then goes to tertiary treatment which involved disinfection by chlorine. However, in this study, the tertiary treatment of all WWTPs was dysfunctional, leading to effluent being discharged without being disinfected.

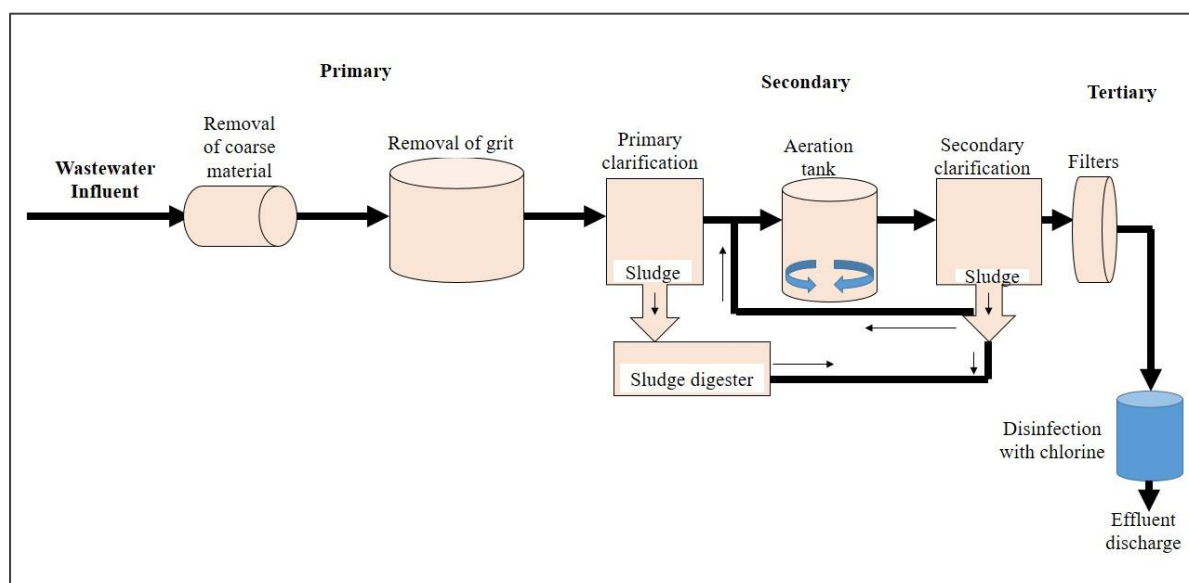


Figure 5.5 Schematic presentation of the selected wastewater treatment plants

5.4.3.1 Occurrence of emerging contaminants in wastewater influents

In influents, the average concentrations of pharmaceuticals and personal care products, such as acetaminophen, carbamazepine, ibuprofen and triclosan, in the spring season were 5.63 mg/l, 0.62 mg/l, 6.34 mg/l, and 0.30 mg/l, correspondingly. Their respective average concentrations during the summer season were 14.80 mg/l, 0.64 mg/l, 10.25 mg/l, and

0.21 mg/l. During the autumn season, their respective average concentrations were 28.15 mg/l, 0.35 mg/l, 7.95 mg/l and 0.62 mg/l. Moreover, the winter season recorded their average concentrations as 11.16 mg/l, 3.06 mg/l, 7.04 mg/l and <LOQ, respectively (Table 4.5). The highest sum average concentration of pharmaceuticals and personal care products was detected in the autumn season and their trend was autumn > summer > winter > spring. The sum average concentration of acetaminophen was the highest in influent samples. The overall mean concentrations of the detected pharmaceuticals and personal care products in the influent samples were descending as acetaminophen > carbamazepine > ibuprofen > triclosan (Figure 5.6). Acetaminophen and ibuprofen are analgesics/non-steroid anti-inflammatory drugs that are commonly used alone or in combination with other formulations to treat a variety of ailments (Ekinci et al., 2020). In a related study, concentrations of acetaminophen and ibuprofen, lower than the current findings, were detected in WWTPs in the North West province of South Africa (Kanama et al., 2018). Carbamazepine belongs to the anticonvulsant group of pharmaceuticals and is a prescription drug used to treat patients with seizures and bipolar disorder (Nannou et al., 2022). A lower concentration was observed for carbamazepine in wastewater influent of two sewage treatment plants in southern India (Subedi et al., 2017). Triclosan as one of the personal care products detected in this study is extensively used in a variety of consumer products because of their excellent antimicrobial and antifungal properties. Most of the consumer products such as soap, disinfectants, toothpaste, body washes and medical disinfectants, may have a concentration of triclosan ranging from 0.1 to 2% (Kanama et al., 2018). A very low concentration of triclosan than in the present study was observed by Lin et al. (2020) in wastewater influents in China. The WWTPs in this study received wastewater from industrial, domestic and hospital wastewater. Consequently, the occurrence of these pharmaceuticals and personal care products in WWTPs may be attributed to the excretion from patients suffering from pain, fever, seizures, headaches, menstrual periods, toothaches, backaches, osteoarthritis or colds and flu, as well as bipolar disorder. Moreover, the presence of triclosan reveals its constant use in households, industries or hospitals.

The average concentrations of targeted herbicides such as atrazine, metolachlor, simazine and terbuthylazine during the spring season were 0.04 mg/l, 0.01 mg/l, 0.37 mg/l and 0.03 mg/l, respectively. During the summer season, their respective mean concentrations were 0.04 mg/l, 0.05 mg/l, 0.32 mg/l and 0.08 mg/l. In the autumn season, their respective average concentrations were 0.04 mg/l, 0.03 mg/l, 0.15 mg/l and 0.04 mg/l. Moreover, in the winter season their respective average concentrations were 0.07 mg/l, 0.07 mg/l, 0.23 mg/l and 0.10 mg/l (Table 4.5). Among the herbicides detected in influent samples, the highest sum average concentration was observed during the summer season and their trend

was summer > winter > spring > autumn. The sum average concentration of simazine was the highest in influent samples and their overall mean concentrations were descending as simazine > terbuthylazine > atrazine > metolachlor (Figure 5.6). Different trends of herbicides in wastewater influent was reported in a study conducted in WWTPs located in the Baoding city of China, showing atrazine with the highest concentration among the herbicides detected (Wang et al., 2022). WWTPs receive municipal domestic wastewater from all residents, including fruit and vegetable cleaning, atmospheric sedimentation adsorption and other irregular uses (Wang et al., 2022). The dominance of these herbicides in WWTPs clearly shows their abundant use in the city, households, agricultural areas and pesticide production factories.

The average concentrations of steroid hormones such as 17-alpha-ethinyl-estradiol, estradiol, progesterone and testosterone in wastewater influents during the spring season were recorded as 31.2 mg/l, <LOQ, 0.02 mg/l and 0.01 mg/l, respectively. During the summer season their respective average concentrations were 32.77 mg/l, <LOQ, <LOQ and 0.002 mg/l. During the autumn season, their average concentrations were 37.53 mg/l, <LOQ, 0.04 mg/l and 0.03 mg/l, respectively. Moreover, their respective average concentrations in the winter season were 21.68 mg/l, <LOQ, 0.01 mg/l and <LOQ (Table 5.5). The highest sum average concentration of these contaminants was observed during the autumn season and their trend was autumn > summer > spring > winter. The sum average concentration of 17-alpha-ethinyl-estradiol was the highest in influent samples and their overall mean concentrations were descending as 17-alpha-ethinyl-estradiol > progesterone > testosterone > estradiol (Figure 5.6). A concentration of 17-alpha-ethinyl-estradiol, which was lower than the present study, was reported in WWTPs in the North West province of South Africa (Kanama et al., 2018). Another study by Manickum and John (2014) in WWTPs in Pietermaritzburg, South Africa, detected maximum concentrations of estradiol, 17-alpha-ethinyl-estradiol, progesterone, and testosterone, which were below those found in this study, except estradiol which concentration was above. Synthetic estrogens such as 17-alpha-ethinyl-estradiol (EE2) are frequently used as the main ingredient in many oral contraceptives (Kanama et al., 2018). Progesterone is a progestogen regarded as a female pregnancy hormone, while testosterone is a major androgen compound necessary for normal spermatogenesis and may decrease the risk of osteoporosis (Hu et al., 2010; Prior, 2019). The presence of these hormones in wastewater influent could be attributed to humans' high excretion rates (Kanama et al., 2018). According to Forghani et al. (2018), even without the use of hormonal drugs, every human excretes estrogens through their bodies. Women and men excrete approximately 2.3–259 and 1.6g per day of estradiol hormones, respectively, which explains their presence in WWTPs within

the study area (Forghani et al., 2018). In summation, high levels of the emerging contaminants in influent samples were recorded in the autumn season. It was mostly contributed by 17-alpha-ethinyl-estradiol, acetaminophen, which make them contaminants of concern in this area (Figure 5.6).

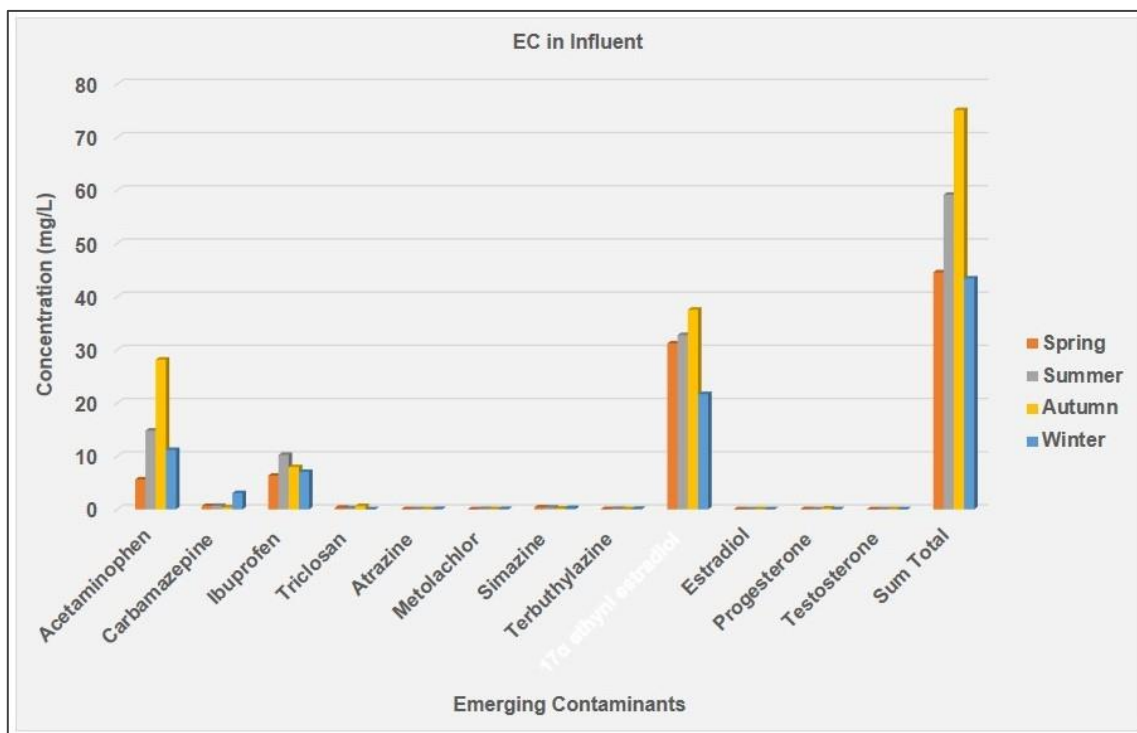


Figure 5.6 Seasonal concentrations of emerging contaminants in influents

5.4.3.2 Occurrence of emerging contaminants in effluents

The targeted compounds acetaminophen, carbamazepine, ibuprofen and triclosan showed different concentrations in effluent samples (Table 5.6). In the spring season, their respective mean concentrations were <LOQ, 0.93 mg/l, 4.30 mg/l and 0.13 mg/l. In the summer season, their mean concentrations were <LOQ, 1.68 mg/l, 3.72 mg/l and <LOQ, respectively. In the autumn season, their mean concentrations were <LOQ, 0.63 mg/l, 2.07 mg/l and <LOQ, respectively. They were also recorded as <LOQ, 0.36 mg/l, 2.19 mg/l and <LOQ in the winter season, respectively. The highest sum average concentration was observed during the summer season and their trend was summer > spring > autumn > winter (Figure 5.7). The sum average concentration of ibuprofen was the highest in effluent samples and their overall mean concentrations were descending as ibuprofen > carbamazepine > triclosan > acetaminophen. Other academics also detected ibuprofen and acetaminophen in the North West province, South Africa (Kanama et al., 2018), carbamazepine in Msunduzi, KwaZulu-Natal (Matongo et al., 2015) and triclosan in

wastewater effluents in the Eastern Cape province, South Africa (Ademoyegun, 2017). The occurrence of pharmaceuticals and personal care products in effluent samples shows poor removal efficiency of these contaminants in WWTPs.

Herbicides atrazine, metolachlor, simazine and terbuthylazine in wastewater effluents were detected and their concentrations are presented in Table 5.6. The mean concentrations of these contaminants in the spring season were 0.06 mg/l, 0.02 mg/l, 0.21 mg/l and 0.06 mg/l, respectively. In the summer season, their respective mean concentrations were 0.04 mg/l, 0.07 mg/l, 0.44 mg/l and 0.07 mg/l. In the autumn season, their mean concentrations were 0.05 mg/l, 0.06 mg/l, 0.24 mg/l and 0.02 mg/l, respectively. Moreover, in the winter season their respective mean concentrations were recorded as 0.03 mg/l, 0.02 mg/l, 4.32 mg/l and 0.02 mg/l. The highest sum average concentration was observed during the winter season and their trend was winter > summer > autumn > spring (Figure 5.7). The sum average concentration of simazine was the highest among the herbicides in effluent samples and their overall mean concentrations were descending as simazine > atrazine > metolachlor = terbuthylazine. A study conducted in Darvill in the KwaZulu-Natal province of South Africa reported average concentrations of simazine and atrazine in effluent samples (Kunene, 2019), which were lower than the findings of this study. The study by Kunene (2019) also detected terbuthylazine in effluent samples around Amanzimtoti at a concentration lower than this study.

Moreover, the concentrations of 17-alpha-ethinyl-estradiol, estradiol, progesterone and testosterone are presented in Table 5.6. In the spring season, the mean concentrations of these steroid hormones were recorded as 16.60 mg/l, <LOQ, 0.01 mg/l and <LOQ, respectively. In the summer season, their respective mean concentrations were 13.58 mg/l, <LOQ, <LOQ and <LOQ. In the autumn season, their mean concentrations were recorded as 41.40 mg/l, <LOQ, <LOQ and <LOQ, respectively. Moreover, in the winter season, only 17-alpha-ethinyl-estradiol was detected among the steroid hormones, with a mean concentration of 17.90 mg/l. The highest sum average concentration was observed during the autumn season and they were trending as autumn > winter > spring > summer (Figure 5.7). The sum average concentration of 17-alpha-ethinyl-estradiol was the highest among the steroid hormones detected samples and their overall mean concentrations were descending as 17-alpha-ethinyl-estradiol > progesterone > testosterone = estradiol. The occurrence of 17-alpha-ethinyl-estradiol and estradiol in effluent samples were also reported in a study conducted in China (Lin et al., 2020). In Pietermaritzburg, South Africa, wastewater treatment effluents also showed occurrence of progesterone and testosterone (Manickum and John, 2014). In summation, a high level of the emerging contaminants in

effluent samples was recorded in the autumn season (Figure 5.7). It was mostly contributed by 17-alpha-ethinyl-estradiol, simazine and ibuprofen. Generally, in this study the concentrations of the emerging contaminants in effluent samples can be described as reduced, not reduced or higher than the influent concentrations. Noteworthy was a negative removal of other emerging contaminants. The negative removal efficiency observed for some emerging contaminants is in accordance with preceding literature (Nannou et al., 2022; Ofrydopoulou et al., 2021). All emerging contaminants quantified at lower concentrations in the effluent than in the influent samples clearly indicated that these WWTPs had significant removal efficiency. Detail information on removal efficiency of WWTPs is presented on the next subsection of this chapter.

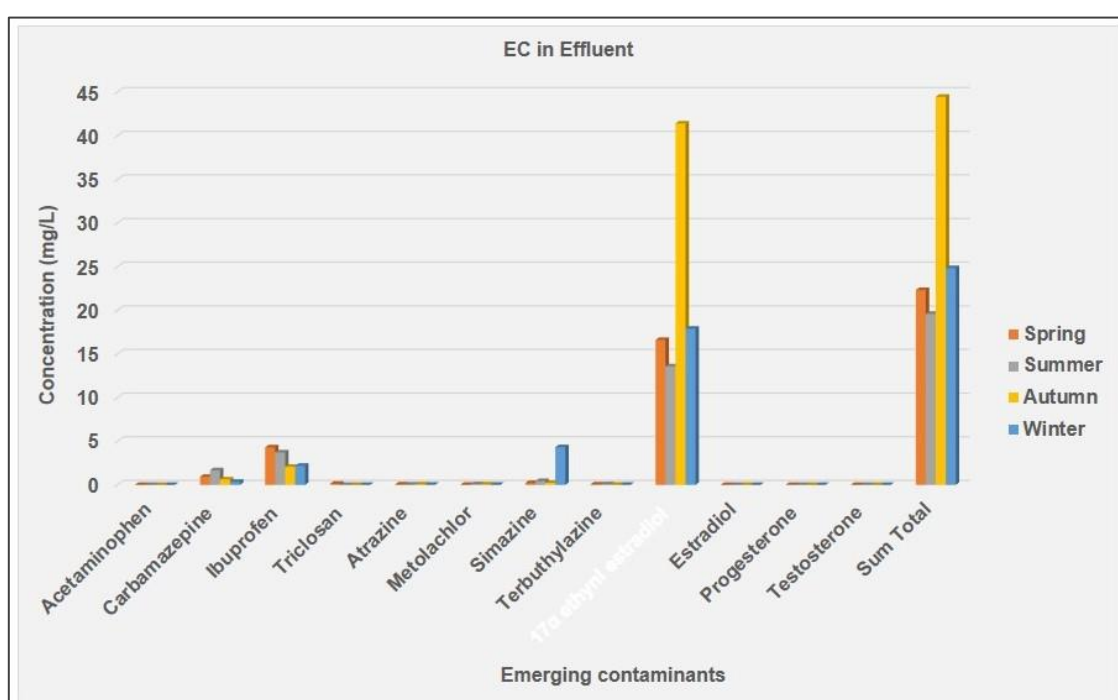


Figure 5.7 Seasonal concentrations of emerging contaminants in effluents

5.4.3.3 Removal efficiency of emerging contaminants in wastewater treatment plants

The removal rate of pollutants in wastewater can be used to assess the performance of WWTPs. Solubility, volatility, adsorption to solids and other factors in WWTPs contribute to the elimination and persistence of pharmaceuticals, personal care products, herbicides and steroid hormones (Kanama et al., 2018). The removal efficiency (%) expresses the decrease in a compound's concentration during treatment and is based on comparison of the average influent and effluent concentrations (Nannou et al., 2022). In this study, the removal

efficiency of emerging contaminants in WWTPs were rated as complete (100%), efficient (70–99%), moderate (50–69%), poor (0–49%) and negative removal (–%).

The results of removal efficiency ranged from complete to negative removal as presented in Table 5.7. There was complete removal (100%) of acetaminophen and testosterone in all seasons. Other compounds such as progesterone (in autumn/winter) and triclosan (in summer/autumn) also showed complete removal. There was a poor removal rate of compounds such as ibuprofen, simazine and terbuthylazine during the spring season. During the summer season, there was a poor removal rate of metolachlor and terbuthylazine, while in the winter season there was a poor removal rate of 17- α -ethinyl-estradiol. Furthermore, the WWTPs also showed a negative removal rate of carbamazepine in the spring, summer and autumn seasons. There was also a negative removal rate during the spring and autumn seasons for atrazine and metolachlor. The negative removal rate of terbuthylazine was only observed during the spring season, while for 17- α -ethinyl-estradiol it was observed during the autumn season. Moreover, the negative removal rate of simazine was observed during summer, autumn and winter. All emerging contaminants quantified at lower concentrations in the effluent than in the influent samples, clearly indicated that these WWTPs had a significant removal efficiency (Figure 5.8).

High removal rates of acetaminophen in WWTPs was also mentioned by other authors (Kanama et al., 2018; Nannou et al., 2022). There was also poor and negative removal rates of the majority of pesticides, which are similar to the work conducted in WWTPs of four Mediterranean river basins (Campo et al., 2013) and in Baoding city, China (Wang et al., 2022). The low or negative removal rates of emerging contaminants can be attributed to particulate matter desorption and hydrolysis, as well as the degradation and transformation of emerging contaminants during the biochemical process (Köck-Schulmeyer et al., 2013; Wang et al., 2022). According to Kortesmäki et al. (2020), non-removal and the presence of higher concentrations of some analytes in effluent than influent, may be attributed to factors such as wastewater composition, structure of analytes and conversion of the conjugated metabolites to the parent compound by enzymatic processes in the WWTPs.

The WWTPs chosen in this study were not built with the intention of removing emerging contaminants received from domestic, industrial and hospital wastewater. All of the WWTPs used primary treatment that involves removal of suspended solids by flotation, settling and screening mechanisms and secondary treatment for removal of remaining organic matter via trickling filters utilising bacteria-coated stones and bacterial-activated sludge. Therefore, it can be said that the processes employed in these treatment plants were unable to remove some of the emerging contaminants and needed improvement. Morin-Crini et al. (2022)

buttressed this finding by mentioning that in order to limit emerging contaminant pollution, tertiary treatment systems should be added in WWTPs. In South Africa, wastewater effluent is typically discharged into nearby streams, introducing pollutants into the aqueous environment. As a result, prioritising these chemicals in pollution monitoring studies is critical. Not only will this protect aquatic life but it will also preserve or sustain South Africa's water resources.

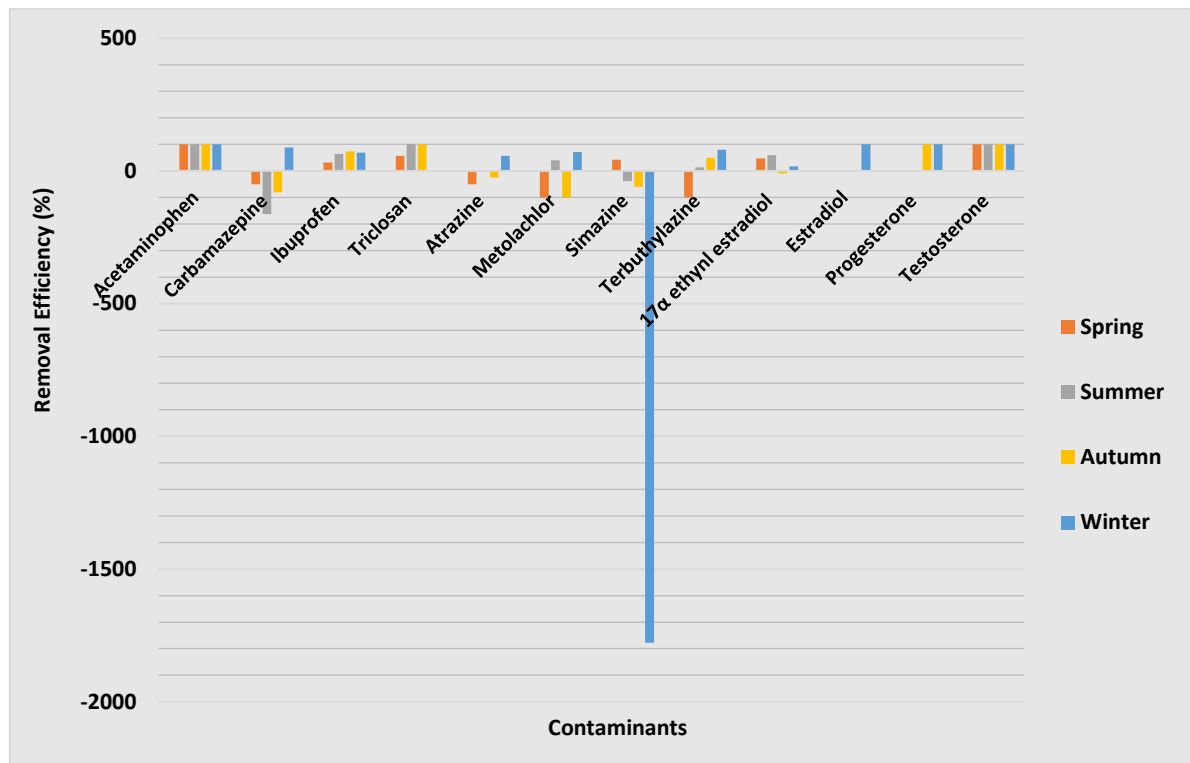


Figure 5.8 Efficiency of wastewater treatment plants in removing emerging contaminants

Table 5.5 Concentration of emerging contaminants in wastewater influents

Compound	Concentration (mg/l)											
	Spring (n=3)			Summer (n=3)			Autumn (n=3)			Winter (n=3)		
	DF	Minimum–Maximum	Mean ±SD	DF	Minimum–Maximum	Mean ±SD	DF	Minimum–Maximum	Mean ±SD	DF	Minimum–Maximum	Mean ±SD
Pharmaceuticals and personal care products												
Acetaminophen	3	2.73–8.81	5.63±3.05	3	14.00–16.10	14.8±1.14	2	<LOQ–39.20	28.15±15.62	3	5.28–18.10	11.16±6.47
Carbamazepine	3	0.16–0.95	0.62±0.41	3	0.54–0.83	0.64±0.16	3	0.25–0.48	0.35±0.12	3	0.08–8.89	3.06±5.05
Ibuprofen	3	3.32–11.10	6.34±4.17	3	8.16–14.20	10.25±3.42	3	5.10–9.46	7.95±2.47	3	5.74–7.80	7.04±1.13
Triclosan	2	<LOQ–0.31	0.3±0.02	3	0.13–0.37	0.21±0.13	3	0.49–0.76	0.62±0.14	0	<LOQ	-
Pesticides (herbicides)												
Atrazine	3	0.02–0.07	0.04±0.03	3	0.02–0.07	0.04±0.02	3	0.02–0.07	0.04±0.02	3	0.01–0.15	0.07±0.07
Metolachlor	3	0.003–0.01	0.01±0.01	3	0.02–0.09	0.05±0.04	3	0.01–0.07	0.03±0.03	3	0.002–0.21	0.07±0.12
Simazine	3	0.04–0.58	0.37±0.29	3	0.11–0.45	0.32±0.19	2	<LOQ–0.19	0.15±0.05	3	0.05–0.54	0.23±0.27
Terbutylazine	3	0.01–0.05	0.03±0.02	3	0.02–0.11	0.08±0.05	3	0.02–0.08	0.04±0.03	3	0.01–0.28	0.10±0.15
Endocrine disrupting compound (steroid hormones)												
17α ethinyl estradiol	3	19.90–47	31.2±14.10	3	23.10–46.10	32.77±11.93	3	17.30–62.10	37.53±22.71	3	6.43–32.8	21.68±13.66
Estradiol	0	<LOQ	–	0	<LOQ	–	0	<LOQ	–	0	<LOQ	–
Progesterone	2	<LOQ–0.03	0.02±0.01	0	<LOQ	–	2	<LOQ–0.05	0.04±0.01	2	<LOQ–0.02	0.01±0.02
Testosterone	3	0.006–0.009	0.01±0.001	2	<LOQ–0.003	0.002±0.001	2	<LOQ–0.04	0.03±0.01	1	<LOQ–0.01	–

Notation: LOQ=limit of quantification, DF=detection frequency, n=number of samples, ±SD=standard deviation; mg/l=milligram per litre.

Table 5.6 Concentration of emerging contaminants in wastewater effluents

Compound	Concentration (mg/l)											
	Spring (n=3)			Summer (n=3)			Autumn (n=3)			Winter (n=3)		
	DF	Minimum-Maximum	Mean $\pm$ SD	DF	Minimum-Maximum	Mean $\pm$ SD	DF	Minimum-Maximum	Mean $\pm$ SD	DF	Minimum-Maximum	Mean $\pm$ SD
Pharmaceuticals and personal care products												
Acetaminophen	0	<LOQ	–	1	<LOQ–8.7	–	1	<LOQ–11.80	–	0	<LOQ	–
Carbamazepine	3	0.51–1.20	0.93 $\pm$ 0.37	3	0.57–2.82	1.68 $\pm$ 1.13	3	0.51–0.81	0.63 $\pm$ 0.16	3	0.16–0.60	0.36 $\pm$ 0.23
Ibuprofen	3	2.86–6.22	4.30 $\pm$ 1.73	3	0.22–7.67	3.72 $\pm$ 3.74	3	0.07–4.08	2.07 $\pm$ 2.01	3	0.42–5.58	2.19 $\pm$ 2.93
Triclosan	2	<LOQ–0.17	0.13 $\pm$ 0.06	1	<LOQ–0.14	–	0	<LOQ	–	0	<LOQ	–
Pesticides (herbicides)												
Atrazine	3	0.02–0.13	0.06 $\pm$ 0.06	3	0.02–0.07	0.04 $\pm$ 0.03	3	0.01–0.11	0.05 $\pm$ 0.06	3	0.02–0.05	0.03 $\pm$ 0.01
Metolachlor	3	0.003–0.03	0.02 $\pm$ 0.01	3	0.03–0.12	0.07 $\pm$ 0.05	3	0.01–0.14	0.06 $\pm$ 0.07	3	0.003–0.03	0.02 $\pm$ 0.01
Simazine	3	0.03–0.32	0.21 $\pm$ 0.16	3	0.13–0.72	0.44 $\pm$ 0.30	3	0.05–0.38	0.24 $\pm$ 0.17	2	<LOQ–8.45	4.32 $\pm$ 5.84
Terbuthylazine	3	0.01–0.10	0.06 $\pm$ 0.04	3	0.03–0.11	0.07 $\pm$ 0.04	3	0.01–0.05	0.02 $\pm$ 0.02	3	0.01–0.02	0.02 $\pm$ 0.002
Endocrine disrupting compound (steroid hormones)												
17 α ethinyl estradiol	3	11.20–20.30	16.60 $\pm$ 4.78	3	2.64–26.40	13.58 $\pm$ 11.99	3	26.20–52.80	41.40 $\pm$ 13.70	3	14.7–20.10	17.90 $\pm$ 2.84
Estradiol	1	<LOQ–0.03	–	0	<LOQ	–	0	<LOQ	–	0	<LOQ	–
Progesterone	2	<LOQ–0.006	0.01 $\pm$ 0.001	0	<LOQ	–	0	<LOQ	–	0	<LOQ	–
Testosterone	1	<LOQ–0.003	–	1	<LOQ–0.002	–	1	<LOQ	–	0	<LOQ	–

Notation: LOQ = limit of quantification, DF = detection frequency, n = number of samples, $\pm$ SD = standard deviation, mg/l = milligram per litre

Table 5.7 Removal efficiency of emerging contaminants from wastewater treatment plants

Analytes	Spring	Summer	Autumn	Winter
Acetaminophen	100	100	100	100
Carbamazepine	-50	-163	-80	88
Ibuprofen	32	64	74	69
Triclosan	57	100	100	<LOQ
Atrazine	-50	0	-25	57
Metolachlor	-100	40	-100	71
Simazine	43	-38	-60	-1 778
Terbutylazine	-100	13	50	80
17- α -ethinyl estradiol	47	59	-10	17
Estradiol	<LOQ	<LOQ	<LOQ	100
Progesterone	<LOQ	<LOQ	100	100
Testosterone	100	100	100	100

5.4.4 Occurrence of emerging contaminants in treated drinking water

Only a few contaminants were detected in treated drinking water as shown in Table 5.8. Among the detected contaminants in treated drinking water, herbicides were the most detected contaminants. During the spring season, the average values of emerging contaminants were carbamazepine (0.13 mg/l), atrazine (0.02 mg/l), metolachlor (0.01 mg/l), terbutylazine (0.02 mg/l) and 17- α -ethinyl-estradiol (1.46 mg/l). During the summer season the average values of the majority of emerging contaminants were <LOQ, except atrazine (0.07 mg/l), metolachlor (0.05 mg/l), terbutylazine (0.09 mg/l) and 17- α -ethinyl-estradiol (0.20 mg/l). In the autumn season, average values of atrazine (0.02 mg/l), metolachlor (0.02 mg/l), terbutylazine (0.01 mg/l) and 17- α -ethinyl-estradiol (0.73 mg/l) were recorded. Moreover, the winter season also showed a majority of emerging contaminants to be below limit of quantification (<LOQ), except atrazine (0.02 mg/l), metolachlor (0.01 mg/l), terbutylazine (0.01 mg/l) and 17- α -ethinyl-estradiol (0.44 mg/l). The highest mean concentrations of detected emerging contaminants in treated drinking water were recorded during the spring season. Their sum average concentrations in treated water were trending as spring > autumn > winter > summer (Figure 5.9). The concentrations of 17- α -ethinyl-estradiol were the highest in all seasons. Their overall average concentrations were ranging as 17- α -ethinyl-estradiol > terbutylazine = atrazine > metolachlor > carbamazepine.

The situation of having pesticides as the most detected contaminants in treated drinking water around the city of Bloemfontein is comparable to the findings of other researchers who also reported the pesticides atrazine and terbutylazine as the most detected contaminants

in treated drinking water (Machado et al., 2016; Odendaal et al., 2015). Van Zijl et al. (2017) reported the occurrence of 17-alpha-ethinyl-estradiol in treated drinking water around Pretoria, South Africa, which is comparable to the findings of this study. The high concentrations of herbicides in treated drinking water may be attributed to the use of herbicides to control weeds in dams used as a source of water in water treatment plants. Rivers that recharge these dams may be polluted by herbicides and 17-alpha-ethinyl-estradiol as they frequently receive wastewater effluents. The high detection of atrazine in water sources may also be connected to their nature of being persistent. Herbicides such as atrazine are persistent in soil and their transport to water, making it the most commonly detected pesticide in water sources (Almberg et al., 2018). Additionally, the occurrence of these compounds in treated drinking water reveals the incapability of the methods applied in selected water treatment plants, which include abstraction, macro/micro sieving, coagulation, flocculation, sedimentation, filtration and disinfection in removing them.

Currently, in South Africa and other parts of the world, there are no drinking water threshold limits or standards for emerging contaminants except for herbicides. Therefore, as shown in Table 5.9, the mean concentrations of atrazine and terbuthylazine in this study were above the South African acceptable limit (Department of Water Affairs and Forestry, 1996; Horak et al., 2021) and their corresponding WHO guidelines (Hamilton et al., 2003) in all seasons, while mean concentrations of metolachlor only exceeded those tolerable limits in the summer and autumns seasons. The outcomes of this study indicated a serious health concern for the population of Bloemfontein. Chronic pesticide exposure through water ingestion can mimic human hormones, lowering immunity, disrupting hormone balance, triggering reproductive issues, posing carcinogenic effects and lowering intelligence, particularly in children at the body development stage (Syafudin et al., 2021). In summation, the sum concentrations of emerging contaminants in treated drinking water were observed in the spring season (Figure 5.9). It was mostly contributed by 17-alpha-ethinyl-estradiol, terbuthylazine and atrazine. These compounds should be prioritised in pollution management campaigns. Moreover, water treatment managers should prioritise them during their treatment processes.

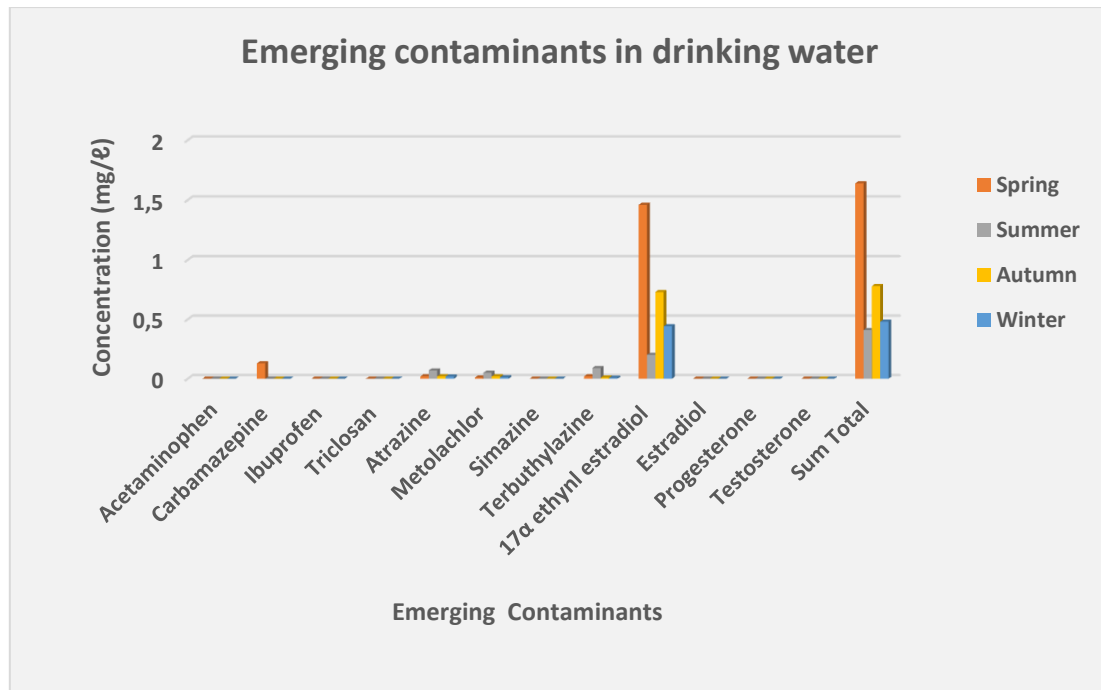


Figure 5.9 Seasonal concentrations of emerging contaminants in treated drinking water

Table 5.8 Concentration of emerging contaminants in treated drinking water

Compound	Concentration (mg/ℓ)											
	Spring (n=2)			Summer (n=2)			Autumn (n=2)			Winter (n=2)		
	DF	Minimum–Maximum	Mean/ ±SD	DF	Minimum–Maximum	Mean/ ±SD	DF	Minimum–Maximum	Mean/ ±SD	DF	Minimum–Maximum	Mean/ ±SD
Pharmaceuticals and personal care products												
Acetaminophen	1	<LOQ–0.10	–	0	<LOQ	–	0	–	–	1	<LOQ–0.28	–
Carbamazepine	2	0.01–0.25	0.13±0.17	0	<LOQ	–	0	<LOQ	–	0	<LOQ	–
Ibuprofen	1	<LOQ–0.01	–	0	<LOQ	–	0	<LOQ	–	0	<LOQ	–
Triclosan	0	<LOQ	–	0	<LOQ	–	0	<LOQ	–	0	<LOQ	–
Pesticides (herbicide)												
Atrazine	2	0.015–0.019	0.02±0.003	2	0.02–0.12	0.07±0.07	2	0.01–0.03	0.02±0.01	2	0.008–0.03 0.002–0.02	0.02±0.01
Metolachlor	2	0.009–0.01	0.01±0.001	2	0.01–0.09	0.05±0.06	2	0.004–0.04	0.02±0.02	2	3	0.01±0.01
Simazine	1	<LOQ–0.03	–	1	<LOQ–0.04	–	0	<LOQ	–	0	<LOQ	–
Terbuthylazine	2	0.019–0.02	0.02±0.001	3	0.02–0.16	0.09±0.10	2	0.004–0.02	0.01±0.01	2	0.006–0.01	0.01±0.003
Endocrine disrupting compound (steroid hormones)												
17α ethinyl estradiol	2	0.15–2.78	1.46±1.86	2	0.14–0.26	0.2±0.08	2	0.42–1.04	0.73±0.44	2	0.16–0.73	0.44±0.40
Estradiol	0	<LOQ	–	0	<LOQ	–	0	<LOQ	–	0	<LOQ	–
Progesterone	0	<LOQ	–	0	<LOQ	–	0	<LOQ	–	0	<LOQ	–
Testosterone	0	<LOQ	–	0	<LOQ	–	0	<LOQ	–	0	<LOQ	–

Notation: LOQ=limit of quantification, DF=detection frequency, n=number of samples, ±SD=standard deviation, mg/ℓ=milligram per millilitre.

Table 5.9 Concentration of pesticides in treated drinking water with guidelines values

Contaminant	Spring (mg/ℓ)	Summer (mg/ℓ)	Autumn (mg/ℓ)	Winter (mg/ℓ)	South Africa (mg/ℓ)	WHO (mg/ℓ)
Atrazine	0.02	0.07	0.02	0.02	0.01	0.002
Metolachlor	0.01	0.05	0.02	0.01	–	0.01
Simazine	0.00	0.00	0.00	0.00	–	0.002
Terbuthylazine	0.02	0.09	0.01	0.01	–	0.007

Notation: WHO=World Health Organisation.

Source: Department of Water Affairs and Forestry (1996); Hamilton et al. (2003).

5.5 Conclusion

The chapter aimed at investigating and monitoring emerging contaminants in various water sources around Bloemfontein. Examining the occurrence of emerging contaminants for the first time in water sources around Bloemfontein brings to an end the dearth of data on emerging contaminant pollution. Both qualitative and quantitative analysis proved that water sources around Bloemfontein are vulnerable to emerging contaminant pollution, which may lead to negative environmental and health risks. The qualitative analysis revealed the majority of unforeseen and unknown analytes that may also contribute to adverse health risks to aquatic and human life. Notably, pesticides (herbicides) and pharmaceuticals (stimulants) were the leading class of emerging contaminants. Considering that the numbers of emerging contaminants are always increasing, qualitative studies should be prioritised in pollution monitoring and risk assessment studies of emerging pollutants. Among the targeted contaminants, the quantitative analysis revealed 17-alpha-ethinyl-estradiol as the contaminant with the highest concentrations in all water sources during all seasons. When compared to the national and international drinking water standards, the majority of pesticides exceeded their acceptable limits, which indicates a serious health concern for the Bloemfontein community. Prioritising these substances in contamination monitoring studies is critical, not only in shielding aquatic life and human health, but also in preserving and sustaining South Africa's water resources. Moreover, WWTPs around Bloemfontein are unable to remove emerging contaminants, in particular pesticides. Wastewater effluent is typically discharged into nearby streams, introducing pollutants into the aqueous environment. Therefore, it can be concluded that the release of wastewater effluent to nearby streams will cause pollution and eventually harmfully upset the aquatic species and population health. The outcomes of this study may be relevant for the prioritisation of hazardous substances in order to address suitable monitoring campaigns and any necessary countermeasures to be adopted for environmental protection and sustainability of water resources. Furthermore, the data could also facilitate the need to develop regulations aimed at reducing the spread of emerging contaminants in water sources around Bloemfontein and other parts of the province.

Chapter 6

ENVIRONMENTAL HEALTH RISK ASSESSMENT OF EMERGING CONTAMINANTS IN WATER SOURCES

Exposure to emerging contaminants in water sources can inflict significant risks to both aquatic life and people's health. This chapter focuses solely on risks of emerging contaminants in water sources. It covers the individual and mixture environmental risks of emerging contaminants in rivers, dams or reservoirs, wastewater effluents and treated drinking water. Moreover, the non-carcinogenic and carcinogenic risks stemming from exposure to pesticides in selected water sources are also presented and discussed.

6.1 Introduction

The most crucial resource on earth is water and it represents 70% of the globe. It is a necessity for the existence of all living organisms, animals and human beings (Fawell and Nieuwenhuijsen, 2003). Water offers sustenance and enables the circulation of oxygen within living cells such as mitochondria. It also serves as a habitation for aquatic organisms and a reproduction home for some terrestrial organisms (Bwire et al., 2020). Water resources are crucial in developing any area as they serve as a major source of potable, agricultural, and industrial water (Babuji et al., 2023). According to Tufenkji et al. (2002), continuous, safe and clean water supplies are requirements for a decent and healthy living. However, the increase in the universal inhabitants (to 8.0 billion as of 2022), manufacturing activities (pharma-ceuticals) and the usage of chemical goods in households such as plastics, cosmetic products, toothpaste and toys, tourism, industrial manufacturing, agricultural activities, as well as in human and animal health care, are producing considerable volumes of chemical waste that pollute our surroundings (Braton-Maclaren et al., 2022; Torres-Padron et al., 2020).

Pollution caused by chemicals is regarded as one of the world's utmost threats to aquatic life and public health (Braton-Maclaren et al., 2022) and water as an indispensable resource for life in the world is most vulnerable to chemical pollutions, including emerging contaminants (Brack et al., 2019). A complex mixture of emerging contaminants occurs in the aquatic environment, posing a significant threat to aquatic species and the health of organisms that consume these contaminants (Ghosh et al., 2023). Pesticides, pharmaceuticals, steroid hormones and personal care products are among the contaminants that threaten the quality

of freshwater (Miraji et al., 2016) and their presence in water sources may make it unfit for daily use and consumption (Babuji et al., 2023; Li et al., 2023a). They also adversely affect aquatic ecosystems and public health due to their likelihood to trigger serious implications (Morin-Crini et al., 2022). The risk of emerging contaminant exposures are well documented with adverse effects such as endocrine disruption, immunotoxicity, neurological disorders, reductions in fertility, spontaneous abortions, birth defects, poisoning of genes, sexual organs annoyance, resistance of antibiotics, and congenital disorders even at low concentration (Ramirez-Malule et al., 2020). Moving up the food chain, chemical pollutants cause biomagnification, endangering aquatic organisms, wildlife animals that depend on water and human health as well as drinking water supplies, recreation and fishing (Mercanti et al., 2023).

On a global scale (Bagnis et al., 2020; Castiglioni et al., 2020; Kasprzyk-Hordern et al., 2021; Ogunbanwo et al., 2022; Okoye et al., 2022; Styszko et al., 2021) and in South Africa (Archer et al., 2021, 2023; Madikizela et al., 2020, 2022; Malisa et al., 2019; Mhuka et al., 2020; Wilkinson et al., 2022;), the occurrence of various emerging contaminants in water sources has received extensive research. However, the number of emerging contaminants in water resources increases year after year and their transformation products are frequently more harmful than the parent compounds (Wilkinson et al., 2022), which is an ecological and a public health concern in the country. Furthermore, regulation of emerging contaminants in wastewater effluents and fresh water, as well as studies focusing on their potential ecological and public health risks, remain limited in South Africa (Archer et al., 2023).

The growing number of chemicals detected in various water sources and lack of regulations, emphasises the need of ongoing identification and evaluation of their loads in water sources as well as to better understand their potential risks for environmental sustainability and protection of aquatic species and human health. In South Africa, particularly in the Free State province, which is the host of the city of Bloemfontein, there is no published work on risks associated with emerging contaminants. In this context, this chapter specifically assesses the environmental health risks emanating from exposure to emerging contaminants in various water sources. To achieve this aim, emphasis is first placed on assessing individual and a mixture of environmental risks of selected contaminants; and second, human health risk by attending to carcinogenic and non-carcinogenic effects of selected herbicides in wastewater effluent, rivers, dams and reservoirs, and treated drinking water around Bloemfontein, South Africa. The findings of this study may improve the knowledge of the occurrence and risks associated with exposure to emerging contaminants.

It may also aid in the development of environmental quality standards for regulatory and environmental sustainability purposes.

6.2 Environmental risk assessment of emerging contaminants in water sources

6.2.1 Individual risk assessment

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

Where the mean effective values (EC_{50}) were not available, the median LC_{50} were used. Even in cases where NOEC were unobtainable, the lowest observed effect concentration (LOEC) values were used. Moreover, in the incident of data gaps, different species and endpoints were selected. In this study, a few contaminants had no toxicity data. For acute toxicity, there was no toxicity data for terbuthylazine on fish. For chronic toxicity, the data for terbuthylazine (algae), 17-alpha-ethinyl-estradiol (algae and daphnids), estradiol (algae and daphnids), testosterone (algae, daphnids and fish) and progesterone (algae and daphnids) were not available. The reason why there is a lack of chronic toxicity data for many of these compounds is due to the fact that most of these compounds have been only recently considered as emerging contaminants. Thus, this is a crucial disadvantage for the determination of the risk assessment, since chronic effects are much more likely to be induced rather than acute ones (Liu et al., 2023a; Nannou et al., 2015, 2022; Pei et al., 2022). The risk assessment covered four seasons of the year (spring, summer, autumn and winter) and the results are presented and discussed in the following sections.

6.2.1.1 Environmental risk assessment of individual emerging contaminant in rivers

The environmental risk assessment of emerging contaminants in rivers, based on acute toxicity on sensitive aquatic species, were assessed in all seasons as presented in Table 6.1. Generally, for acute toxicity, the risks ranged from medium ($0.1 < RQ < 1$) to high ($RQ \geq 1$) risks. During the spring season, carbamazepine, ibuprofen, triclosan, atrazine, simazine, terbuthylazine, 17-alpha-ethinyl-estradiol, and estradiol posed high risks on algae. Regarding *Daphnia*, acetaminophen, carbamazepine, ibuprofen, triclosan, atrazine, simazine, terbuthylazine, 17-alpha-ethinyl-estradiol and estradiol posed high risks. For fish, carbamazepine, ibuprofen, triclosan, atrazine, metolachlor, simazine, terbuthylazine, 17-alpha-ethinyl-estradiol and estradiol posed high risks. During the summer season, carbamazepine, ibuprofen, atrazine, simazine, terbuthylazine and 17-alpha-ethinyl-estradiol posed high environmental risks on algae. Carbamazepine, ibuprofen, atrazine, metolachlor, simazine, terbuthylazine and 17-alpha-ethinyl-estradiol posed high ecological risks on daphnids. Carbamazepine, ibuprofen, atrazine, metolachlor, simazine, terbuthylazine and 17-alpha-ethinyl-estradiol posed high environmental risks on fish. During the autumn season, carbamazepine, ibuprofen, atrazine, simazine, terbuthylazine and 17-alpha-ethinyl-estradiol posed high acute risks on algae. For daphnids, carbamazepine, ibuprofen, atrazine, simazine, and 17-alpha-ethinyl-estradiol showed high acute ecological risks. It was carbamazepine, ibuprofen, atrazine, metolachlor, simazine, terbuthylazine and 17-alpha-ethinyl-estradiol that posed high acute risks on fish. Furthermore, during the winter season, high acute environmental risks on algae, daphnids and fish were posed by carbamazepine, ibuprofen, atrazine, metolachlor, simazine, terbuthylazine and 17-alpha-ethinyl-estradiol.

The chronic toxicity risk results of emerging contaminants on sensitive aquatic species are presented in Table 6.1. For chronic toxicity, the risks ranged from low ($RQ \leq 0.1$) to high ($RQ \geq 1$). During the spring season, algae were likely to suffer high risks as a result of exposure to carbamazepine, ibuprofen, triclosan, atrazine and simazine. Daphnids were likely to suffer high risks from exposure to carbamazepine, ibuprofen, atrazine and simazine. Fish were likely to suffer high risks from exposure to ibuprofen, simazine, terbuthylazine, 17-alpha-ethinyl-estradiol and estradiol. In the summer season, algae were likely to suffer high risks from exposure to ibuprofen, atrazine, metolachlor and simazine. Daphnids were likely to suffer high risks from exposure to carbamazepine, ibuprofen, atrazine, simazine and terbuthylazine. Fish were likely to suffer high chronic risks from exposure to ibuprofen, simazine, terbuthylazine and 17-alpha-ethinyl-estradiol. During the autumn season, algae were more likely to suffer high chronic risks from exposure to carbamazepine, ibuprofen, atrazine and simazine. Daphnids were more likely to suffer high risks from exposure to

carbamazepine, ibuprofen, atrazine, simazine and 17-alpha-ethinyl-estradiol, while fish were more likely to suffer high risks from ibuprofen, atrazine, simazine and 17-alpha-ethinyl-estradiol. Moreover, during the winter season, algae and daphnids were likely to suffer high risks from exposure to carbamazepine, ibuprofen, atrazine, metolachlor and simazine, while fish were more likely to suffer high chronic risks from exposure to ibuprofen, metolachlor, terbuthylazine and 17-alpha-ethinyl-estradiol.

From the results of individual environmental risks in rivers, high environmental risks were generally posed by acetaminophen, carbamazepine, ibuprofen, triclosan, atrazine, simazine, terbuthylazine, metolachlor, 17-alpha-ethinyl-estradiol and estradiol. The majority (83%) of targeted emerging contaminants showed the possibilities of high acute risks, while 75% of them showed high chronic ecological risks. Most notable for acute risks were the high risks of carbamazepine, ibuprofen, atrazine, simazine and 17-alpha-ethinyl-estradiol which occurred on all species in all seasons, while for chronic risks, only ibuprofen and simazine showed high risks on all species in all seasons. The assessed high environmental risks of carbamazepine, ibuprofen, triclosan, terbuthylazine and 17-alpha-ethinyl-estradiol in this study were in good accordance with other studies around the world (Čelić et al., 2021; Duarte et al., 2022; Grung et al., 2008; Guruge et al., 2019; Hernando et al., 2006; Jiang et al., 2015; Nannou et al., 2015). The observation of high environmental risks in river water clearly indicated that the rivers were not safe and these contaminants may have improper environmental health effects to the ecosystem and surrounding communities that may be exposed to rivers contaminated by these compounds. Domestic animals such as donkeys, cows, sheep and goats seen during site visits drinking water from some of the rivers may also suffer some health effects. Most concerning in this study is the high risks of carbamazepine, ibuprofen, atrazine, simazine and 17-alpha-ethinyl-estradiol which were observed on all species in all seasons. There is evidence that ibuprofen entering the body for a long time may lead to kidney failure (Wu et al., 2020). Wanda et al. (2017) stated that carbamazepine may disrupt the production of red blood cells, white blood cells, and platelets in humans and animals, even at lower concentrations. Atrazine and simazine are of serious concern in human health as they may gather in the human cell membrane and interferes with normal body functioning (Syafrudin et al., 2021). Exposure to these triazines, herbicides may lead to irritation, carcinogenic and teratogenic effects (Sathiakumar et al., 2011). Moreover, exposure to low levels of 17-alpha-ethinyl-estradiol may expand fish livers and affect the sexual characteristics of male fish in surface water (Ngqwala and Muchesa, 2020).

Table 6.1 Acute and chronic risks of individual contaminants in rivers

Contaminant	Species	Spring		Summer		Autumn		Winter	
		HQ mean	Risk	HQ mean	Risk	HQ mean	Risk	HQ mean	Risk
Acute toxicity									
Acetaminophen	Algae	0.92	Medium	–	–	–	–	–	–
	Daphnids	13	High	–	–	–	–	–	–
	Fish	0.32	Medium	–	–	–	–	–	–
Carbamazepine	Algae	15.8	High	22	High	7.81	High	9.81	High
	Daphnids	95	High	117	High	41.67	High	48.74	High
	Fish	16.3	High	20	High	7.14	High	8.76	High
Ibuprofen	Algae	16.4	High	4	High	2.92	High	6.98	High
	Daphnids	69 375	High	38 667	High	30 667	High	68 750	High
	Fish	22.2	High	12	High	9.2	High	22	High
Triclosan	Algae	160.7	High	–	–	–	–	–	–
	Daphnids	230.7	High	–	–	–	–	–	–
	Fish	34.6	High	–	–	–	–	–	–
Atrazine	Algae	508.47	High	833	High	11 695	High	1 356	High
	Daphnids	4.35	High	7	High	100	High	11.59	High
	Fish	6.67	High	11	High	153	High	17.78	High
Metolachlor	Algae	0.17	Medium	1	High	0.35	Medium	2	High
	Daphnids	0.5	Medium	3	High	0.83	Medium	5	High
	Fish	2.5	High	15	High	5.13	High	31	High
Simazine	Algae	45 500	High	26 000	High	17 250	High	9 250	High
	Daphnids	1 820	High	1 040	High	627	High	336	High
	Fish	202	High	104	High	77	High	41	High
Terbutylazine	Algae	3 000	High	4 000	High	500	High	2 500	High
	Daphnids	1.54	High	2	High	0.26	Medium	1.27	High
	Fish	16.67	High	20	High	2.78	High	14	High
17α-ethinyl-estradiol	Algae	16 000 000	High	97 375 000	High	39 437 500	High	15 425 000	High
	Daphnids	10 666 666	High	6 491 667	High	26 291 667	High	10 283 333	High
	Fish	6 400 000	High	3 895 000	High	15 775 000	High	617 000	High
Estradiol	Algae	43 750	High	–	–	–	–	–	–
	Daphnids	2 333	High	–	–	–	–	–	–
	Fish	2 333	High	–	–	–	–	–	–
Progesterone	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	–	–	–	–	–	–	–	–
Testosterone	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	–	–	–	–	–	–	–	–
Chronic toxicity									
Acetaminophen	Algae	0.26	Medium	–	–	–	–	–	–
	Daphnids	1	Medium	–	–	–	–	–	–
	Fish	0.1	Medium	–	–	–	–	–	–
Carbamazepine	Algae	5.7	High	0.7	Medium	2.5	High	3	High
	Daphnids	1 140	High	140	High	500	High	620	High

Contaminant	Species	Spring		Summer		Autumn		Winter	
		HQ mean	Risk	HQ mean	Risk	HQ mean	Risk	HQ mean	Risk
Ibuprofen	Fish	0.2	Medium	0.14	Medium	0.1	Medium	0.1	Medium
	Algae	22 200	High	11 600	High	9 200	High	22 000	High
	Daphnids	111	High	47	High	36.8	High	89	High
	Fish	22 200	High	464	High	9 200	High	22 000	High
Triclosan	Algae	450	High	–	–	–	–	–	–
	Daphnids	0.02	Low	–	–	–	–	–	–
	Fish	0.01	Low	–	–	–	–	–	–
Atrazine	Algae	30	High	50	High	690	High	80	High
	Daphnids	15	High	25	High	345	High	40	High
	Fish	0.15	Medium	0.25	Medium	3.45	High	0.4	Medium
Metolachlor	Algae	0.33	Medium	2	High	0.67	Medium	4	High
	Daphnids	0.17	Medium	1	Medium	0.33	Medium	2	High
	Fish	0.1	Medium	0.6	Medium	0.2	Medium	1.2	High
Simazine	Algae	303	High	173	High	115	High	62	High
	Daphnids	182	High	87	High	57.5	High	31	High
	Fish	26	High	15	High	9.86	High	5	High
Terbuthylazine	Algae	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
	Daphnids	14.28	Medium	19	High	2.38	High	0.001	Low
	Fish	46.15	High	6	High	0.77	Medium	4	High
17 α -ethinyl-estradiol	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	4 060	High	2 597	High	10 517	High	4 113	High
Estradiol	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	1.66	High	–	–	–	–	–	–
Progesterone	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	–	–	–	–	–	–	–	–
Testosterone	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	–	–	–	–	–	–	–	–

Notation: HQ = Hazard quotient

6.2.1.2 Environmental risk assessment of individual emerging contaminant in dams

The environmental risks of emerging contaminants in dams are presented in Table 6.2. The risk assessment was based on acute and chronic toxicity on most sensitive aquatic species. For acute toxicity, their risks in dams/reservoirs ranged from low ($RQ \leq 0.1$) to high environmental risks ($RQ \geq 1$). During the spring season, acute toxicity results showed that exposure to carbamazepine, atrazine, simazine, terbuthylazine and 17-alpha-ethinyl-estradiol may possibly pose high risks to algae. Exposure to acetaminophen, carbamazepine, ibuprofen, atrazine, simazine and 17-alpha-ethinyl-estradiol showed possibilities of high risks on daphnids. Exposure to carbamazepine, ibuprofen, atrazine,

metolachlor, simazine, terbutylazine and 17-alpha-ethinyl-estradiol showed possibilities of high risk on fish. During the summer season, the risks results revealed that exposure to carbamazepine, atrazine, simazine, terbutylazine and 17-alpha-ethinyl-estradiol may cause high acute risks on algae. For daphnids, the results showed possibilities of high risks from exposure to carbamazepine, atrazine, metolachlor, simazine, terbutylazine and 17-alpha-ethinyl-estradiol. For fish, the results showed high acute risks from exposure to carbamazepine, metolachlor, simazine, terbutylazine and 17-alpha-ethinyl-estradiol. During the autumn season, the possibilities of high acute risks on algae were posed by carbamazepine, atrazine, simazine, terbutylazine and 17-alpha-ethinyl-estradiol. For daphnids, only carbamazepine, atrazine, simazine and 17-alpha-ethinyl-estradiol showed the possibilities of high risks while exposure to carbamazepine, atrazine, metolachlor, simazine, terbutylazine and 17-alpha-ethinyl-estradiol showed possibilities of high risks on fish. Moreover, acute toxicity results during the winter season showed the possibilities of carbamazepine, atrazine, simazine, terbutylazine and 17-alpha-ethinyl-estradiol to pose high risks on fish. For daphnids, carbamazepine, atrazine, simazine and 17-alpha-ethinyl-estradiol showed the possibilities of high risks while on fish the possibilities of high risks were likely to occur as a result of exposure to carbamazepine, atrazine, metolachlor, simazine, terbutylazine and 17-alpha-ethinyl-estradiol.

The results of chronic toxicity on most sensitive aquatic species are also presented in Table 6.2. The environmental risks of emerging contaminants based on chronic toxicity were also ranging from low ($RQ \leq 0.1$) to high risks ($RQ \geq 1$). During the spring season, exposure to carbamazepine, ibuprofen, atrazine and simazine showed possibilities of high risks on algae. For daphnids, exposure to carbamazepine, ibuprofen, atrazine and simazine showed the possibilities of high risks. For fish, exposure to ibuprofen, simazine, terbutylazine and 17-alpha-ethinyl-estradiol showed the possibilities of high risks. During the summer season, exposure to carbamazepine, atrazine and simazine showed possibilities of high risks on algae. Exposure to carbamazepine, atrazine, simazine and terbutylazine showed the possibilities of high risks on daphnids, while exposure to simazine, terbutylazine and 17-alpha-ethinyl-estradiol showed possibilities of high risks on fish. During the autumn season, there were possibilities of high risks on algae as a result of exposure to ibuprofen, atrazine and simazine. Exposure to carbamazepine, atrazine, simazine and terbutylazine showed the possibilities of high risks on daphnids while exposure to ibuprofen, simazine, terbutylazine and 17-alpha-ethinyl-estradiol posed high risks on fish. During the winter season, there were possibilities of high risks on algae from exposure to atrazine and simazine. Exposure to carbamazepine, atrazine, simazine and terbutylazine posed high

risks on daphnids. Moreover, exposure to terbutylazine, simazine and 17-alpha-ethinyl-estradiol posed high risks on fish.

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

Table 6.2 Acute and chronic risks of individual contaminant in dams

Contaminant	Species	Spring		Summer		Autumn		Winter	
		HQ mean	Risk	HQ mean	Risk	HQ mean	Risk	HQ mean	Risk
Acute toxicity									
Acetaminophen	Algae	0.52	Medium	–	–	–	–	–	–
	Daphnids	7.6	High	–	–	–	–	–	–
	Fish	0.2	Medium	–	–	–	–	–	–
Carbamazepine	Algae	8	High	3.75	High	2.5	High	1.9	High
	Daphnids	48.3	High	20	High	12.5	High	9	High
	Fish	8.3	High	3.43	High	2.26	High	1.67	High
Ibuprofen	Algae	0.9	Medium	–	–	0.06	Low	–	–
	Daphnids	9 375	High	–	–	625	High	–	–
	Fish	3	High	–	–	0.2	Medium	–	–
Triclosan	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	–	–	–	–	–	–	–	–
Atrazine	Algae	338.98	High	500	High	169	High	678	High
	Daphnids	2.9	High	4.29	High	1.45	High	6	High
	Fish	4.44	High	0.6	Medium	2.22	High	9	High
Metolachlor	Algae	0.17	Medium	0.5	Medium	0.18	Medium	0.18	Medium
	Daphnids	0.5	Medium	1.5	High	0.43	Medium	0.43	Medium
	Fish	2.5	High	7.5	High	2.53	High	3	High

Contaminant	Species	Spring		Summer		Autumn		Winter	
		HQ mean	Risk	HQ mean	Risk	HQ mean	Risk	HQ mean	Risk
Simazine	Algae	2 500	High	3 250	High	3 000	High	3 500	High
	Daphnids	100	High	130	High	109	High	127	High
	Fish	11.11	High	14.44	High	13.33	High	16	High
Terbutylazine	Algae	1 500	High	2 500	High	500	High	1 000	High
	Daphnids	0.77	Medium	1.25	High	0.25	Medium	0.51	Medium
	Fish	8.33	High	12.5	High	2.56	High	6	High
17 α -ethinyl-estradiol	Algae	4 587 500	High	2 287 500	High	8 625 000	High	3 475 000	High
	Daphnids	3 058 333	High	1 525 000	High	5 750 000	High	231 667	High
	Fish	1 835 000	High	91 500	High	3 450 000	High	1 390 000	High
Estradiol	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	–	–	–	–	–	–	–	–
Progesterone	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	–	–	–	–	–	–	–	–
Testosterone	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	–	–	–	–	–	–	–	–

Chronic toxicity

Acetaminophen	Algae	0.1	Medium	–	–	–	–	–	–
	Daphnids	0.6	Medium	–	–	–	–	–	–
	Fish	0.07	Low	–	–	–	–	–	–
Carbamazepine	Algae	2.9	High	1.2	High	0.8	Medium	0.6	Medium
	Daphnids	580	High	240	High	16	High	120	High
	Fish	0.1	Medium	0.05	Low	0.03	Low	0.024	Low
Ibuprofen	Algae	3 000	High	–	–	200	High	–	–
	Daphnids	15	High	–	–	0.8	Medium	–	–
	Fish	3 000	High	–	–	2	High	–	–
Triclosan	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	–	–	–	–	–	–	–	–
Atrazine	Algae	20	High	3	High	10	High	40	High
	Daphnids	10	High	15	High	5	High	20	High
	Fish	0.1	Medium	0.15	Medium	0.005	Low	0.2	Medium
Metolachlor	Algae	0.33	Medium	1	Medium	0.33	Medium	0.33	Medium
	Daphnids	0.17	Medium	0.5	Medium	0.17	Medium	0.17	Medium
	Fish	0.1	Medium	0.3	Medium	0.1	Medium	0.10	Medium
Simazine	Algae	16.67	High	22	High	20	High	23	High
	Daphnids	10	High	11	High	10	High	100	High
	Fish	1.43	High	2	High	1.71	High	117	High
Terbutylazine	Algae	–	–	–	–	–	–	–	–
	Daphnids	0.71	Medium	12	High	2.38	High	4.76	High
	Fish	2.3	High	4	High	0.77	Medium	1.54	High
17- α -ethinyl-estradiol	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–

Contaminant	Species	Spring		Summer		Autumn		Winter	
		HQ mean	Risk	HQ mean	Risk	HQ mean	Risk	HQ mean	Risk
Estradiol	Fish	1 223	High	610	High	1 150	High	927	High
	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	–	–	–	–	–	–	–	–
Progesterone	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	–	–	–	–	–	–	–	–
	Algae	–	–	–	–	–	–	–	–
Testosterone	Daphnids	–	–	–	–	–	–	–	–
	Fish	–	–	–	–	–	–	–	–
	Algae	–	–	–	–	–	–	–	–

Notation: HQ = hazard quotient

6.2.1.3 Environmental risk assessment of individual emerging contaminants in wastewater effluents

As presented in Table 6.3, the risk assessment of emerging contaminants in effluents was based on acute and chronic toxicity on most sensitive aquatic species. Their risk assessment results were generally ranging from medium ($0.1 < RQ < 1$) to high ($RQ \geq 1$). During the spring season, the high acute risks on algae were presented by acetaminophen, ibuprofen, triclosan, atrazine, simazine, terbuthylazine, estradiol, 17-alpha-ethinyl-estradiol and progesterone. On daphnids, the high risks were presented by acetaminophen, ibuprofen, triclosan, atrazine, simazine, terbuthylazine, estradiol, 17-alpha-ethinyl-estradiol and progesterone. On fish, the high risks were presented by acetaminophen, ibuprofen, triclosan, atrazine, metolachlor, simazine, terbuthylazine, estradiol and 17-alpha-ethinyl-estradiol. During the summer season, high acute risks on algae were presented by carbamazepine, ibuprofen, atrazine, metolachlor, simazine, terbuthylazine and 17-alpha-ethinyl-estradiol. On daphnids, the high risks were presented by carbamazepine, ibuprofen, atrazine, metolachlor, simazine, terbuthylazine and 17-alpha-ethinyl-estradiol. On fish, the high risks were posed by carbamazepine, ibuprofen, atrazine, metolachlor, simazine, terbuthylazine and 17-alpha-ethinyl-estradiol. During the autumn season, the high acute risks on algae were presented by carbamazepine, ibuprofen, atrazine, metolachlor, simazine, terbuthylazine and 17-alpha-ethinyl-estradiol. On daphnids, the high risks were presented by carbamazepine, ibuprofen, atrazine, atrazine, metolachlor, simazine and 17-alpha-ethinyl-estradiol. On fish, the high risks were presented by carbamazepine, ibuprofen, atrazine, metolachlor, simazine, terbuthylazine and 17-alpha-ethinyl-estradiol. Moreover, the high acute risks on algae during the winter season were presented by carbamazepine, ibuprofen, atrazine, simazine, terbuthylazine, and 17-alpha-ethinyl-estradiol. On daphnids, the high risks were presented by carbamazepine, ibuprofen, atrazine, metolachlor, simazine

and 17- α -ethinyl-estradiol, while on fish, they were presented by carbamazepine, ibuprofen, atrazine, metolachlor, simazine, terbuthylazine and 17- α -ethinyl-estradiol.

Moreover, the results of chronic risks on most sensitive aquatic species are also presented in Table 6.3. The chronic toxicity of emerging contaminants in wastewater effluents also ranged from medium ($0.1 < RQ < 1$) to high ($RQ \geq 1$) risks. During the spring season, the high chronic risks on algae were presented by carbamazepine, ibuprofen, triclosan, atrazine and simazine. On daphnids, the high risks were presented by carbamazepine, ibuprofen, atrazine, simazine and terbuthylazine. On fish, the high risks were presented by ibuprofen, simazine, terbuthylazine and 17- α -ethinyl-estradiol. During the summer season, the high chronic risks on algae were presented by carbamazepine, ibuprofen, atrazine, metolachlor and simazine. On daphnids, the high risks were presented by carbamazepine, ibuprofen, atrazine, simazine and terbuthylazine. On fish, the high risks were presented by ibuprofen, simazine, terbuthylazine and 17- α -ethinyl-estradiol. The high chronic risks on algae during the autumn season were presented by carbamazepine, ibuprofen, atrazine, metolachlor and simazine. On daphnids, the high risks were presented by carbamazepine, ibuprofen, atrazine, simazine and terbuthylazine. On fish, the high chronic risks were presented by ibuprofen, simazine, terbuthylazine and 17- α -ethinyl-estradiol. During the winter season, the high chronic risks on algae were presented by carbamazepine, ibuprofen, atrazine and simazine. On daphnids, the high risks were presented by carbamazepine, ibuprofen, atrazine, simazine and terbuthylazine. On fish, the high risks were presented by ibuprofen, simazine, terbuthylazine and 17- α -ethinyl-estradiol.

In wastewater effluent, the majority (92%) of the targeted emerging contaminants showed the possibilities of high acute risks, while 67% of them showed possibilities of high chronic risks. In general, high risks were mostly from acetaminophen, carbamazepine, ibuprofen, triclosan, atrazine, metolachlor, simazine, terbuthylazine, estradiol, 17- α -ethinyl-estradiol and progesterone. Most notable for acute risks were high risks of carbamazepine, ibuprofen, atrazine, simazine and 17- α -ethinyl-estradiol that occurred on all species in all seasons. Additionally, only ibuprofen and simazine high chronic risks were observed on all species in all seasons. The high ecological risks of acetaminophen, ibuprofen, triclosan, atrazine, simazine, terbuthylazine, estradiol, 17- α -ethinyl-estradiol, progesterone and metolachlor in effluent were reported by other researchers (Cardini et al., 2021; Lin et al., 2020; Santos et al., 2007; Shao et al., 2019; Ying et al., 2009). Their high ecological risks may be credited to their low elimination rate in WWTPs (Cardin et al., 2021). Moreover, their high RQ values may be caused by some working faults of the WWTPs and current electricity load shedding problems in the country. These factors may cause the composition of influent wastewater not

to change much in effluent samples. Most of the time, wastewater effluent is discharged into downstream rivers after being treated by WWTPs. The release of effluents with unremoved pollutants into nearby water streams may contribute to the river contamination, which may lead to detrimental effects to aquatic organisms and human beings. At the same time, the combined effects of multiple emerging contaminants may further increase the level of environmental risks that will adversely affect the survival of aquatic organisms (Pei et al., 2022).

Exposure to pharmaceuticals and personal care products such as ibuprofen and triclosan may decrease reproduction rate in fish, increase the level of estradiol hormones (Veldhoen et al., 2014), reduce sperm counts in male fish, and reduce the time of producing eggs in fish (Olujimi et al., 2010). Exposure to steroids hormones such as estradiol, progesterone and 17-alpha-ethinyl-estradiol is associated with serious medical conditions on both aquatic and terrestrial animals (Olujimi et al., 2010). Their exposure is associated with the development of vaginal and breast cancers in humans and uterine cancers in animals (Birnbbaum and Fenton, 2003). Moreover, they cause embryo deformation and mortality; impaired reproduction and growth in fish (Yazdan et al., 2022). Herbicides are another class of chemical pesticides that have been related to endocrine disrupting effects and reproductive toxicity (Jin et al., 2014). During fieldwork it was noticed that wastewater effluent was being used by small-scale farmers for irrigating vegetables. Therefore, the threats of these compounds are not only limited to aquatic organisms but also to human beings as the consumption of such vegetables being grown entails a potential threat to human health due to the bioaccumulation of these organisms (Wang et al., 2018). To avoid such consequences around Bloemfontein, continuous monitoring and improvement of the treatment methods should be implemented in order to decrease the high environmental risks of these compounds for safer reuse in the future and for environmental sustainability.

Table 6.3 Acute and chronic risks of individual contaminants in effluents

Contaminant	Species	Spring		Summer		Autumn		Winter	
		HQ mean	Risk	HQ mean	Risk	HQ mean	Risk	HQ mean	Risk
Acute toxicity									
Acetaminophen	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	–	–	–	–	–	–	–	–
Carbamazepine	Algae	25.8	High	52.5	High	19.69	High	11	–
	Daphnids	155	High	255	High	99.05	High	57	–
	Fish	26.5	High	48	High	17.8	High	7	–
Ibuprofen	Algae	13.6	High	11.81	High	6.57	High	7	–

Contaminant	Species	Spring		Summer		Autumn		Winter	
		HQ mean	Risk	HQ mean	Risk	HQ mean	Risk	HQ mean	Risk
Triclosan	Daphnids	134 375	High	116 250	High	64 688	High	68 438	–
	Fish	43	High	37	High	20.7	High	22	–
	Algae	214	High	–	–	–	–	–	–
	Daphnids	308	High	–	–	–	–	–	–
	Fish	461	High	–	–	–	–	–	–
Atrazine	Algae	1017	High	678	High	847	High	508	–
	Daphnids	8.69	High	5.79	High	7.25	High	4	–
	Fish	13.33	High	8.89	High	11.11	High	7	–
Metolachlor	Algae	0.33	Medium	1.22	High	1.05	High	0.04	Low
	Daphnids	1	Medium	2.98	High	2.55	High	0.85	Medium
	Fish	5	High	17.95	High	15.38	High	5	High
Simazine	Algae	5 250	High	11 000	High	6 000	High	108 000	High
	Daphnids	210	High	400	High	218	High	3 927	High
	Fish	23.33	High	48.89	High	26.67	High	480	High
Terbuthylazine	Algae	3 000	High	3 500	High	1 000	High	1 000	High
	Daphnids	15.38	High	1.78	High	0.51	Medium	0.51	Medium
	Fish	16.66	High	19.44	High	5.56	High	6	High
17 α -ethinyl-estradiol	Algae	20 750 000	High	16 975 000	High	51 750 000	High	22 375 000	High
	Daphnids	13 833 333	High	11 316 667	High	34 500 000	High	14 916 667	High
	Fish	8 300 000	High	6 790 000	High	20 700 000	High	8 950 000	High
Estradiol	Algae	18 750	High	–	–	–	–	–	–
	Daphnids	1 000	High	–	–	–	–	–	–
	Fish	1 000	High	–	–	–	–	–	–
Progesterone	Algae	10 000	High	–	–	–	–	–	–
	Daphnids	1 428	High	–	–	–	–	–	–
	Fish	–	–	–	–	–	–	–	–
Testosterone	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	–	–	–	–	–	–	–	–
Chronic toxicity									
Acetaminophen	Algae	–	–	–	–	–	–	–	–
	Daphnids	–	–	–	–	–	–	–	–
	Fish	–	–	–	–	–	–	–	–
Carbamazepine	Algae	9.3	High	17	High	6.3	High	3.6	High
	Daphnids	1 860	High	3 360	High	1 260	High	720	High
	Fish	0.4	Medium	0.67	Medium	0.25	Medium	0.144	Medium
Ibuprofen	Algae	43 000	High	37 200	High	20 700	High	21 900	High
	Daphnids	215	High	151	High	84.15	High	89	High
	Fish	43 000	High	37 200	High	20 700	High	21 900	High
Triclosan	Algae	60	High	–	–	–	–	–	–
	Daphnids	0.03	Medium	–	–	–	–	–	–
	Fish	0.02	Medium	–	–	–	–	–	–
Atrazine	Algae	60	High	40	High	50	High	30	High
	Daphnids	30	High	20	High	25	High	15	High

Contaminant	Species	Spring		Summer		Autumn		Winter	
		HQ mean	Risk	HQ mean	Risk	HQ mean	Risk	HQ mean	Risk
Metolachlor	Fish	0.3	Medium	1	Medium	0.25	Medium	0.15	Medium
	Algae	0.67	Medium	2	High	2	High	0.67	Medium
	Daphnids	0.33	Medium	1	Medium	1	Medium	0.33	Medium
	Fish	0.2	Medium	0.7	Medium	0.6	Medium	0.2	Medium
Simazine	Algae	35	High	73	High	40	High	720	High
	Daphnids	21	High	37	High	20	High	3 600	High
	Fish	3	High	6	High	3.43	High	62	High
	Algae	-	-	-	-	-	-	-	-
Terbuthylazine	Daphnids	14.28	High	17	High	4.76	High	4.80	High
	Fish	4.61	High	5	High	1.54	High	1.54	High
	Algae	-	-	-	-	-	-	-	-
	Daphnids	-	-	-	-	-	-	-	-
17 α -ethinyl-estradiol	Fish	5 533	High	4 527	High	13 800	High	5 967	High
	Algae	-	-	-	-	-	-	-	-
	Daphnids	-	-	-	-	-	-	-	-
	Fish	0.7	Medium	-	-	-	-	-	-
Estradiol	Algae	-	-	-	-	-	-	-	-
	Daphnids	-	-	-	-	-	-	-	-
	Fish	-	-	-	-	-	-	-	-
	Algae	-	-	-	-	-	-	-	-
Progesterone	Daphnids	-	-	-	-	-	-	-	-
	Fish	-	-	-	-	-	-	-	-
	Algae	-	-	-	-	-	-	-	-
	Daphnids	-	-	-	-	-	-	-	-
Testosterone	Fish	-	-	-	-	-	-	-	-
	Algae	-	-	-	-	-	-	-	-

Notation: HQ = hazard quotient

6.2.1.4 Environmental risk assessment of individual emerging contaminants in treated drinking water

The results in Table 6.4 present the risks of emerging contaminants in treated drinking water, which were also based on acute and chronic toxicity on most sensitive species. Their risks assessment results ranged from medium ($0.1 < RQ < 1$) to high ($RQ \geq 1$). The acute toxicity of emerging contaminants in treated drinking water during the spring season showed carbamazepine, atrazine, simazine, terbuthylazine and 17-alpha-ethinyl-estradiol to have the possibility of high risks on algae. On daphnids, high ecological risks were contributed by acetaminophen, carbamazepine, ibuprofen, atrazine, simazine and 17-alpha-ethinyl-estradiol. On fish, high risks were contributed by carbamazepine, atrazine, metolachlor, simazine, terbuthylazine and 17-alpha-ethinyl-estradiol. During the summer season, high acute risks on algae were contributed by atrazine, terbuthylazine and 17-alpha-ethinyl-estradiol. On daphnids, high risks were contributed by atrazine, metolachlor, terbuthylazine and 17-alpha-ethinyl-estradiol. On fish, high risks were contributed by atrazine, metolachlor, terbuthylazine and 17-alpha-ethinyl-estradiol. During the autumn season, high acute risks on

algae were contributed by atrazine, terbuthylazine and 17-alpha-ethinyl-estradiol. On daphnids high risks were contributed by atrazine and 17-alpha-ethinyl-estradiol, while on fish it was contributed by atrazine, metolachlor and 17-alpha-ethinyl-estradiol. Moreover, during the winter season, the acute risks on algae were contributed by atrazine, terbuthylazine and 17-alpha-ethinyl-estradiol. On daphnids high risks were contributed by atrazine and 17-alpha-ethinyl-estradiol, while on fish it was contributed by atrazine, metolachlor, terbuthylazine and 17-alpha-ethinyl-estradiol.

The chronic risks emanating from emerging contaminants in treated drinking water are also presented in Table 6.4. Their risks ranged from low ($RQ \leq 0.1$) to high environmental risks ($RQ \geq 1$). For acute toxicity on algae, the high risks were presented by carbamazepine, ibuprofen, atrazine and simazine. On daphnids, high risks were presented by carbamazepine, atrazine, simazine and terbuthylazine. On fish, ibuprofen and 17-alpha-ethinyl-estradiol presented high risks. During the summer season, high acute toxicity on algae was posed by atrazine and metolachlor. On daphnids, the high risks were presented by atrazine and terbuthylazine. On fish, the high risks were presented by terbuthylazine and 17-alpha-ethinyl-estradiol. During the autumn and winter seasons, only atrazine posed high risks on algae. On daphnids, atrazine and terbuthylazine presented high risks, while 17-alpha-ethinyl-estradiol presented high risks on fish.

In treated drinking water, 67% of the targeted emerging contaminants showed the possibilities of high acute risks, while 58% of them showed possibilities of high chronic risks. Generally, high risks were mostly from carbamazepine, acetaminophen, ibuprofen, atrazine, simazine, terbuthylazine, metolachlor and 17-alpha-ethinyl-estradiol. Most notable in drinking water, atrazine and 17-alpha-ethinyl-estradiol were high acute risks, which occurred on all species in all seasons. In South Africa, there are no reported guidelines for emerging contaminants (carbamazepine, acetaminophen, ibuprofen, atrazine, simazine, terbuthylazine, metolachlor and 17-alpha-ethinyl-estradiol) that showed high risks in this study, except for atrazine. The high environmental risks of these compounds in treated drinking water may put serious risks to the water consumers (Shipingana et al., 2022). Residues of pesticides are often suspected of being carcinogens or disrupting endocrine activities in drinking water (Kumar et al., 2013). Exposure to ibuprofen may increase vitellogenin production in male fish; decrease reproduction rate in fish; rise estradiol hormone levels and aromatase enzyme activity, and decrease testosterone hormone levels (Veldhoen et al., 2014). The 17-alpha-ethinyl-estradiol may cause embryo deformation and mortality, impaired reproduction and growth in fish. Yazdan et al. (2022) showed that progesterone at pollutant levels can cause oocyte maturation in female and sperm motility in

male fish. Triazine herbicides are another class of chemical pesticides that have been related to endocrine disrupting effects and reproductive toxicity (Jin et al., 2014). Studies have also shown a possible statistical relationship between triazine herbicides and the incidence of breast cancer (Nicolopoulou-Stamati et al., 2016). It is of paramount importance to note that the combined effect of these emerging contaminants may further threaten the safety of drinking water in the area (Pei et al., 2022).

Table 6.4 Acute and chronic risks of individual contaminants in treated drinking water

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

Contaminant	Species	Spring		Summer		Autumn		Winter	
		HQ mean	Risk	HQ mean	Risk	HQ mean	Risk	HQ mean	Risk
	Daphnids	-	-	-	-	-	-	-	-
	Fish	-	-	-	-	-	-	-	-
Chronic toxicity									
Acetaminophen	Algae	0.22	Medium	-	-	-	-	-	-
	Daphnids	0.91	Medium	-	-	-	-	-	-
	Fish	0.1	Medium	-	-	-	-	-	-
Carbamazepine	Algae	1.3	High	-	-	-	-	-	-
	Daphnids	260	High	-	-	-	-	-	-
	Fish	0.05	Low	-	-	-	-	-	-
Ibuprofen	Algae	10	High	-	-	-	-	-	-
	Daphnids	0.5	Medium	-	-	-	-	-	-
	Fish	10	High	-	-	-	-	-	-
Triclosan	Algae	-	-	-	-	-	-	-	-
	Daphnids	-	-	-	-	-	-	-	-
	Fish	-	-	-	-	-	-	-	-
Atrazine	Algae	20	High	70	High	2	High	20	High
	Daphnids	10	High	35	High	10	High	10	High
	Fish	0.1	Medium	0.35	Medium	0.1	Medium	0.25	Medium
Metolachlor	Algae	0.33	Medium	1.67	High	0.67	Medium	0.33	Medium
	Daphnids	0.17	Medium	0.83	Medium	0.33	Medium	0.17	Medium
	Fish	0.1	Medium	0.5	Medium	0.2	Medium	0.10	Medium
Simazine	Algae	5	High	-	-	-	-	-	-
	Daphnids	3	High	-	-	-	-	-	-
	Fish	0.43	Medium	-	-	-	-	-	-
Terbutylazine	Algae	n/a	n/a	-	-	-	-	-	-
	Daphnids	4.76	High	21	High	2.38	High	2.34	High
	Fish	0.15	Medium	7	High	0.77	Medium	0.77	Medium
17 α -ethinyl - estradiol	Algae	-	-	-	-	-	-	-	-
	Daphnids	-	-	-	-	-	-	-	-
	Fish	487	High	67	High	243	High	147	High
Estradiol	Algae	-	-	-	-	-	-	-	-
	Daphnids	-	-	-	-	-	-	-	-
	Fish	-	-	-	-	-	-	-	-
Progesterone	Algae	-	-	-	-	-	-	-	-
	Daphnids	-	-	-	-	-	-	-	-
	Fish	-	-	-	-	-	-	-	-
Testosterone	Algae	-	-	-	-	-	-	-	-
	Daphnids	-	-	-	-	-	-	-	-
	Fish	-	-	-	-	-	-	-	-

6.2.2 Mixture risk assessment

Ecological risk assessment of emerging contaminants in water sources is still frequently done substance by substance ignoring mixture effects which may underestimate the true risks to the ecosystem (Maasz et al., 2019). As the knowledge on the mixture toxicity of emerging contaminants towards various aquatic organisms in water sources around Bloemfontein is still limited, the study adopted the concentration addition method to assess the mixture toxicity of emerging contaminants towards most sensitive aquatic species such as algae, daphnids and fish. Concentration addition in this study was approximated by RQmix and TUs_{sum} approaches (Backhaus and Faust, 2012; Backhaus and Karlsson, 2014; Backhaus et al., 2013; Białk-Bielińska et al., 2022; Kienzler et al., 2019; Maasz et al., 2019).

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

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

6.2.2.1 Mixture environmental risk assessment of emerging contaminants in rivers

Acute and chronic mixture toxicity estimates for various contaminants in rivers during all seasons of the year are presented in Table 6.5. Based on the RQmix, the acute mixture risks of contaminants on algae, daphnids and fish far exceeded the 1 threshold during all seasons. As presented in Figure 6.1, the highest mixture risks for algae were observed in

the summer season, indicating that it is likely to suffer more acute risks in the summer seasons. For daphnids and fish, the highest mixture risks were observed during the autumn season, indicating that these aquatic species are likely to suffer more acute risks in such seasons. The risk mixture (RQ_{mix}) results based on chronic toxicity in rivers also exceeded the acceptable limit (RQ_{mix} > 1) for all selected aquatic organisms in all seasons, as presented in Table 6.5. The highest chronic mixture risks for algae, daphnids and fish in water sources around Bloemfontein were observed during the spring season, indicating that aquatic organisms are more likely to suffer chronic toxicity risks during the spring season. Furthermore, mixture risks were assessed using the TU_{sum} as presented in Table 6.5. For acute mixture risks, algae had the highest TU_{sum} in all seasons, while for chronic risks, fish showed the highest mixture risks in the summer, autumn and winter, while during the spring season it was algae that showed the highest mixture risks (Figure 6.1). Therefore, the TU_{sum} results for both acute and chronic toxicity revealed high mixture risks (TU_{sum} > 1) for algae, daphnids and fish in all seasons.

The findings of this study are comparable to those of Bouzas-Monroy et al. (2022), who reported that the risk mixtures (RQ_{mix}) of emerging contaminants in rivers in Africa, Asia, Europe, South and North America were greater than one. Based on TU_{sum}, the trophic level with the highest toxic unit sum should be used to assess the final mixture risks (Kienzler et al., 2019). Therefore, for acute mixture risks, algae has the highest TU_{sum} in all seasons (Figure 6.1), which is consistent with previous research (Kienzler et al., 2019). In case studies from European rivers (Kienzler et al., 2019) and the Erft River in Germany (Markert et al., 2020), risk mixtures based on TU_{sum}, were also found to be above the acceptable limit, which supports the findings of this study. The findings of this study proved that the majority of the rivers in this area were not safe and were likely to have acute and chronic effects on most sensitive aquatic species, which is concerning. According to Thrupp et al. (2018), regardless of the chemical composition, the exposed organism and the considered biological endpoint, a chemical mixture will always have a greater toxic effect than the individual effect of each of its constituents, which supports the findings of this study. There are evidence showing that mixtures of emerging contaminants often have unexpected toxicity when compared to individual chemicals, resulting in immobilisation, higher rates of death and deformity in exposed organisms, than predicted by a single pollutant (Shore et al., 2014; Heys et al., 2016).

Table 6.5 Acute and chronic mixture risks of contaminants in rivers

Species	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter
Acute RQmix				Acute TUs				
Algae	16 092 952	93 382 460	39 466 956	15 438 125	15 318 534	9 768 874	3 9470 510	15 438 125
Daphnids	10 740 539	6 531 503	26 323 104	10 352 486	10 244 105	6 529 067	2 630 4771	10 352 153
Fish	6 402 634	3 895 182	15 775 254	617 135	6 113 265	3 895 205	15 765 267	6 170 134
Chronic RQmix				Chronic TUs				
Algae	22 990	11 826	10 008	22 149	22 536	11 859	10 009	22 149
Daphnids	1463	319	942	782	1 431	5 930	941	794
Fish	26 335	3 083	19 731	26124	14 222	26 295	19 735	26 124

Notation: RQmix=risk quotient mixture; TUs=toxic unit sum (Σ).

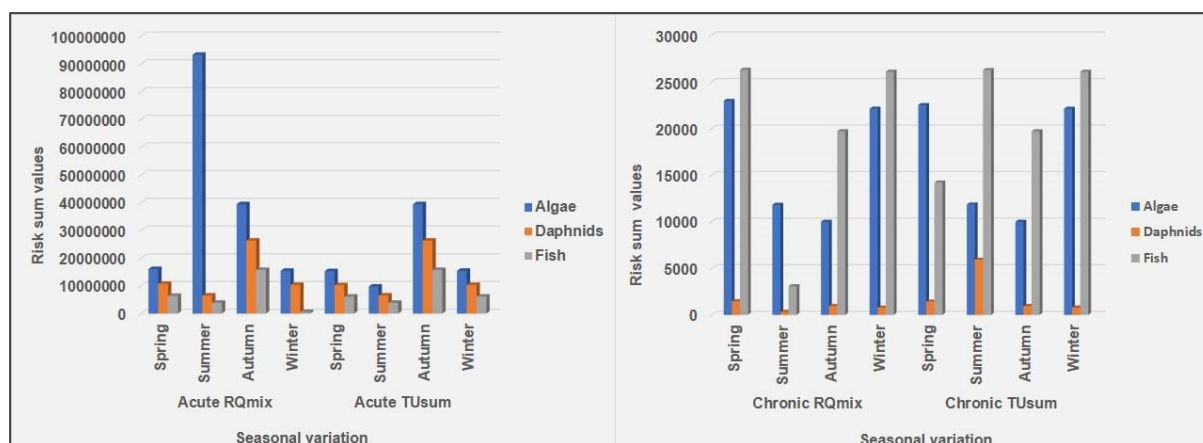


Figure 6.1 Seasonal mixture risks of emerging contaminants on aquatic species in rivers

6.2.2.2 Mixture environmental risk assessment of emerging contaminants in dams

As shown in Table 6.6, the acute mixture risks based on RQmix on algae, daphnids and fish exceeded the threshold of 1 by a wide margin in all seasons. The highest acute mixture risks on selected species in dams were observed during the autumn season, indicating that these species are likely to suffer from high acute risks during the autumn season (Figure 6.2). For chronic risks on algae, daphnids and fish, the RQmix values (Table 6.6) exceeded the acceptable limit in all seasons. The highest chronic mixture risks on all selected aquatic organisms were observed during the autumn season, indicating that aquatic organisms are more likely to suffer chronic risks during the autumn season (Figure 6.2). Furthermore, according to Kienzler et al. (2019), the trophic level with the highest TUs should be used to assess the final mixture risks, which in this study were algae in all seasons for acute toxicity and fish for chronic risk values in all seasons (Table 6.6). Therefore, the results for both acute and chronic risks based on the TUs in dams demonstrated high mixture risks ($TUs > 1$) on all selected aquatic species in all seasons (Figure 6.2).

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

Table 6.6 Acute and chronic mixture risks of contaminants in dams

Species	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter
Acute RQmix				Acute TUs				
Algae	4 591 849	2 293 755	8 628 672	3 480 180	4 592 430	2 294 760	8 635 023	3 480 180
Daphnids	3 067 868	1 525 157	5 750 749	231 810	3 067 131	1 525 137	5750 752	2 317 143
Fish	1 835 037	91 539	3 450 023	1 390 036	1 835 034	915 043	2 300 020	1 390 034
Chronic RQmix				Chronic TUs				
Algae	3 040	26	231	64	3 030	54	231	64
Daphnids	617	279	34	245	633	288	179	161
Fish	4 227	617	1 155	1 046	4224	616	2 313	931

Notation: RQmix=risk quotient mixture; TUs= toxic unit sum (Σ).

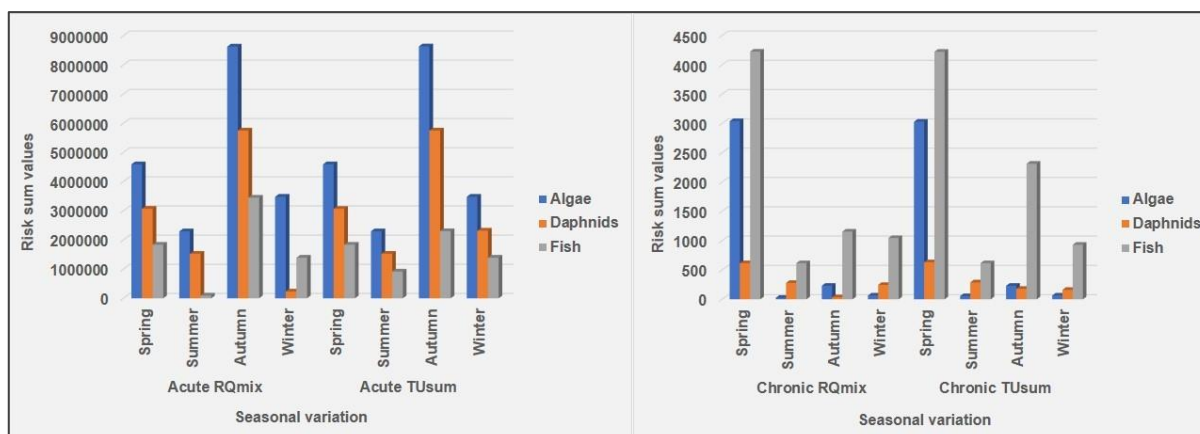


Figure 6.2 Seasonal mixture risks of emerging contaminants on aquatic species in dams

6.2.2.3 Mixture environmental risk assessment of emerging contaminants in wastewater effluents

The RQmix based on acute toxicity on algae, daphnids and fish in wastewater effluents revealed risk mixture values greater than one in all seasons, as presented in Table 6.7. The highest acute RQmix values for contaminants in effluents on algae, daphnids and fish were observed during the autumn season (Figure 6.3), indicating that these organisms are not safe in the autumn season. The mixture risk assessment based on chronic risks on algae, daphnids and fish in effluent in all seasons were also above the acceptable limit. The highest chronic mixture risk of emerging contaminants was observed on fish in all seasons (Figure 6.3). Based on TUsum, the highest toxic unit summation values for acute toxicity were observed on algae in all seasons. Fish had the highest toxic unit summation value for chronic toxicity (Figure 6.3). Therefore, both acute and chronic mixture risks on algae, daphnids and fish exceeded the risk threshold limit ($TU_{sum} > 1$) in all seasons (Table 6.7).

The RQmix findings are comparable to those of a study conducted in European WWTPs (Finckh et al., 2022) and in wastewater effluent from the Republic of Ireland (Rapp-Wright et al., 2023), both of which reported that the mixture risk assessment of emerging contaminants in effluent samples were greater than one. Finckh et al. (2022) found that the TUsum value of contaminants in effluents exceeded the risk threshold, which is consistent with the findings of this study. From the results of both the RQmix and TUsum, it is clear that effluents in this study were not safe as they were significantly higher than the acceptable limit. The majority of wastewater effluents are discharged into nearby streams. This is concerning, given that environmental mixtures of emerging contaminants may unexpectedly have negative effects on aquatic ecosystems and, eventually, humans. The discharge of these wastewater effluents into natural water bodies, such as rivers, exposes aquatic

organisms to emerging contaminants. Furthermore, rivers that receive effluent from treatment plants discharge their water in dams, potentially endangering the water ecosystem. As a result, it causes morbidity and mortality in organisms by interfering with processes such as reproduction and development (Heys et al., 2016). Advance treatment should be implemented to remove these compounds. When treating wastewater, WWTPs should also prioritise these contaminants. This will help to reduce their concentration and, as a result, their potential risks as they are used to irrigate vegetables by small-scale farmers around the area.

Table 6.7 Acute and chronic mixture risks of contaminants in wastewater effluents

Species	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter
Acute RQmix				Acute TUs_{sum}				
Algae	2 078 8271	16 990 244	51 757 874	22 484 526	20 764 817	16 990 744	51 811 881	22 484 527
Daphnids	13 970 834	11 433 583	34 565 015	14 989 094	13 969 110	11 433 675	34 565 348	14 989 427
Fish	8 301 589	6 790 180	20 700 097	8 950 527	8 300 627	6 790 179	20 700 110	8 950 530
Chronic RQmix				Chronic TUs_{sum}				
Algae	43 165	37 322	20 798	22 654	43 097	162 433	20 798	22 654
Daphnids	2 141	3 586	1 395	4 429	408	3 574	1385	1 189
Fish	48 542	41 740	34 506	27 931	48 535	41 827	34 506	27 930

Notation: RQmix=risk quotient mixture; TUs_{sum}=toxic unit sum (Σ).

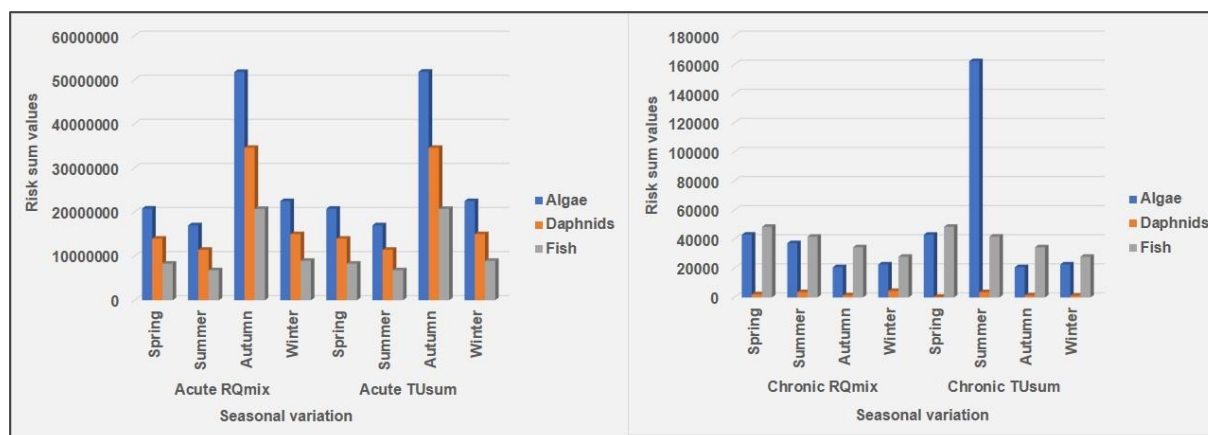


Figure 6.3 Seasonal mixture risks of emerging contaminants in wastewater effluent on aquatic species

6.2.2.4 Mixture environmental risk assessment of emerging contaminants in treated drinking water

The RQmix based on acute risks on algae, daphnids and fish in treated drinking water revealed mixture risk values greater than one in all seasons, as shown in Table 6.8. The results of acute mixture risks revealed that the spring season had the highest mixture risk values for all aquatic organisms studied (Figure 6.4). The mixture risk values were also above the acceptable limit based on chronic toxicity on algae, daphnids and fish in all seasons as presented in Table 6.8. The results of chronic mixture risks revealed that the spring season had the highest values of mixture risks on all aquatic organisms (Figure 6.4). Furthermore, acute and chronic mixture risks on algae, daphnids and fish based on TUsum were investigated (Table 6.8). In all seasons, algae showed the worst case scenario for acute mixture toxicity in all seasons. Fish had the highest toxic unit summation value for chronic mixture risks in all seasons (Figure 6.4). Therefore, the TUsum results for both acute and chronic toxicity showed high mixture risks values ($TU_{sum} > 1$) on aquatic species.

These findings are concerning for water consumers because exposure to water contaminated by compounds with such high risks could have serious consequences as most of them are known toxins. Long-term exposure to contaminated water may have negative consequences for both water consumers and aquatic species. Once the various emerging contaminants are taken up by the organisms, biotransformation may occur with the production of secondary metabolites with possible interactions between chemicals in the mixture, such as synergism or antagonism (Ojemaye et al., 2022). The environmental health risks linked to the exposure of mixture of emerging contaminants for aquatic species and water consumers include olfactory tissue damage, lowering of the immune responses, alteration of steroidogenic pathways, thyroid disease, low sperm quality and causing reproductive system disorders among women (Belden et al., 2007; Ferrari et al., 2017; Heys et al., 2016; Hunt et al., 2016; Ojemaye et al., 2022; Selvaraju et al., 2021). The outcomes of this study will play a significant role in raising awareness on cumulative effects of chemical mixtures and in protecting the environmental and community health. For the sustainability of the water sources, further and continuous monitoring of emerging contaminants in water sources around Bloemfontein is necessary.

Table 6.8 Acute and chronic mixture risks of contaminants in treated drinking water

Species	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter
Acute RQmix				Acute TUsum				
Algae	1 827 094	255 687	913 339	55 839	1 826 343	256 001	913 840	550 839
Daphnids	1 217 045	166 681	608 337	366 671	1 217 024	167 014	608004	366 670
Fish	730 020	100 054	365 012	220 010	730 017	100 042	365 017	220 010
Chronic RQmix				Chronic TUsum				
Algae	37	72	3	20	22	72	94	20
Daphnids	280	57	13	13	265	57	13	13
Fish	498	75	244	148	492	77	241	148

Notation: RQmix=risk quotient mixture; TUsum=toxic unit sum (Σ).

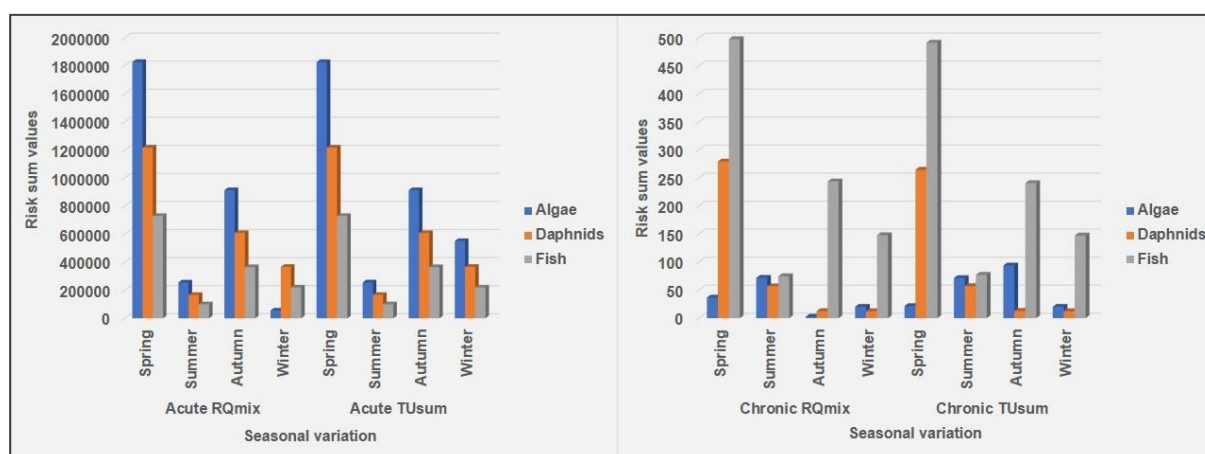


Figure 6.4 Seasonal mixture risks of emerging contaminants in treated drinking water on aquatic species

6.3 Human health risk assessment of selected pesticides in water sources

The evaluation of human health risks was assessed based on both non-carcinogenic and carcinogenic risks. The determination of health risks associated with the exposure of pesticides – atrazine, metolachlor, simazine and terbuthylazine – to effluent, rivers, dams or reservoirs, and treated drinking water, was based on the ingestion route. The outcomes of non-carcinogenic and carcinogenic risks are presented in Table 6.9 and Table 6.10, respectively. In terms of non-carcinogenic risk, all pesticides in all water sources had the hazard quotients below 1 in all seasons of the year, which is a sign of low non-carcinogenic risks to the entire population around Bloemfontein. Similar results were also reported by other authors (Guo et al., 2023; Huang et al., 2014; Shah and Parveen, 2023). Seasonally (Figure 6.5), summer had the highest total HQ in effluent and dams, contributed by simazine on both adults and children. In rivers, the highest total HQs were recorded in the autumn

season on both adults and children. They were mostly contributed by simazine. In drinking water, the spring season showed the highest total hazard quotient on adults contributed mostly by simazine, while for children summer had the highest total HQ, contributed mostly by atrazine (Figure 6.5).

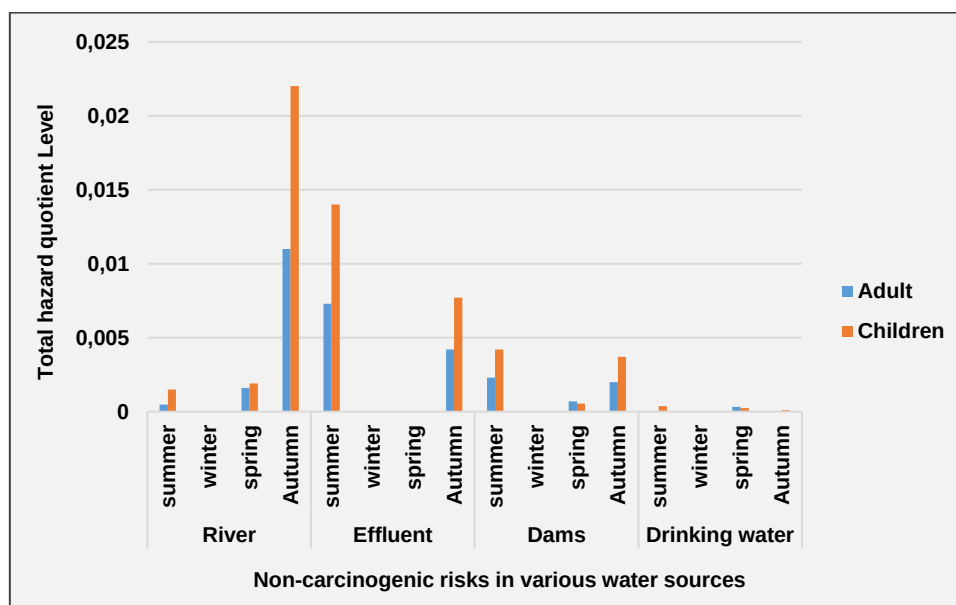


Figure 6.5 Seasonal variation of non-carcinogenic risks in various water sources

The results of carcinogenic risks ranged from very low to high risks. In wastewater effluent, all the targeted pesticides had low risks to the entire population in all seasons. In rivers, only atrazine posed high carcinogenic risk to the adult group during the summer season. During spring, autumn and winter, all the pesticides showed low carcinogenic risks to both the adult and children groups. Similar outcomes of low carcinogenic risks of pesticide exposure were also reported in Ganga River, India (Shah and Parveen, 2023). In dams and treated drinking water, all the targeted pesticides showed very low risks to the entire population in all seasons. Dong et al. (2023) also reported low carcinogenic risks of the pesticide atrazine in drinking water sources in Dalian, China. Seasonally, in effluent, the highest total carcinogenic risk (TCR) on adults was recorded in autumn, which was mostly contributed by simazine (Figure 6.6). On children, TRC was recorded during summer, also mostly contributed by atrazine. In rivers, the utmost TCR on adults was recorded during summer, contributed mostly by atrazine, while on children; it was recorded during summer and contributed mostly by simazine. In dams, the highest TCR was recorded during summer, contributed mostly by simazine for the entire population (Figure 6.6). Moreover, in treated drinking water, the highest TCR was recorded during summer on adults and during autumn on children, contributed mostly by atrazine.

The most noticeable and alarming risk was the high carcinogenic risks of atrazine found in rivers around Bloemfontein, which may be attributed to the fact that most of the rivers are surrounded by intensive agricultural fields and industrial activities that are likely to release these compounds. Both Ganie et al. (2023) and Wani et al. (2019) stated that anthropogenic pollution of water sources can come from a variety of sources, including chemical industry discharge and agricultural runoff.

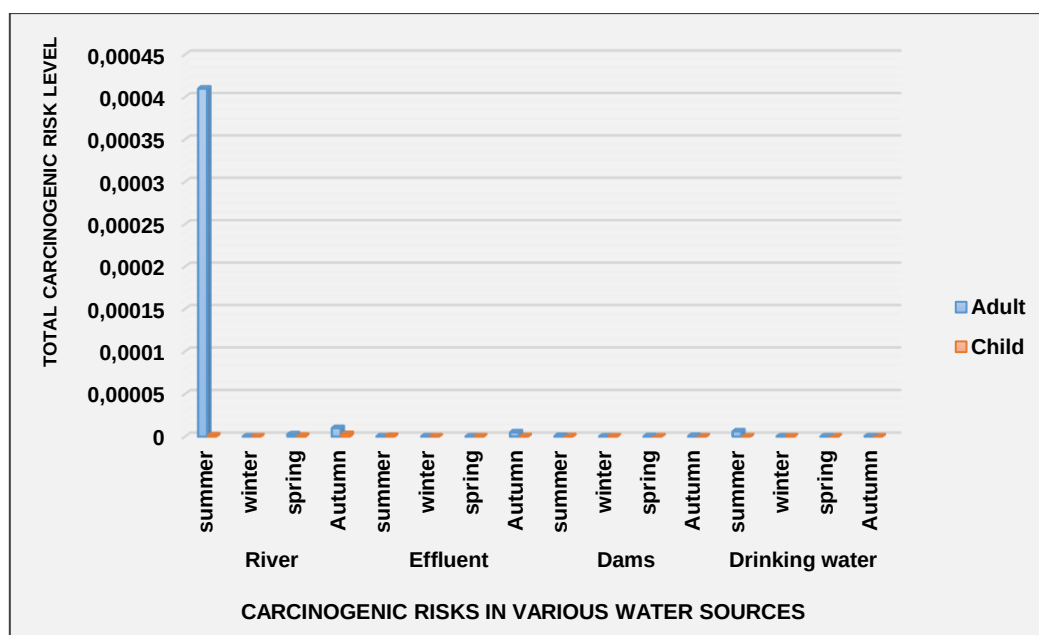


Figure 6.6 Seasonal variation of carcinogenic risks in various water sources

Moreover, most of the wastewater effluents in the study area are discharged in nearby streams thus introducing traces of pesticide in natural waters thus compromising the quality of water sources. The high carcinogenic risk of herbicide atrazine in rivers in this area is a public health concern as the water from rivers around Bloemfontein is used to help agriculturalists and local people for growing crops and drinking purposes particularly in rural areas. During field sampling domestic animals such as goats, sheep and cows were also seen drinking river water. The use and drinking of river water contaminated with pesticides may lead to their build-up in soils, grown crops, build-up in animal organs and eventually transfer to persons (Shahid et al., 2020; Abera et al., 2022). Exposure to water with high carcinogenic risks associated with atrazine may cause cancers, reproduction deficiency, antibiotic resistance, hypospadias, cryptorchidism and small penis (Syafudin et al., 2021; Kumar et al., 2013).

Additionally, exposure to water sources contaminated by other pesticides identified in this study may lead to health effects such as endocrine effects, stress, intestinal secretion, cancer and reproductive effects (Nicolopoulou-Stamati et al., 2016). The results of this study pointed out the significance of raising awareness on pesticides pollution in the aquatic ecosystem among the farmers and local residents. This will enable water resources sustainability around Bloemfontein. Moreover, the risks of these pesticides should be reduced by identifying places that are more susceptible to pesticides pollution, particularly reservoirs that are utilised as sources of water for drinking water treatment plants.

Table 6.9 Non-carcinogenic risks of selected pesticides in various water sources

Seasons	Compound	WWTP effluent		Rivers		Reservoir		Drinking water	
		ADD	HQ	ADD	HQ	ADD	HQ	ADD	HQ
Adults									
Spring	Atrazine	1.64×10^{-6}	4.69×10^{-8}	8.2×10^{-7}	2.3×10^{-7}	5.5×10^{-7}	1.6×10^{-4}	5.5×10^{-7}	1.6×10^{-4}
	Metolachlor	5.48×10^{-6}	3.65×10^{-9}	2.7×10^{-7}	1.8×10^{-6}	2.7×10^{-7}	1.8×10^{-6}	2.7×10^{-7}	1.8×10^{-6}
	Simazine	5.75×10^{-9}	1.2×10^{-6}	5.0×10^{-5}	1.6×10^{-2}	2.7×10^{-6}	5.4×10^{-4}	8.2×10^{-7}	1.6×10^{-4}
	Terbuthylazine	1.64×10^{-9}	-	1.6×10^{-6}	-	8.2×10^{-7}	-	5.5×10^{-7}	-
	Total	7.13×10^{-6}	1.3×10^{-6}	5.3×10^{-5}	1.6×10^{-2}	4.3×10^{-6}	7.0×10^{-4}	2.2×10^{-6}	3.2×10^{-4}
Summer	Atrazine	3.3×10^{-6}	9.4×10^{-5}	4.1×10^{-6}	1.2×10^{-4}	2.5×10^{-6}	7.1×10^{-5}	5.8×10^{-6}	1.7×10^{-4}
	Metolachlor	5.8×10^{-6}	3.9×10^{-5}	4.9×10^{-6}	3.3×10^{-5}	2.5×10^{-6}	1.7×10^{-5}	4.1×10^{-6}	2.7×10^{-5}
	Simazine	2.0×10^{-5}	7.2×10^{-3}	1.6×10^{-6}	3.2×10^{-4}	1.1×10^{-5}	2.2×10^{-3}	-	-
	Terbuthylazine	5.8×10^{-6}	-	6.6×10^{-6}	-	4.1×10^{-6}	-	4.6×10^{-9}	-
	Total	3.5×10^{-5}	7.3×10^{-3}	1.7×10^{-5}	4.7×10^{-4}	2.0×10^{-5}	2.3×10^{-3}	1.0×10^{-5}	4.4×10^{-5}
Autumn	Atrazine	4.1×10^{-6}	1.2×10^{-4}	5.7×10^{-5}	1.6×10^{-3}	8.2×10^{-7}	2.3×10^{-5}	1.6×10^{-6}	4.6×10^{-6}
	Metolachlor	4.9×10^{-9}	3.3×10^{-5}	1.6×10^{-6}	1.1×10^{-5}	8.2×10^{-7}	5.5×10^{-6}	1.6×10^{-6}	1.1×10^{-5}
	Simazine	2.0×10^{-7}	4.0×10^{-3}	5.7×10^{-5}	1.1×10^{-2}	9.8×10^{-6}	2.0×10^{-3}	-	-
	Terbuthylazine	1.6×10^{-6}	-	8.2×10^{-7}	-	8.2×10^{-7}	-	-	-
	Total	5.9×10^{-6}	4.2×10^{-3}	1.6×10^{-4}	1.1×10^{-2}	1.2×10^{-5}	2.0×10^{-3}	3.2×10^{-6}	1.6×10^{-5}
Winter	Atrazine	8.22×10^{-10}	2.35×10^{-8}	2.20×10^{-9}	6.30×10^{-8}	1.09×10^{-9}	3.11×10^{-8}	5.48×10^{-10}	1.60×10^{-8}
	Metolachlor	5.48×10^{-10}	3.89×10^{-9}	3.30×10^{-9}	2.2×10^{-8}	2.74×10^{-10}	1.83×10^{-9}	2.74×10^{-10}	1.83×10^{-9}
	Simazine	1.20×10^{-7}	2.4×10^{-5}	1.01×10^{-8}	2.02×10^{-6}	3.83×10^{-9}	7.7×10^{-9}	-	-
	Terbuthylazine	5.48×10^{-10}	-	1.40×10^{-9}	-	5.48×10^{-10}	-	2.74×10^{-10}	-
	Total	1.2×10^{-7}	2.0×10^{-5}	1.7×10^{-8}	2.1×10^{-6}	5.7×10^{-9}	4.1×10^{-8}	1.1×10^{-9}	1.8×10^{-8}

Seasons	Compound	WWTP effluent		Rivers		Reservoir		Drinking water	
		ADD	HQ	ADD	HQ	ADD	HQ	ADD	HQ
Children									
Spring	Atrazine	3.08×10^{-9}	8.80×10^{-8}	1.5×10^{-6}	4.3×10^{-4}	4.1×10^{-7}	1.2×10^{-4}	4.1×10^{-7}	1.2×10^{-4}
	Metolachlor	1.03×10^{-9}	6.87×10^{-9}	5.0×10^{-7}	3.3×10^{-6}	2.0×10^{-7}	1.3×10^{-6}	2.0×10^{-7}	1.3×10^{-6}
	Simazine	1.10×10^{-8}	2.2×10^{-6}	9.3×10^{-5}	1.9×10^{-2}	2.1×10^{-6}	4.2×10^{-4}	6.1×10^{-7}	1.2×10^{-4}
	Terbutylazine	3.08×10^{-9}	-	3.1×10^{-6}	-	6.1×10^{-7}	-	4.1×10^{-7}	-
	Total	1.8×10^{-8}	2.3×10^{-6}	9.8×10^{-5}	1.9×10^{-2}	3.3×10^{-7}	5.4×10^{-4}	1.6×10^{-7}	2.4×10^{-4}
Summer	Atrazine	6.2×10^{-6}	1.8×10^{-4}	7.7×10^{-4}	7.7×10^{-4}	4.6×10^{-6}	1.3×10^{-4}	1.1×10^{-5}	3.1×10^{-4}
	Metolachlor	1.1×10^{-5}	7.3×10^{-5}	9.2×10^{-6}	6.1×10^{-5}	4.6×10^{-6}	3.1×10^{-5}	7.7×10^{-6}	5.1×10^{-5}
	Simazine	6.8×10^{-5}	1.4×10^{-2}	3.1×10^{-6}	6.2×10^{-4}	2.0×10^{-5}	4.0×10^{-3}	-	-
	Terbutylazine	1.1×10^{-5}	-	1.2×10^{-5}	-	7.7×10^{-6}	-	4.62×10^{-9}	-
	Total	9.6×10^{-5}	1.4×10^{-2}	7.9×10^{-4}	1.5×10^{-3}	3.7×10^{-5}	4.2×10^{-3}	1.9×10^{-5}	3.6×10^{-4}
Autumn	Atrazine	7.7×10^{-6}	2.2×10^{-4}	1.1×10^{-6}	3.1×10^{-5}	1.5×10^{-6}	4.3×10^{-5}	3.1×10^{-6}	8.9×10^{-5}
	Metolachlor	9.2×10^{-6}	6.1×10^{-5}	3.1×10^{-6}	2.1×10^{-5}	1.5×10^{-6}	1.0×10^{-5}	3.1×10^{-6}	2.1×10^{-5}
	Simazine	3.7×10^{-5}	7.4×10^{-3}	1.1×10^{-4}	2.2×10^{-2}	1.8×10^{-5}	3.6×10^{-3}	-	-
	Terbutylazine	3.1×10^{-6}	-	1.5×10^{-6}	-	1.5×10^{-6}	-	-	-
	Total	5.7×10^{-5}	7.7×10^{-3}	1.2×10^{-4}	2.2×10^{-2}	2.3×10^{-5}	3.7×10^{-3}	3.5×10^{-6}	1.1×10^{-4}
Winter	Atrazine	1.54×10^{-9}	4.40×10^{-8}	4.11×10^{-9}	1.20×10^{-7}	2.05×10^{-9}	5.86×10^{-6}	1.03×10^{-9}	2.94×10^{-8}
	Metolachlor	1.03×10^{-9}	6.8×10^{-9}	6.20×10^{-9}	4.13×10^{-8}	5.14×10^{-10}	3.43×10^{-9}	5.14×10^{-10}	3.43×10^{-9}
	Simazine	2.22×10^{-7}	4.4×10^{-5}	1.90×10^{-8}	3.80×10^{-6}	7.20×10^{-9}	1.40×10^{-6}	-	-
	Terbutylazine	5.14×10^{-9}	-	2.60×10^{-9}	-	1.03×10^{-9}	-	5.14×10^{-10}	-
	Total	2.3×10^{-7}	4.4×10^{-5}	3.2×10^{-8}	4.0×10^{-6}	1.1×10^{-8}	7.2×10^{-6}	2.2×10^{-8}	3.3×10^{-8}

ADD=average daily dose; HQ=hazard quotient.

Table 6.10 Carcinogenic risks of selected pesticides in various water sources

Seasons	Compound	WWTP effluent		Rivers		Reservoir		Drinking water	
		ADD	CR	ADD	CR	ADD	CR	ADD	CR
Adults									
Spring	Atrazine	7.05×10^{-10}	1.62×10^{-10}	3.5×10^{-7}	8.0×10^{-8}	2.3×10^{-7}	5.3×10^{-8}	2.3×10^{-7}	5.3×10^{-8}
	Metolachlor	2.35×10^{-10}	2.16×10^{-12}	1.2×10^{-7}	1.10×10^{-9}	1.2×10^{-5}	1.1×10^{-7}	1.2×10^{-7}	1.1×10^{-9}
	Simazine	2.50×10^{-9}	2.3×10^{-10}	2.1×10^{-5}	2.5×10^{-6}	1.2×10^{-6}	1.4×10^{-7}	3.5×10^{-8}	4.2×10^{-9}
	Terbuthylazine	7.05×10^{-10}	-	7.0×10^{-7}	-	3.5×10^{-7}	-	2.3×10^{-7}	-
	Total	4.1×10^{-9}	3.9×10^{-10}	2.2×10^{-5}	2.5×10^{-6}	1.4×10^{-5}	3.0×10^{-7}	6.5×10^{-7}	5.8×10^{-8}
Summer	Atrazine	1.4×10^{-6}	3.2×10^{-7}	1.8×10^{-7}	4.1×10^{-4}	1.1×10^{-6}	2.5×10^{-7}	2.5×10^{-6}	5.8×10^{-7}
	Metolachlor	2.5×10^{-6}	2.3×10^{-8}	2.1×10^{-6}	1.9×10^{-8}	1.1×10^{-6}	1.0×10^{-8}	1.8×10^{-6}	1.7×10^{-8}
	Simazine	1.5×10^{-5}	1.4×10^{-6}	3.7×10^{-5}	3.4×10^{-6}	4.6×10^{-6}	4.2×10^{-7}	-	-
	Terbuthylazine	2.5×10^{-6}	-	9.4×10^{-7}	-	1.8×10^{-6}	-	1.06×10^{-9}	-
	Total	2.1×10^{-5}	1.7×10^{-6}	4.0×10^{-5}	4.1×10^{-4}	8.6×10^{-6}	6.8×10^{-7}	4.3×10^{-6}	6.0×10^{-6}
Autumn	Atrazine	1.8×10^{-5}	4.1×10^{-6}	2.4×10^{-5}	5.5×10^{-6}	3.5×10^{-7}	8.1×10^{-8}	7.0×10^{-7}	1.6×10^{-7}
	Metolachlor	2.1×10^{-6}	1.9×10^{-8}	7.0×10^{-7}	6.4×10^{-9}	3.5×10^{-7}	3.2×10^{-9}	7.0×10^{-7}	6.4×10^{-9}
	Simazine	8.4×10^{-6}	7.7×10^{-7}	2.4×10^{-5}	2.2×10^{-6}	4.2×10^{-6}	3.9×10^{-7}	-	-
	Terbuthylazine	7.0×10^{-7}	-	3.5×10^{-7}	-	3.5×10^{-7}	-	-	-
	Total	2.9×10^{-5}	5.0×10^{-6}	5.0×10^{-5}	1.0×10^{-5}	5.3×10^{-6}	5.0×10^{-7}	1.4×10^{-6}	1.7×10^{-7}
Winter	Atrazine	3.52×10^{-10}	8.10×10^{-10}	9.40×10^{-10}	2.20×10^{-10}	4.70×10^{-10}	4.14×10^{-11}	2.35×10^{-10}	5.41×10^{-11}
	Metolachlor	2.35×10^{-10}	2.16×10^{-9}	1.41×10^{-9}	1.30×10^{-11}	1.20×10^{-10}	4.05×10^{-13}	1.20×10^{-10}	1.10×10^{-12}
	Simazine	5.07×10^{-8}	2.54×10^{-10}	4.34×10^{-9}	4.09×10^{-10}	1.64×10^{-9}	5.67×10^{-11}	-	-
	Terbuthylazine	2.35×10^{-10}	-	5.90×10^{-10}	-	2.34×10^{-4}	-	1.20×10^{-10}	-
	Total	5.2×10^{-8}	3.2×10^{-9}	3.2×10^{-9}	6.4×10^{-10}	2.3×10^{-4}	9.9×10^{-11}	4.7×10^{-10}	5.5×10^{-11}

Seasons	Compound	WWTP effluent		Rivers		Reservoir		Drinking water	
		ADD	CR	ADD	CR	ADD	CR	ADD	CR
Children									
Spring	Atrazine	2.68×10^{-10}	6.07×10^{-11}	1.3×10^{-7}	2.9×10^{-8}	8.8×10^{-8}	2.0×10^{-8}	8.8×10^{-8}	2.0×10^{-8}
	Metolachlor	8.81×10^{-11}	8.11×10^{-13}	4.3×10^{-8}	3.9×10^{-10}	4.3×10^{-8}	3.9×10^{-10}	4.3×10^{-8}	3.9×10^{-10}
	Simazine	9.2×10^{-10}	8.51×10^{-11}	8.0×10^{-6}	9.6×10^{-7}	4.3×10^{-7}	5.2×10^{-8}	1.3×10^{-8}	1.5×10^{-9}
	Terbuthylazine	2.64×10^{-10}	-	2.6×10^{-7}	-	1.2×10^{-7}	-	4.3×10^{-7}	-
	Total	1.5×10^{-9}	1.5×10^{-10}	8.4×10^{-6}	9.9×10^{-7}	6.8×10^{-7}	7.2×10^{-8}	5.7×10^{-7}	2.2×10^{-8}
Summer	Atrazine	5.3×10^{-7}	1.2×10^{-7}	6.6×10^{-8}	1.5×10^{-8}	4.0×10^{-7}	9.2×10^{-8}	9.2×10^{-7}	2.1×10^{-8}
	Metolachlor	9.2×10^{-7}	8.5×10^{-9}	7.9×10^{-7}	7.3×10^{-9}	4.0×10^{-7}	3.7×10^{-9}	6.6×10^{-7}	6.1×10^{-10}
	Simazine	5.8×10^{-6}	5.3×10^{-7}	1.4×10^{-5}	1.3×10^{-6}	1.7×10^{-6}	1.6×10^{-7}	-	-
	Terbuthylazine	9.2×10^{-7}	-	1.1×10^{-6}	-	6.6×10^{-7}	-	3.96×10^{-10}	-
	Total	8.2×10^{-6}	6.6×10^{-7}	1.6×10^{-5}	1.3×10^{-6}	3.2×10^{-6}	2.6×10^{-7}	1.6×10^{-6}	2.2×10^{-8}
Autumn	Atrazine	6.6×10^{-7}	1.5×10^{-7}	9.1×10^{-6}	2.1×10^{-6}	1.3×10^{-7}	3.0×10^{-8}	2.6×10^{-7}	6.0×10^{-8}
	Metolachlor	7.9×10^{-7}	7.3×10^{-9}	2.6×10^{-7}	2.4×10^{-9}	1.3×10^{-7}	1.2×10^{-9}	2.6×10^{-7}	2.4×10^{-9}
	Simazine	3.2×10^{-5}	8.5×10^{-8}	9.1×10^{-6}	8.4×10^{-7}	1.6×10^{-6}	1.5×10^{-7}	-	-
	Terbuthylazine	2.6×10^{-7}	-	1.3×10^{-8}	-	1.32×10^{-7}	-	-	-
	Total	3.4×10^{-5}	2.4×10^{-7}	1.8×10^{-5}	2.9×10^{-6}	2.0×10^{-6}	1.8×10^{-7}	5.2×10^{-7}	6.2×10^{-8}
Winter	Atrazine	6.60×10^{-10}	1.52×10^{-10}	3.52×10^{-10}	8.09×10^{-11}	1.80×10^{-10}	4.14×10^{-11}	8.81×10^{-11}	2.03×10^{-11}
	Metolachlor	4.40×10^{-10}	4.05×10^{-9}	5.28×10^{-10}	4.86×10^{-12}	4.40×10^{-11}	4.05×10^{-13}	4.40×10^{-11}	4.05×10^{-13}
	Simazine	9.51×10^{-8}	8.75×10^{-9}	1.63×10^{-9}	1.50×10^{-10}	6.16×10^{-10}	5.67×10^{-11}	-	-
	Terbuthylazine	9.51×10^{-8}	-	2.20×10^{-10}	-	8.81×10^{-11}	-	4.40×10^{-11}	-
	Total	1.9×10^{-7}	9.3×10^{-9}	2.7×10^{-9}	2.4×10^{-10}	9.2×10^{-10}	9.9×10^{-11}	1.8×10^{-10}	2.1×10^{-11}

ADD=average daily dose; CR=carcinogenic risks.

6.4 Conclusion

This chapter solely aimed at assessing the risks of emerging contaminants in water sources around Bloemfontein where there is no published data on environmental health risks of emerging contaminants. It can be concluded that the high individual and mixture ecological risks reported in this study may seriously impair the ecosystem and adversely affect aquatic species. Moreover, the high carcinogenic risk of atrazine is a serious public health concern as its exposure is associated with certain types of cancer. The findings of this study will raise awareness on the risks associated with exposure to emerging contaminants. It may also help in the development of environmental quality standards for regulatory purposes, environmental sustainability, as well as risk reduction. It is recommended that regular monitoring of chemicals in water sources be implemented around the area to protect the health of the living organisms. Wastewater treatment managers should also incorporate risk assessment before discharging the effluent into nearby streams.

Chapter 7

SOURCE APPORTIONMENT OF EMERGING CONTAMINANT POLLUTION IN WATER SOURCES AND THEIR MITIGATION STRATEGIES

Multivariate statistical methods have become widely used in pollution source apportionment in recent years as they are useful in determining the sources of chemical contaminants in water environments, which in turn provide valuable insights into effective preventative measures and controls against emerging contaminant pollution. Therefore, this chapter presents and discusses the sources of emerging contaminants based on multivariate statistical analysis such as the Pearson correlation coefficient analysis, the hierarchical cluster analysis and PCA. It also discusses the possible mitigation measures based on the sources identified in this study.

7.1 Introduction

Water is a treasured and limited resource that is essential for the survival of all known life forms (Bonecker et al., 2020; Isah et al., 2013). Dams, rivers and lagoons are important water sources for both human welfare and aquatic life (Isah et al., 2013). They are critical for domestic use, agricultural endeavours, industrial growth, leisure and aquatic habitation and reproduction (Ma et al., 2020). The majority of urban areas were built on or near freshwater sources (Bonecker et al., 2020). As a result of industrialisation and population growth, various pollutants such as emerging contaminants from manufacturing, WWTPs, agricultural practises and household tasks find their way into water sources, contaminating and degrading their quality (Wang et al., 2015). Many urban areas have high levels of production and consumption of emerging contaminants as a result of economic development and population growth (Yang et al., 2014). The occurrence of emerging contaminants (i.e. steroid hormones, personal care products, pesticides and pharmaceuticals) in water sources have become widespread and of great concern in recent years due to their high potency and specificity of undesirable ecological effects when interacting with biological systems and human society (Huang et al., 2023). Ma et al. (2020) also stated that their presence in water sources not only endangers aquatic and human life, but also impedes public and monetary development.

South Africa currently uses mostly surface water, with groundwater accounting for only 15% of the total water consumption (Sililo et al., 2001). The land use in Bloemfontein and its

surrounding areas is primarily urban, industrial and agricultural (Pretorius et al., 2005). Oke and Alowo (2021) found that there have been changes, trends and threats to water resources in the area as a result of population growth and urbanisation. Changes such as population growth and urbanisation have been reported to cause pollution, causing water sources to gradually lose their original quality state, hydromorphological characteristics and be accumulated by concentrations of pollutants (e.g., emerging contaminants) which may trigger undesirable effects on the aquatic ecosystem (Lin et al., 2020) and threaten the sustainability of high-quality water supplies (Enyigwe et al., 2022). Moreover, the WHO (2017) stated that the countries with the most limited access to drinking water are primarily those in sub-Saharan Africa, including South Africa. Water resources in South Africa are scarce and unevenly distributed. It is expected that competition for water among users will intensify in the near future. As a result, monitoring water quality and emerging contaminant pollution in water sources is critical in preventing water pollution and implementing corrective measures (Ma et al., 2020).

While the quantity of researches investigating and monitoring the presence of emerging contaminants in South African water environments has increased (Madikizela and Ncube, 2021; Madikizela et al., 2020; Mashile et al., 2021; Ojemaye et al., 2022; Vumazonke et al., 2020; Wilkinson et al., 2022), there is still a dearth of studies monitoring emerging contaminants in the Free State province, which is the host of the city of Bloemfontein. Furthermore, water sources face substantial risks from both point and nonpoint sources pollution, which act as major pathways for the enrichment of emerging contaminants in water sources. Nevertheless, there are no published studies determining the sources of emerging contaminants in water sources around Bloemfontein. Multivariate statistical methods have become widely used in pollution source apportionment in recent years (Chen et al., 2015, 2016; Enyigwe et al., 2022; Selvaraju et al., 2013; Shrestha and Kazama, 2007; Wang et al., 2015). They are useful in determining the source of chemical contaminants in water environments (Ma et al., 2020) which in turn, provide valuable insights into effective preventative measures and controls against emerging contaminant pollution (Hong et al., 2023).

Therefore, in this chapter, the researcher presents and discusses the sources of emerging contaminant pollution in various water sources. The possible mitigation strategies based on the sources identified in this study will also be presented and discussed. To trace the sources of emerging contaminant pollution in water sources, the following statistical methods were used in this study: Pearson correlation coefficient analysis, hierarchical cluster analysis, and PCA. The outcomes of this research may be very crucial in preventing water

pollution from emerging contaminants for the protection and sustainability of the water sources around Bloemfontein.

7.2 Pollution source profiling

Emerging contaminants are introduced into the water environment through various sources and pathways. They can be discharged into the water environment either from a point source or nonpoint source (Chen et al., 2012; Stefanakis and Becker, 2016). From the field survey (Table 7.1), the main possible source of pollution for emerging contaminants around the city of Bloemfontein include point sources such as household waste, sewage runoff, septic tanks, industrial activities, agricultural activities and wastewater effluents containing domestic, industrial and hospital wastewater. Moreover, some rivers are near the highway roads, passes through settlements and urban areas. Therefore, runoff from roads, settlements, and parks may be attributed as nonpoint sources in this study (Stefanakis and Becker, 2016). It should be noted that a definitive signature of a source may not exist because pollutant emissions rely on many factors that may vary significantly during the transportation process. In addition, source profiles may also be affected by physical, chemical and biological degradation of water quality variables before they enter the receptor sites. So the bias is reasonable between the emission profiles and loading factors (Chen et al., 2012).

Table 7.1 Sampling points around the study area

Item	Sample identity	Coordinates			Site description
		Latitude	Longitude	Elevation	
Surface water (Dam)					
1	SWMSO1	29°01'4.9" S	26°24'2.7" E	1 344 m	It serves as a resort and conference centre. Few houses with septic tanks nearby.
2	SWMD02	29°02'8.4" S	26°27'5.8" E	1 354 m	It also serves as a resort. Surrounded by farm houses with septic tanks.
3	SWKD08	28°53'03" S	25°57'21" E	1 226 m	Few houses, fishing activities and some agricultural fields.
4	SWSD09	29°12'10" S	26°47'38" E	1 460 m	Approximately 1 km away from residential area. Household waste is dumped nearby. Sewage runoff directed to the dam.
5	SWRUSD10	29°16'20" S	26°37'00" E	1 370 m	Around agricultural areas. A few houses near the dam. Aquatic sports.
Surface water (River)					
6	SWRS03	29°06'9.6" S	26°19'7.2" E	1 379 m	Intense agricultural activities within a 500 m range. Near national and regional roads.
7	SWBS04	29°07'2.4" S	26°17'1.5" E	1 390 m	It is close to wastewater treatment work. Bisect residential and industrial areas.
8	SWKOR05	29°12'8.3" S	26°31'0.4" E	1 334 m	Around agricultural activities, farm houses and old mechanical workshop.
9	SWMOR06	29°09'39.3" S	26°34'20.3" E	1 327 m	Near a national road and railway line.
10	SWKLM07	29°14'34.3" S	26°40'26.2" E	1 373 m	It passes through a township, receives wastewater effluent, and polluted by domestic waste.
Wastewater treatment plants					
11	WWTP01I	29°05'29" S	26°19'12" E	1 386 m	Receives domestic, industrial and hospital wastewater.

Item	Sample	Coordinates			Site description
12	WWTP01E	29°05'51" S	26° 19' 33" E	1 384 m	Discharged to Bloemspruit.
13	WWTP02I	29°14'2.8" S	26° 41'12.9" E	1 380 m	Receives domestic, industrial and hospital wastewater.
14	WWTP02E	29°14'25.4" S	26°41' 6.2" E	1 376 m	Discharged to Klein Modder River.
15	WWTP03I	29°07'27.4" S	26°14' 46.7" E	1 558 m	Receives domestic, industrial and hospital wastewater.
16	WWTP03E	29°07'31.8" S	26°14'51.8" E	1 364 m	Discharged to Bloemspruit.
Treated drinking water					
17	TWWRUS01	29°16'31" S	26°37'51" E	1 366 m	Supplied by Rustfontein dam. Supply water to Botshabelo Township.
18	TWWMSP02	29°01'10.3" S	26°24'9.2" E	1 339 m	Supplied by Maselspoort dam. Supply water to the city of Bloemfontein.

7.3 Identification of pollution source with Pearson correlation coefficient analysis

The Pearson correlation analysis was performed to establish emerging contaminant relationships and make inferences on their sources of origin. When the degree of correlation (r) was >0.7 , it was regarded as strong; $0.5 < r < 0.7$ connoted a moderate correlation; and <0.5 suggested weak correlations (Li et al., 2023b). As stated by Zhao et al. (2019) and Mugudamani et al. (2022), a good correlation between contaminants suggests a possible common sources or similar chemical behaviour. The results of the Pearson correlation analysis in this study are discussed as per the water sources.

7.3.1 Identification of pollution source in rivers

Table 7.2 and 7.3 shows the Pearson correlation matrix of the emerging contaminants in rivers during the wet season (spring and summer) and the dry season (autumn and winter).

In the spring season, a strong correlation among the contaminants was between terbutylazine and atrazine; carbamazepine and atrazine; metolachlor and atrazine; ibuprofen and carbamazepine; 17- α -ethinyl-estradiol and atrazine; 17- α -ethinyl-estradiol and carbamazepine, as well as between 17- α -ethinyl-estradiol and metolachlor (Table 7.2).

In the summer season, as represented by the bold numbers in Table 7.2, the analysis produced a strong positive correlation between atrazine and simazine; terbutylazine and simazine; terbutylazine and atrazine; metolachlor and simazine; metolachlor and atrazine; metolachlor and terbutylazine; ibuprofen and carbamazepine; 17- α -ethinyl-estradiol and metolachlor; 17- α -ethinyl-estradiol and simazine; 17- α -ethinyl-estradiol and atrazine; 17- α -ethinyl-estradiol and terbutylazine; 17- α -ethinyl-estradiol and metolachlor, as well as between 17- α -ethinyl-estradiol and ibuprofen (Table 7.2).

Table 7.2 Correlation coefficients among emerging contaminants during the wet season in rivers

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

Notation: Numbers in bold represent a strong correlation.

In the autumn season, there was a strong correlation between atrazine and simazine; terbutylazine and simazine; terbutylazine and atrazine; carbamazepine and simazine; carbamazepine and atrazine; carbamazepine and terbutylazine; metolachlor and atrazine; metolachlor and terbutylazine; metolachlor and carbamazepine; 17-alpha-ethinyl-estradiol and simazine; 17-alpha-ethinyl-estradiol and atrazine; 17-alpha-ethinyl-estradiol and terbutylazine; 17-alpha-ethinyl-estradiol and carbamazepine and 17-alpha-ethinyl-estradiol and metolachlor (Table 7.3).

In the winter season, the strong correlation was between terbutylazine and atrazine; metolachlor and simazine; ibuprofen and simazine; ibuprofen and metolachlor; 17-alpha-ethinyl-estradiol and atrazine; 17-alpha-ethinyl-estradiol and terbutylazine and 17-alpha-ethinyl-estradiol and metolachlor (Table 7.3).

Table 7.3 Correlation coefficients among emerging contaminants during the dry season in rivers

Contaminants	Acetaminophen	Simazine	Atrazine	Terbutylazine	Carbamazepine	Metolachlor	Testosterone	Progesterone	Ibuprofen	Estradiol	Triclosan	17-alpha-ethinylestradiol
Autumn												
Acetaminophen	1											
Simazine	0.00	1										
Atrazine	0.00	0.74	1									
Terbutylazine	0.00	0.98	0.82	1								
Carbamazepine	0.00	0.74	0.86	0.85	1							
Metolachlor	0.00	0.60	0.93	0.71	0.93	1						
Testosterone	0.00	0.00	0.00	0.00	0.00	0.00	1					
Progesterone	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1				
Ibuprofen	0.00	0.23	0.24	0.35	0.39	0.20	0.00	0.00	1			
Estradiol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1		
Triclosan	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1	
17-alpha-ethinylestradiol	0.00	0.91	0.78	0.95	0.93	0.78	0.00	0.00	0.31	0.00	0.00	1
Winter												
Acetaminophen	1											
Simazine	-0.25	1										
Atrazine	-0.31	0.12	1									
Terbutylazine	-0.36	0.32	0.98	1								
Carbamazepine	0.07	0.34	0.30	0.36	1							
Metolachlor	-0.38	0.94	0.46	0.63	0.43	1						
Testosterone	0.00	0.00	0.00	0.00	0.00	0.00	1					
Progesterone	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1				
Ibuprofen	0.29	0.83	0.15	0.31	0.52	0.77	0.00	0.00	1			
Estradiol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1		
Triclosan	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1	
17-alpha-ethinylestradiol	-0.30	0.53	0.80	0.88	0.74	0.76	0.00	0.00	0.54	0.00	0.00	1

Notation: Numbers in bold represent a strong correlation.

Generally, in this study, these strong positive correlations may be an indication of the same sources of pollution, potentially from man-made activities such as agricultural activities, wastewater effluents, poor waste management, industrial, roads and nearby household runoffs. The strong positive correlation witnessed between pesticides such as atrazine and simazine; terbutylazine and atrazine; terbutylazine and simazine; metolachlor and simazine; metolachlor and atrazine and metolachlor and terbutylazine may be attributed to agricultural activities, wastewater effluents and stormwater runoff (runoff from roads, settlements and urban areas). Most of the rivers are surrounded by agricultural activities producing maize, soy beans, wheat, sorghum, and sunflower, which compel the use of herbicides before, during and after farming to manage unwanted weeds. Moreover, the city of Bloemfontein is a developed area with well-built highways, a civic country park, industrial areas and golf clubs. With all these evident spaces, substantial quantities of herbicides are utilised to manage unwanted plants (weeds) in paved areas, gardens, country parks, golf clubs, waysides, office blocks and industrial areas. Therefore, wastewater or runoff from these areas may be attributed as the possible source of these herbicides in nearby streams.

The strong positive correlations between compounds such as ibuprofen and carbamazepine; 17- α -ethinyl-estradiol and ibuprofen and 17- α -ethinyl-estradiol and carbamazepine also suggest similar sources of origin. These contaminants are medicinal drugs and their origin can be linked to wastewater effluents and illegal dumping of household waste nearby streams. Wastewater treatment plants receive domestic, industrial and hospital wastewater that contain loads of various pharmaceutical compounds used in daily lives. As WWTPs are not intended to eliminate these organic substances, they may end up in rivers due to wastewater effluent discharge. Illegal dumping of domestic wastes containing unused or expired drugs may also introduce traces of these compounds. Moreover, the strong positive correlations between contaminants such as carbamazepine and atrazine; carbamazepine and simazine; carbamazepine and terbuthylazine; metolachlor and carbamazepine; ibuprofen and metolachlor; ibuprofen and simazine; 17- α -ethinyl-estradiol and atrazine; 17- α -ethinyl-estradiol and simazine; 17- α -ethinyl-estradiol and terbuthylazine and 17- α -ethinyl-estradiol and metolachlor are an indication of similar sources of their emissions. Some of the rivers run through townships and cities; hence, runoff from clogged sewage systems or improper waste disposal may have introduced these contaminants into rivers. Additionally, because the selected WWTPs receive wastewater from households, industries and hospitals, their wastewater effluents discharged into these rivers may introduce traces of these emerging contaminants generally categorised as medicinal drugs and pesticides.

7.3.2 Identification of pollution sources in dams and or reservoirs

From the correlation analysis in Table 7.4, the spring season showed strong positive correlations between pairs of terbuthylazine and simazine; terbuthylazine and atrazine; carbamazepine and acetaminophen; metolachlor and simazine; metolachlor and atrazine; metolachlor and terbuthylazine; ibuprofen and acetaminophen; ibuprofen and carbamazepine; 17- α -ethinyl-estradiol and acetaminophen and 17- α -ethinyl-estradiol and carbamazepine. During the summer season, strong positive correlations were witnessed between pairs of atrazine and simazine; terbuthylazine and simazine; terbuthylazine and atrazine; carbamazepine and terbuthylazine; metolachlor and atrazine; and 17- α -ethinyl-estradiol and carbamazepine (Table 7.4).

Table 7.4 Correlation coefficients among emerging contaminants during the wet season in dams

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

Notation: Numbers in bold represent a strong correlation.

In the autumn season, strong positive correlations between atrazine and simazine; terbuthylazine and simazine; terbuthylazine and atrazine; metolachlor and simazine; metolachlor and atrazine; metolachlor and terbuthylazine; ibuprofen and atrazine; 17-alpha-ethinyl-estradiol and carbamazepine, and 17-alpha-ethinyl-estradiol and ibuprofen was witnessed, as shown in bold in Table 7.5. The winter season had strong positive correlations between pairs of terbuthylazine and simazine; metolachlor and simazine; metolachlor and terbuthylazine, as well as 17-alpha-ethinyl-estradiol and terbuthylazine (Table 7.5).

Table 7.5 Correlation coefficients among emerging contaminants during the dry season in dams

Contaminants	Aceta- minophen	Simazine	Atrazine	Terbu- thylazine	Carba- mazepine	Metola- chlor	Testos- terone	Proges- terone	Ibuprofen	Estradiol	Triclosan	17-alpha- ethinyl- estradiol
Autumn												
Acetaminophen	1											
Simazine	-0.25	1										
Atrazine	-0.41	0.89	1									
Terbuthylazine	-0.27	0.99	0.86	1								
Carbamazepine	-0.45	-0.23	0.22	-0.24	1							
Metolachlor	-0.24	0.81	0.83	0.86	0.14	1						
Testosterone	0.00	0.00	0.00	0.00	0.00	0.00	1					
Progesterone	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1				
Ibuprofen	-0.49	0.41	0.77	0.33	0.67	0.41	0.00	0.00	1			
Estradiol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1		
Triclosan	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1	
17-alpha-ethinyl- estradiol	-0.29	-0.20	0.27	-0.24	0.96	0.11	0.00	0.00	0.76	0.00	0.00	1

Acetaminophen	1											
Simazine	0.00	1										
Atrazine	0.00	0.05	1									
Terbuthylazine	0.00	0.84	-0.24	1								
Carbamazepine	0.00	0.35	0.48	0.38	1							
Metolachlor	0.00	0.97	0.20	0.76	0.51	1						
Testosterone	0.00	0.00	0.00	0.00	0.00	0.00	1					
Progesterone	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1				
Ibuprofen	0.00	-0.08	-0.60	0.47	-0.06	-0.22	0.00	0.00	1			
Estradiol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1		
Triclosan	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1	
17-alpha-ethinyl- estradiol	0.00	0.61	-0.16	0.87	0.69	0.60	0.00	0.00	0.52	0.00	0.00	1

Notation: Numbers in bold represent a strong correlation.

Generally, the strong positive degree of correlations between herbicides such as terbuthylazine and simazine; metolachlor and atrazine; metolachlor and simazine; metolachlor and terbuthylazine; atrazine and simazine and terbuthylazine and atrazine indicate a similar source of origin. As mentioned by Wang et al. (2022), herbicides may be applied before and after planting to control broadleaf and grassy weeds in farming land. Considering that most of the dams are bordered by farming activities, runoff from those sites could be a contributory factor. Another strong positive correlation in dams were between ibuprofen and acetaminophen; carbamazepine and acetaminophen; ibuprofen and carbamazepine; 17-alpha-ethinyl-estradiol and carbamazepine; 17-alpha-ethinyl-estradiol and acetaminophen and 17-alpha-ethinyl-estradiol and ibuprofen, which suggest a similar source of origin. These emerging contaminants are medicinal drugs used to control seizures (carbamazepine); treat inflammatory diseases, arthritis, fever and dysmenorrhea (ibuprofen), pains, headaches, fever in humans and animals (acetaminophen) and are used as the active ingredients in many oral contraceptives and postmenopausal hormone therapies (17-alpha-ethinyl-estradiol) among many communities (Ekinici et al., 2020; Nannou, et al., 2022). Therefore, their strong positive correlations suggest that they are associated with similar

sources such as domestic sewage runoff from nearby communities witnessed during the field visit. Illegal dumping of medical waste from nearby households, during aquatic sports activities, conferences or picnics may also be attributed as one of their possible sources. Moreover, the strong positive correlations between contaminants such as 17-alpha-ethinyl-estradiol and simazine; ibuprofen and atrazine and carbamazepine and terbuthylazine may be linked to sources such as agricultural runoff and wastewater effluent discharged in rivers that recharge these dams.

7.3.3 Identification of pollution source in wastewater treatment plants

The analysis results of the Pearson correlation coefficients of targeted emerging contaminants in wastewater influents are presented in Table 7.6.

Table 7.6 Correlation coefficients among emerging contaminants during the wet season in influents

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

Notation: Numbers in bold represent a strong correlation.

During the spring season, the influent samples (Table 7.6) showed a strong positive correlation between atrazine and simazine; terbuthylazine and atrazine; carbamazepine and simazine; carbamazepine and terbuthylazine; metolachlor and simazine; metolachlor and terbuthylazine; metolachlor and carbamazepine; progesterone and testosterone; ibuprofen

and acetaminophen; ibuprofen and carbamazepine; ibuprofen and metolachlor; triclosan and simazine; triclosan and terbuthylazine; triclosan and carbamazepine; triclosan and metolachlor; triclosan and ibuprofen and 17-alpha-ethinyl-estradiol and testosterone. In the summer season, the strong positive correlations were witnessed between atrazine and simazine; terbuthylazine and simazine; terbuthylazine and atrazine; metolachlor and atrazine; metolachlor and terbuthylazine; testosterone and acetaminophen; ibuprofen and atrazine; ibuprofen and terbuthylazine; ibuprofen and metolachlor; estradiol and progesterone; triclosan and carbamazepine; 17-alpha-ethinyl-estradiol and carbamazepine; and 17-alpha-ethinyl-estradiol and triclosan.

Table 7.7 Correlation coefficients among emerging contaminants during the dry season in influents

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

Notation: Numbers in bold represent a strong correlation.

In the autumn season (Table 7.7), the results showed strong positive correlations between contaminants such as terbuthylazine and atrazine; carbamazepine and acetaminophen; metolachlor and atrazine; metolachlor and terbuthylazine; testosterone and acetaminophen; testosterone and carbamazepine; progesterone and acetaminophen; progesterone and carbamazepine; progesterone and testosterone; ibuprofen and acetaminophen; ibuprofen and carbamazepine; ibuprofen and testosterone; ibuprofen and progesterone; triclosan and

acetaminophen; triclosan and carbamazepine; triclosan and testosterone; triclosan and progesterone; triclosan and ibuprofen; 17-alpha-ethinyl-estradiol and acetaminophen; 17-alpha-ethinyl-estradiol and carbamazepine; 17-alpha-ethinyl-estradiol and testosterone; 17-alpha-ethinyl-estradiol and progesterone; 17-alpha-ethinyl-estradiol and ibuprofen and 17-alpha-ethinyl-estradiol and triclosan. The winter season revealed a strong positive correlation between atrazine and simazine; terbuthylazine and simazine; terbuthylazine and atrazine; metolachlor and simazine; metolachlor and atrazine; progesterone and acetaminophen; ibuprofen and acetaminophen; 17-alpha-ethinyl-estradiol and carbamazepine; 17-alpha-ethinyl-estradiol and testosterone as well as 17-alpha-ethinyl-estradiol and ibuprofen (Table 7.7).

Generally, in wastewater influent, strong positive correlations between atrazine and simazine; terbuthylazine and atrazine; terbuthylazine and simazine; metolachlor and simazine; metolachlor and terbuthylazine and metolachlor and atrazine were witnessed, which is an indication of similar man-made sources. These contaminants are herbicides mostly used in industrial areas, roadsides and public squares to control weeds. Wastewater treatment plants in this area receive municipal domestic wastewater from all residents, industrial areas, including fruit and vegetable cleaning areas. Therefore, their sources may be linked to industrial wastewater and runoff from roadsides, industrial, residential and public squares. There was also strong positive correlations between medicinal drugs such as carbamazepine and acetaminophen; testosterone and acetaminophen; progesterone and testosterone; progesterone and acetaminophen; progesterone and carbamazepine; ibuprofen and acetaminophen; ibuprofen and carbamazepine; ibuprofen and testosterone; ibuprofen and progesterone; estradiol and progesterone; testosterone and carbamazepine; 17-alpha-ethinyl-estradiol and testosterone; 17-alpha-ethinyl-estradiol carbamazepine; 17-alpha-ethinyl-estradiol and ibuprofen; 17-alpha-ethinyl-estradiol and acetaminophen and 17-alpha-ethinyl-estradiol and progesterone. These correlations indicate that these contaminants are probably derived from the same anthropogenic sources such as hospital and domestic wastewaters. The strong positive correlations between compounds under pharmaceuticals and personal care product groups such as triclosan and carbamazepine; triclosan and acetaminophen; triclosan and ibuprofen; triclosan and testosterone; triclosan and progesterone, and 17-alpha-ethinyl-estradiol and triclosan may also be linked to hospital and domestic wastewater received by these WWTPs. Other emerging contaminants such as carbamazepine and simazine; carbamazepine and terbuthylazine; metolachlor and carbamazepine; ibuprofen and metolachlor; ibuprofen and atrazine; ibuprofen and terbuthylazine; triclosan and simazine; triclosan and terbuthylazine and triclosan and metolachlor also showed the strong positive correlations. Their strong positive correlations

are an indication of similar sources such as surface runoff, domestic, industrial and hospital wastewater.

In effluent samples during the spring season, there was the strong positive correlations between terbutylazine and simazine; terbutylazine and atrazine; metolachlor and simazine; metolachlor and atrazine; metolachlor and terbutylazine; testosterone and atrazine; testosterone and terbutylazine; ibuprofen and atrazine; ibuprofen and testosterone; estradiol and ibuprofen; triclosan and carbamazepine; triclosan and progesterone; 17-alpha-ethinyl-estradiol and simazine; 17-alpha-ethinyl-estradiol and terbutylazine; as well as 17-alpha-ethinyl-estradiol and metolachlor as presented in Table 7.8. The summer season revealed strong positive correlations between atrazine and simazine; terbutylazine and atrazine; carbamazepine and acetaminophen; testosterone and acetaminophen; testosterone and carbamazepine; testosterone and metolachlor; ibuprofen and acetaminophen; ibuprofen and testosterone; estradiol and progesterone; triclosan and acetaminophen; triclosan and carbamazepine; triclosan and metolachlor; triclosan and testosterone; triclosan and ibuprofen; 17-alpha-ethinyl-estradiol and acetaminophen; 17-alpha-ethinyl-estradiol and testosterone; 17-alpha-ethinyl-estradiol and ibuprofen; and 17-alpha-ethinyl-estradiol and triclosan (Table 7.8).

Table 7.8 Correlation coefficients among emerging contaminants during the wet season in effluents

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

estradiol

Notation: Numbers in bold represent a strong correlation.

The autumn season showed strong positive correlations between atrazine and simazine; terbuthylazine and simazine; terbuthylazine and atrazine; carbamazepine and atrazine; carbamazepine and terbuthylazine; metolachlor and simazine; metolachlor and atrazine; metolachlor and terbuthylazine; metolachlor and carbamazepine; testosterone and acetaminophen; ibuprofen and acetaminophen; ibuprofen and testosterone and 17-alpha-ethinyl-estradiol and simazine (Table 7.9). In the winter season, the strong positive correlations were between carbamazepine and terbuthylazine; metolachlor and atrazine as well as ibuprofen and carbamazepine (Table 7.9).

Table 7.9 Correlation coefficients among emerging contaminants during the dry season in effluents

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

Notation: Numbers in bold represent a strong correlation.

The presence of emerging contaminants in wastewater effluent may be attributed mainly to their inefficient removal in influents. The general results of the correlation matrix in effluent samples showed strong positive correlations between terbuthylazine and simazine; terbuthylazine and atrazine; metolachlor and simazine; metolachlor and terbuthylazine; metolachlor and atrazine and atrazine and simazine, which suggest similar sources. These

contaminants are herbicides which possibly may have been introduced into WWTPs by wastewater from industrial and settlement areas. The strong positive correlations between ibuprofen and testosterone; estradiol and ibuprofen; progesterone and carbamazepine; ibuprofen and acetaminophen; ibuprofen and carbamazepine; carbamazepine and acetaminophen; testosterone and acetaminophen; testosterone and carbamazepine; 17-alpha-ethinyl-estradiol and acetaminophen; 17-alpha-ethinyl-estradiol and testosterone and 17-alpha-ethinyl-estradiol and ibuprofen, which are pharmaceutical products that may have been introduced into WWTPs by domestic and hospital wastewater received in these treatment plants. This can be supported by the fact that these contaminants are medicinal drugs mostly found in hospitals and many homes for the treatment of various diseases. The strong positive correlations between contaminants such as triclosan and carbamazepine; triclosan and acetaminophen; triclosan and ibuprofen; triclosan and testosterone; triclosan and progesterone and 17-alpha-ethinyl-estradiol and triclosan, which are pharmaceuticals and personal care products that may be linked to domestic and hospital wastewater received in this WWTPs. The strong positive relationships between other contaminants such as 17-alpha-ethinyl-estradiol and simazine; 17-alpha-ethinyl-estradiol and terbuthylazine; 17-alpha-ethinyl-estradiol and metolachlor; carbamazepine and terbuthylazine; carbamazepine and atrazine; carbamazepine and terbuthylazine; metolachlor and acetaminophen; metolachlor and carbamazepine; ibuprofen and atrazine; testosterone and atrazine; testosterone and terbuthylazine, and testosterone and metolachlor may also be linked to stormwater runoff, hospital, domestic and industrial wastewater entering these treatment plants.

7.3.4 Identification of pollution source in treated drinking water

The Pearson correlation analysis (Table 7.10) revealed that most of the emerging contaminants had some strong positive correlations in the spring season. There was strong positive correlations between compounds such as simazine and acetaminophen; terbuthylazine and atrazine; carbamazepine and acetaminophen; carbamazepine and simazine; metolachlor and acetaminophen; metolachlor and simazine; metolachlor and carbamazepine; ibuprofen and acetaminophen; ibuprofen and simazine; ibuprofen and carbamazepine; ibuprofen and metolachlor; 17-alpha-ethinyl-estradiol and acetaminophen; 17-alpha-ethinyl-estradiol and simazine; 17-alpha-ethinyl-estradiol and carbamazepine; 17-alpha-ethinyl-estradiol and metolachlor and 17-alpha-ethinyl-estradiol and ibuprofen. During the summer season, atrazine and simazine; terbuthylazine and simazine; terbuthylazine and atrazine; metolachlor and simazine; metolachlor and atrazine; metolachlor and terbuthylazine; 17-alpha-ethinyl-estradiol and simazine; 17-alpha-ethinyl-estradiol and

atrazine; 17-alpha-ethinyl-estradiol and terbuthylazine and 17-alpha-ethinyl-estradiol and metolachlor showed strong positive correlations as shown in bold in Table 7.10.

Table 7.10 Correlation coefficients among emerging contaminants during the wet season in treated drinking water

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

Notation: Numbers in bold represent a strong correlation.

Both the autumn and winter seasons showed strong positive correlations between terbuthylazine and atrazine; metolachlor and atrazine; metolachlor and terbuthylazine; 17-alpha-ethinyl-estradiol and atrazine; 17-alpha-ethinyl-estradiol and terbuthylazine and 17-alpha-ethinyl-estradiol and metolachlor (Table 7.11).

Table 7.11 Correlation coefficients among emerging contaminants during the dry season in treated drinking water

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

Notation: numbers in bold represent strong correlation.

Generally, there was strong positive relationships between pairs of herbicides such as terbuthylazine and atrazine; terbuthylazine and simazine; atrazine and simazine; metolachlor and simazine; metolachlor and atrazine and metolachlor and terbuthylazine, which indicate that they were probably derived from the same anthropogenic sources. Application of herbicides in surrounding agricultural fields, in lawns around the dams, and paved areas for management of weeds, may lead to their introduction in reservoirs or dams (considered as the water source for water treatment plants) as a result of agricultural runoff and stormwater runoff from lawns used for picnics or paved areas around the dams. Consequently, they are detected in treated drinking water. The strong positive relationships between pairs of carbamazepine and acetaminophen; ibuprofen and acetaminophen; ibuprofen and carbamazepine; 17-alpha-ethinyl-estradiol and acetaminophen; 17-alpha-ethinyl-estradiol and carbamazepine and 17-alpha-ethinyl-estradiol and ibuprofen which are medicinal drugs clearly suggest same sources of origin which may possibly be illegal dumping of medical drugs during conference, fishing and other aquatic sports in dams considered as the water source for water treatment plants. Rivers that receive wastewater effluents may introduce traces of emerging contaminants in dams which eventually can be traced in treated drinking

water. Moreover, the strong positive correlations between simazine and acetaminophen; carbamazepine and simazine; metolachlor and acetaminophen; metolachlor and carbamazepine; ibuprofen and simazine; ibuprofen and metolachlor; simazine and acetaminophen; 17-alpha-ethinyl-estradiol and simazine; 17-alpha-ethinyl-estradiol and metolachlor; 17-alpha-ethinyl-estradiol and atrazine, and 17-alpha-ethinyl-estradiol and terbutylazine may be indicative of similar man-made sources such as stormwater runoff, agricultural runoff, wastewater effluents or illegal dumping of medical waste around some of the dams.

7.4 Identification of pollution sources using hierarchical cluster analysis

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

7.4.1 Identification of pollution source in rivers

The hierarchical cluster analysis in rivers clustered the 12 targeted emerging contaminants into four clusters in all seasons. In the spring season, Cluster 1 (C1) was characterised by one contaminant (simazine), which may be linked to wastewater effluent, agricultural runoff and urban surface runoff. Cluster 2 (C2) was a combination of seven contaminants (carbamazepine, atrazine, progesterone, testosterone, metolachlor, terbutylazine and estradiol), possibly from wastewater treatment effluent, agricultural runoff, illegal dumping and urban surface runoff. Cluster 3 (C3) was made up of three contaminants (acetaminophen, triclosan and ibuprofen) which may be linked to wastewater treatment effluent and illegal dumping. Cluster 4 (C4) only had one contaminant (17-alpha-ethinyl-estradiol) which may be associated with wastewater treatment effluent and illegal dumping in the study area (Figure 7.1; Table 7.12). In summer, C1 was characterised by one contaminant (simazine), which may be linked to wastewater effluent, agricultural runoff and urban surface runoff. C2 was characterised by eight contaminants (acetaminophen, progesterone, testosterone, estradiol, metolachlor, atrazine, terbutylazine and triclosan), which may be linked to wastewater treatment effluent, agricultural runoff, illegal dumping and urban surface runoff. C3 had two contaminants (ibuprofen and carbamazepine), which may be linked to wastewater treatment effluent, and illegal dumping. C4 had one contaminant

(17- α -ethinyl-estradiol), which may be linked to wastewater treatment effluent and illegal dumping in this study (Figure 7.1; Table 7.12).

Moreover, as shown in Figure 7.2 and Table 7.12, sources of emerging contaminants were also identified during the autumn season, where C1 was seen with six contaminants (acetaminophen, metolachlor, progesterone, testosterone, atrazine and terbuthylazine), which may have been introduced by wastewater effluent, agricultural runoff, illegal dumping and urban surface runoff. C2 was dominated by three contaminants (estradiol, carbamazepine, and simazine), which may have been introduced by wastewater effluent, agricultural runoff, illegal dumping and urban surface runoff. Additionally, C3 had two contaminants (triclosan and ibuprofen) which were possibly a result of wastewater effluent, and C4 had one contaminant (17- α -ethinyl-estradiol), probably from wastewater effluent and illegal dumping. During the winter season, C1 was seen with nine contaminants (atrazine, terbuthylazine, metolachlor, acetaminophen, progesterone, testosterone, estradiol, simazine and carbamazepine), which link very well with wastewater effluent, illegal dumping, stormwater runoff, domestic sewage and agricultural runoff. C2 was characterised by triclosan, which may have been introduced in rivers by wastewater effluent and illegal dumping. The contaminants in C3 (ibuprofen) and C4 (17- α -ethinyl-estradiol) in rivers may also link very well to wastewater effluent and illegal dumping (Figure 7.2; Table 7.12).

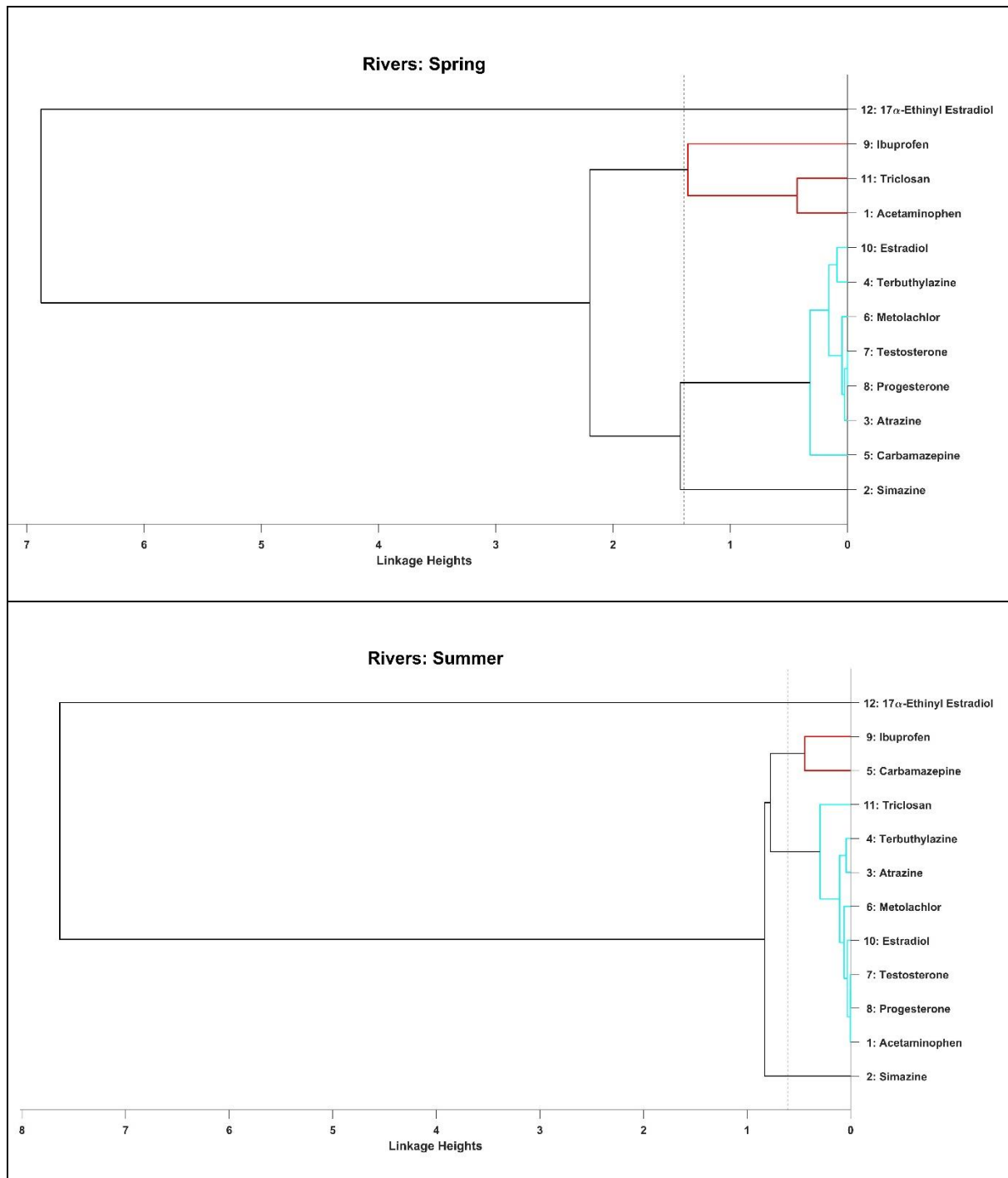


Figure 7.1 Cluster diagram showing similarities of emerging contaminants in rivers during the wet season

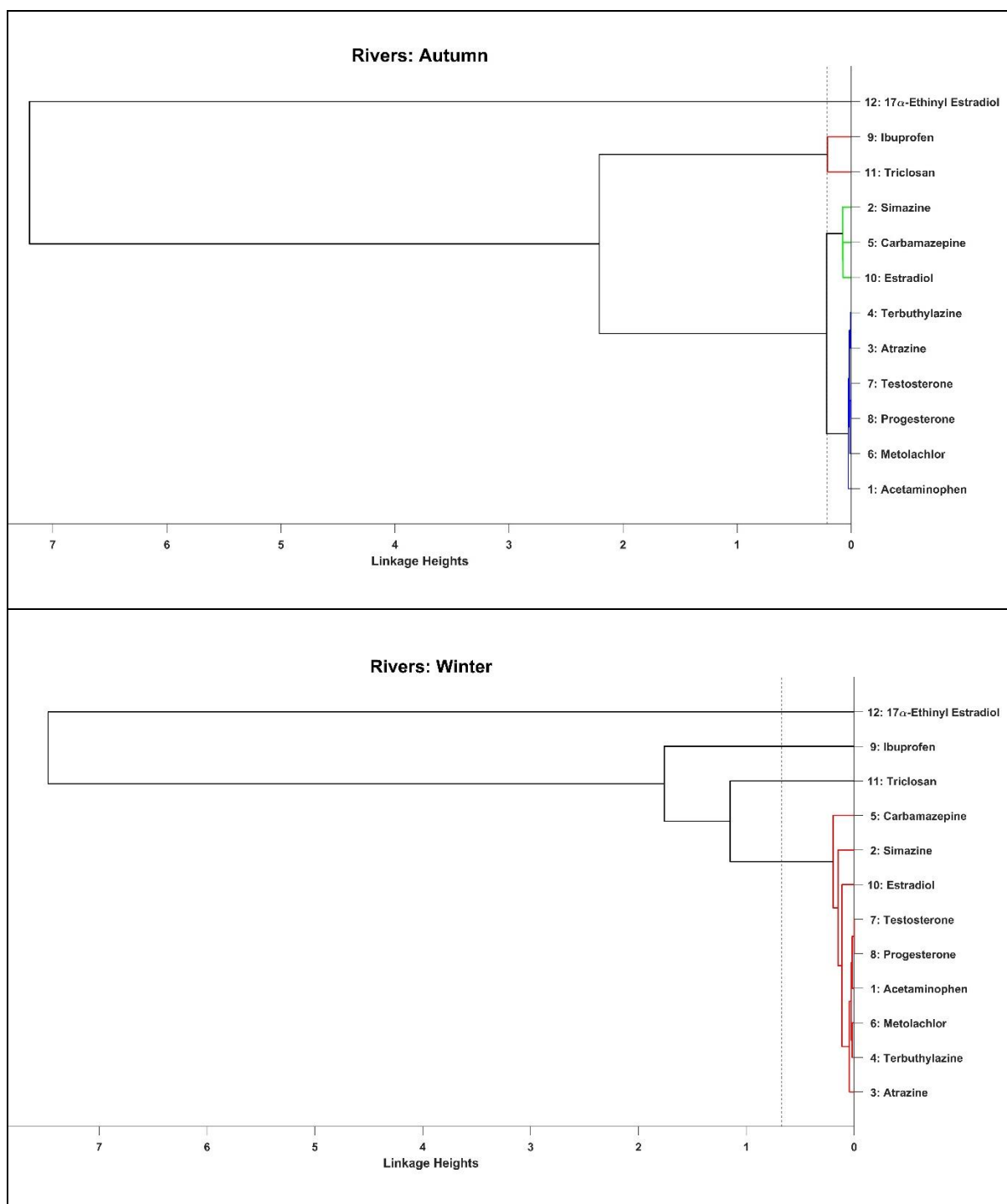


Figure 7.2 Cluster diagram showing similarities of emerging contaminants in rivers during the dry season

Agricultural activities (crop production) that surround most of the rivers around Bloemfontein may influence the occurrence of pesticides in rivers as a result of agricultural runoff. The use of herbicides to regulate unwanted weeds in paved spaces, community squares, gardens, golf courts and industrial areas in the city of Bloemfontein may also lead to the detection of

traces of herbicides due to urban stormwater runoff. In other studies, agricultural runoff and urban surface runoff were also identified as potential sources of pesticides in natural water sources (Hou et al., 2022; Yang et al., 2020). Moreover, it was also observed during field sampling that some farm houses had septic tanks, rivers received effluent from WWTPs, were surrounded by activities such as animal husbandry and were polluted by household wastes from nearby settlements. Therefore, it was reasonable to link emerging contaminants such as acetaminophen, ibuprofen, carbamazepine, estradiol, triclosan, progesterone, testosterone and 17-alpha-ethinyl-estradiol to domestic sewage (leakage from septic tanks at farm houses), discharge of wastewater effluents in streams, runoff from animal husbandry and illegal dumping of household waste (containing unused or expired drugs) nearby the streams. In many parts of the world, human activities such as crop production, animal husbandry, illegal dumping and wastewater effluents have been pin-pointed as main potential sources of many organic or chemical pollutants in water sources (Bella-Atangana et al., 2023; Das, 2022; Khan and Wen et al., 2021; Rashid et al., 2019, 2022).

7.4.2 Identification of pollution sources in dams and or reservoirs

The hierarchical cluster analysis in dams produced dendograms with four clusters in both the wet season (spring and summer) and the dry season (autumn and winter). During the spring season, two contaminants (ibuprofen and carbamazepine) are linked together in C1, which may be associated with wastewater effluent, domestic sewage and illegal dumping. In C2, six contaminants (acetaminophen, testosterone, metolachlor, simazine, terbutylazine and atrazine) were linked together which may have originated from wastewater effluent, illegal dumping, domestic sewage and agricultural runoff. In C3, three contaminants (estradiol, triclosan and progesterone) were linked together, possibly due to wastewater effluent, domestic sewage and illegal dumping. Cluster 4 was seen with one contaminant (17-alpha-ethinyl-estradiol) due to discharge of wastewater effluent, domestic sewage and illegal dumping around the area. In summer, C1 was linked with two contaminants (simazine and carbamazepine) which may be associated with wastewater effluent, illegal dumping, agricultural runoff and domestic sewage. C2 was linked with seven contaminants (acetaminophen, progesterone, testosterone, estradiol, metolachlor, atrazine and terbutylazine), likely emanating from wastewater effluent, illegal dumping, domestic sewage, agricultural runoff and urban surface runoff. C3 is linked with two contaminants (triclosan and ibuprofen), which may be associated with wastewater effluent, illegal dumping and domestic sewage. C4 is linked with only one contaminant (17-alpha-ethinyl-estradiol), which may be associated with wastewater effluent, illegal dumping, and domestic sewage (Figure 7.3; Table 7.12).

As shown in Figure 7.4 and Table 7.12, the hierarchical cluster analysis also produced four clusters in the autumn and winter seasons. During the autumn season, C1 was linked with nine contaminants (acetaminophen, testosterone, progesterone, atrazine, terbuthylazine, estradiol, metolachlor, ibuprofen and carbamazepine), which may be connected to wastewater effluent, illegal dumping, domestic sewage and agricultural runoff. C2 was linked with one contaminant (simazine), most likely from wastewater effluent and agricultural runoff. C3 was linked with one contaminant (triclosan), possibly from wastewater effluent, while C4 was also linked with one contaminant (17- α -ethinyl-estradiol), possibly from wastewater effluent, illegal dumping and domestic sewage. During the winter season, C1 was linked with seven contaminants (simazine, acetaminophen, progesterone, testosterone, metolachlor, terbuthylazine and estradiol) as a result of wastewater effluent, illegal dumping, domestic sewage and agricultural runoff. C2 was linked with two contaminants (carbamazepine and atrazine), which were likely a result of wastewater effluent, illegal dumping and agricultural runoff. C3 was also linked with two contaminants (triclosan and ibuprofen) which may be linked to wastewater effluent, illegal dumping and domestic sewage. C4 was linked with only one contaminant (17- α -ethinyl-estradiol), which may be connected to wastewater effluent, illegal dumping and domestic sewage (Figure 7.4; Table 7.12).

Around Bloemfontein, agricultural activities such as crop production and animal husbandry are the most prominent. Therefore, agricultural runoff may be a contributing element to the sign of some emerging contaminants in surface water such as dams. Hou et al. (2022) and Yang et al. (2020) reported agricultural runoff as one of the potential sources of organic contaminants in surface water sources. Illegal dumping of domestic wastes (unused or expired drugs) may also introduce traces of emerging contaminants in local reservoirs and dams, as some of them are open to the public for picnics, aquatic sports activities and events at conference centres. Illegal dumping of domestic wastes was also cited by other authors as one of the potential sources of chemical water contamination (Rashid et al., 2019, 2022). There was a raw sewage runoff from a nearby settlement flowing into one of the dams during fieldwork, which may have contributed to traces of some pharmaceuticals, steroid hormones and personal care products. Many studies have also reported urban sewage and domestic wastewater discharge as main potential sources of many chemical pollutants in water sources (Bella-Atangana et al., 2023; Das, 2022; Rashid et al., 2022). According to Gosset et al. (2021), emerging contaminants are continuously released in trace amounts into receiving streams due to inefficiency of WWTPs to remove them. Considering this case, these contaminants end up being introduced into local reservoirs and dams during the recharging period.

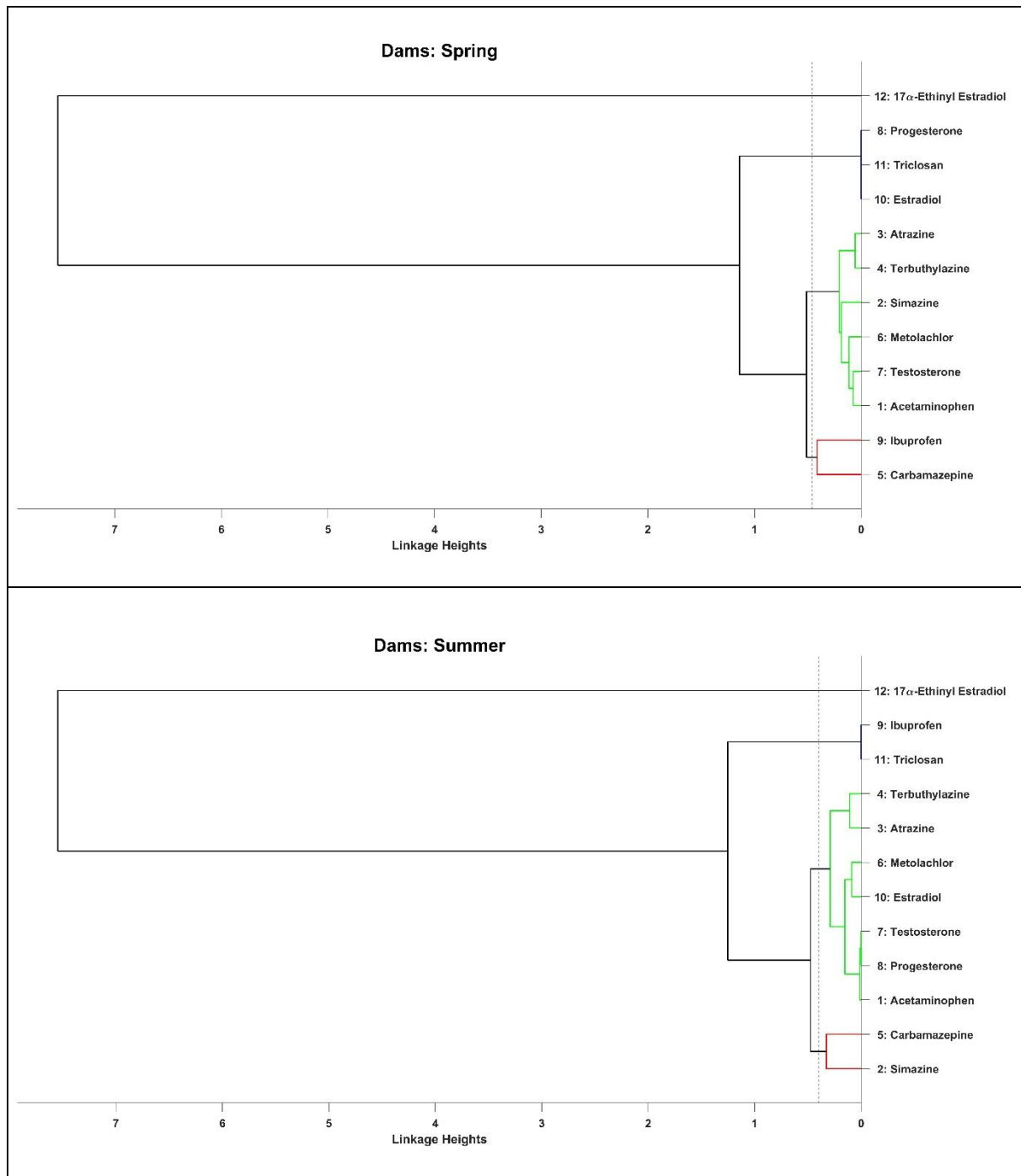


Figure 7.3 Cluster diagram showing similarities of emerging contaminants in dams during the wet season

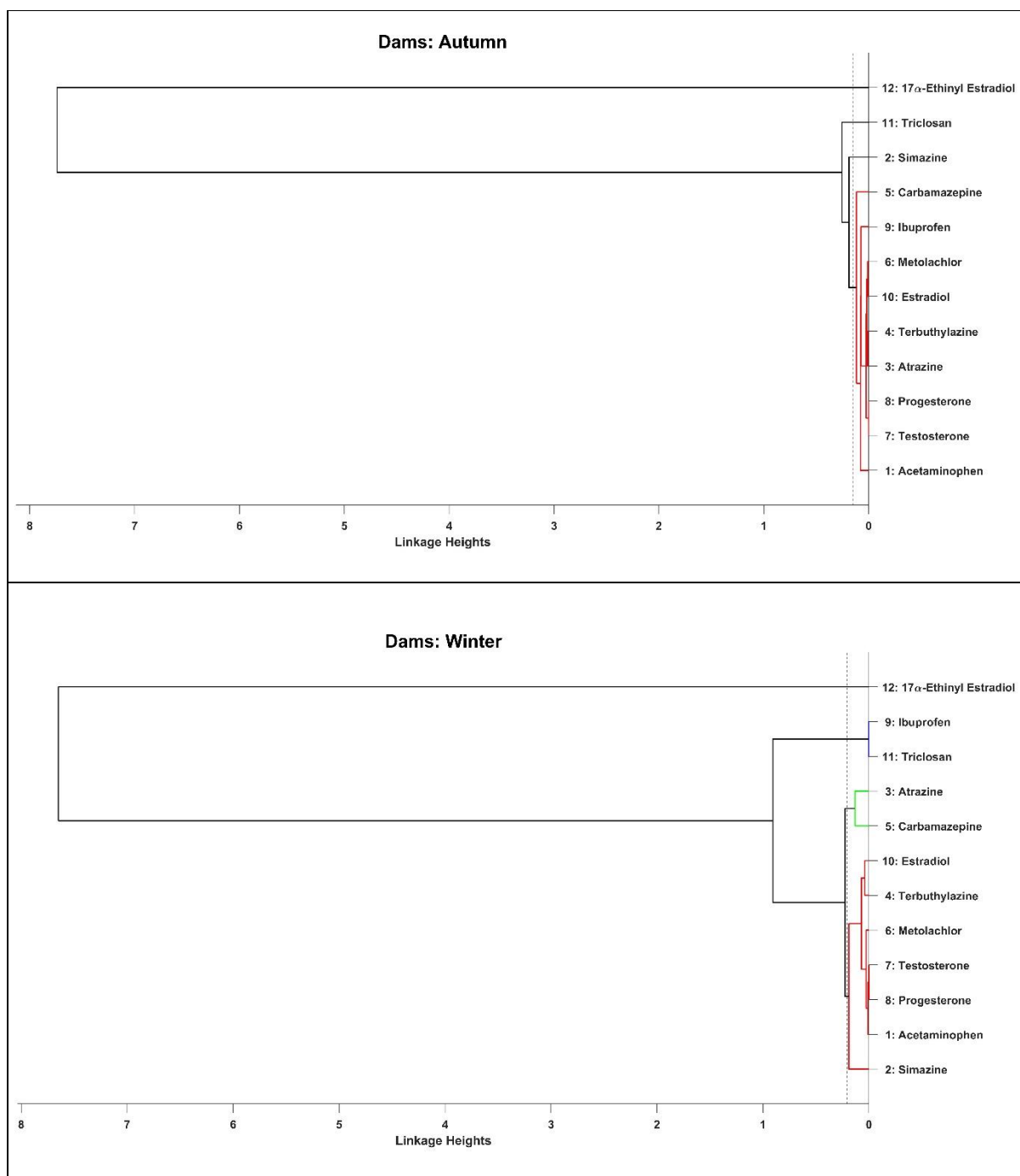


Figure 7.4 Cluster diagram showing similarities of emerging contaminants in dams during the dry season

7.4.3 Identification of pollution sources in wastewater treatment plants

Sources of emerging contaminants in wastewater treatment influent were also determined using hierarchical cluster analysis in all seasons (spring, summer, autumn and winter). In the spring season, C1 was a host of nine contaminants (progesterone, testosterone, metolachlor, terbutylazine, atrazine, estradiol, triclosan, simazine and carbamazepine),

indicating that they have been introduced by one source, which may be domestic, industrial, or hospital wastewater, as well as urban stormwater. C2 was a host of one contaminant (acetaminophen) possibly from domestic, industrial and hospital wastewater received by these WWTPs. C3 was a host of one contaminant (ibuprofen), which linked well with wastewater from hospitals, industrial and residential areas. C4 was also a host of one contaminant (17-alpha-ethinyl-estradiol) possibly from domestic, industrial and hospital wastewater received in these WWTPs. In the summer season, C1 hosted nine contaminants (testosterone, atrazine, metolachlor, terbuthylazine, estradiol, progesterone, triclosan, simazine and carbamazepine), which clearly showed similar pathways such as domestic, industrial and hospital wastewater, as well as urban stormwater. C2 hosted one contaminant (ibuprofen), which may be linked well with wastewater from hospitals, industrial and residential areas. C3 hosted one contaminant (acetaminophen) emanating from hospitals, industrial and domestic wastewater, while C4 also hosted one contaminant (17-alpha-ethinyl-estradiol) also from domestic, hospital and industrial wastewater (Figure 7.5; Table 7.12).

Moreover, the autumn season showed C1 connected to nine contaminants (progesterone, testosterone, estradiol, metolachlor, atrazine, terbuthylazine, simazine, carbamazepine and triclosan) connoting a similar source of origin, possibly domestic, industrial and hospital wastewater as well as urban stormwater. C2 was connected to one contaminant (ibuprofen) from domestic, industrial and hospital wastewater. C3 was connected to one contaminant (acetaminophen), possibly from domestic, industrial and hospital wastewater and C4 was connected to one contaminant (17-alpha-ethinyl-estradiol), also from domestic, industrial and hospital wastewater. In the winter season, C1 was connected to one contaminant (17-alpha-ethinyl-estradiol), C2 was connected to one contaminant (acetaminophen) and C3 was connected to one contaminant (ibuprofen), which may all have been introduced by domestic, industrial and hospital wastewater. C4 was connected to nine contaminants (simazine, terbuthylazine, atrazine, metolachlor, triclosan, estradiol, progesterone, testosterone and carbamazepine). The connection of these contaminants in C4 may have represented similar sources of origin in this study, possibly domestic, industrial and hospital wastewater, as well as urban stormwater (Figure 7.6; Table 7.12).

In this area, WWTPs receive all sorts of wastewater such as domestic, industrial and hospital wastewater. Lim et al. (2017) indicated that WWTPs receive wastewater from various areas containing various chemical pollutants, which support the situation in this study. Therefore, it is rational to deduce domestic wastewater, industrial wastewater, hospital wastewater and urban stormwater as the carriers of emerging contaminants in

wastewater influents in this study. Domestic and hospital wastewater are considered the foremost contributors of pharmaceuticals and personal care products (Khan et al., 2021; Tormo-Budowski et al., 2021; Ulvi et al., 2022). Urban stormwater may also introduce pharmaceuticals and personal care products as a result of illegal dumping of unused or expired drugs in residential and industrial areas (Rodriguez-Mozaz et al., 2015). Moreover, urban stormwater may introduce traces of pesticides in WWTPs as a result of the application of sewage sludge to ensure soil fertility in community gardens, recreational parks and other public areas in this study area (Čelić et al., 2019).

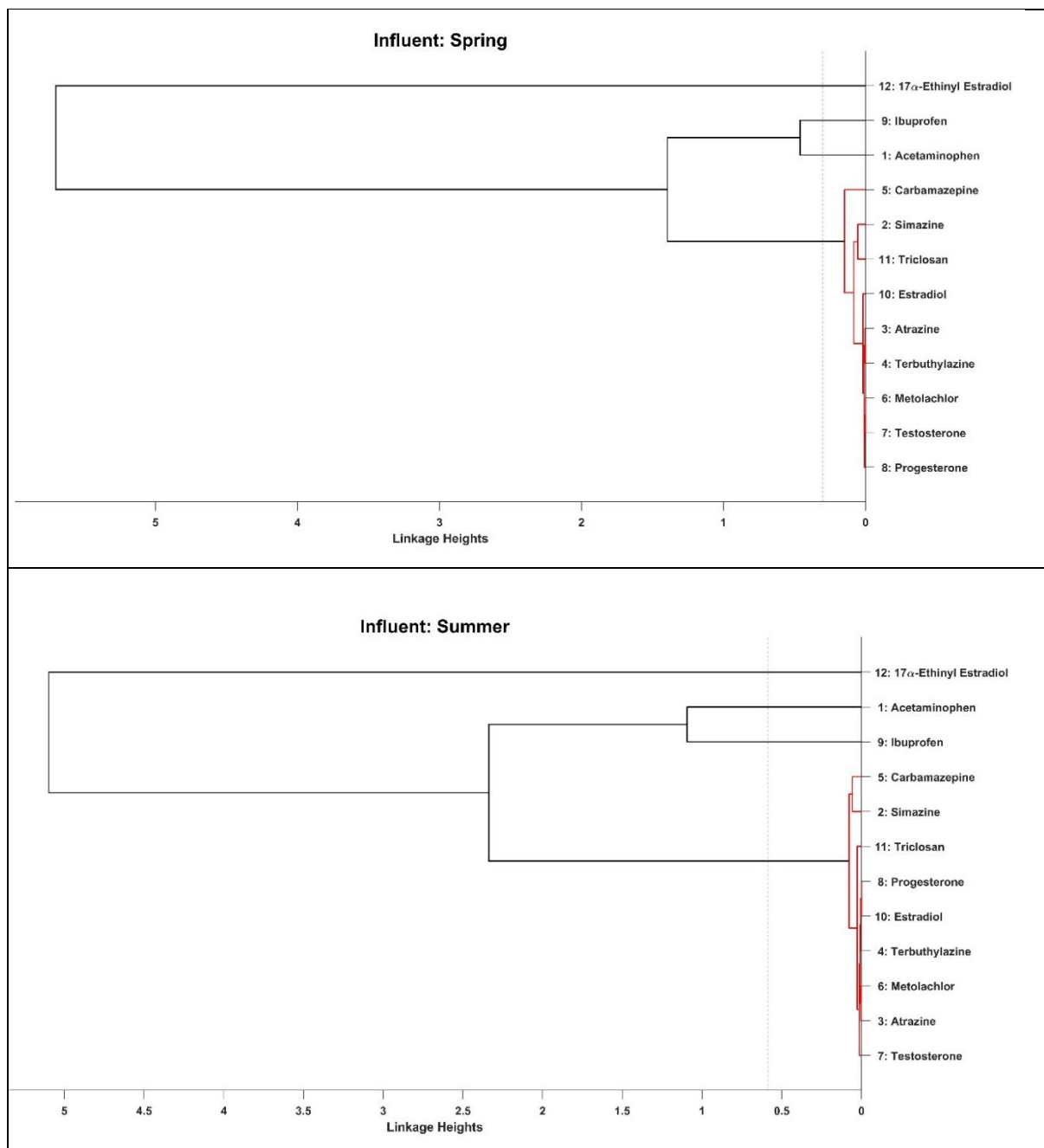


Figure 7.5 Cluster diagram showing similarities of emerging contaminants in wastewater influent during the wet season

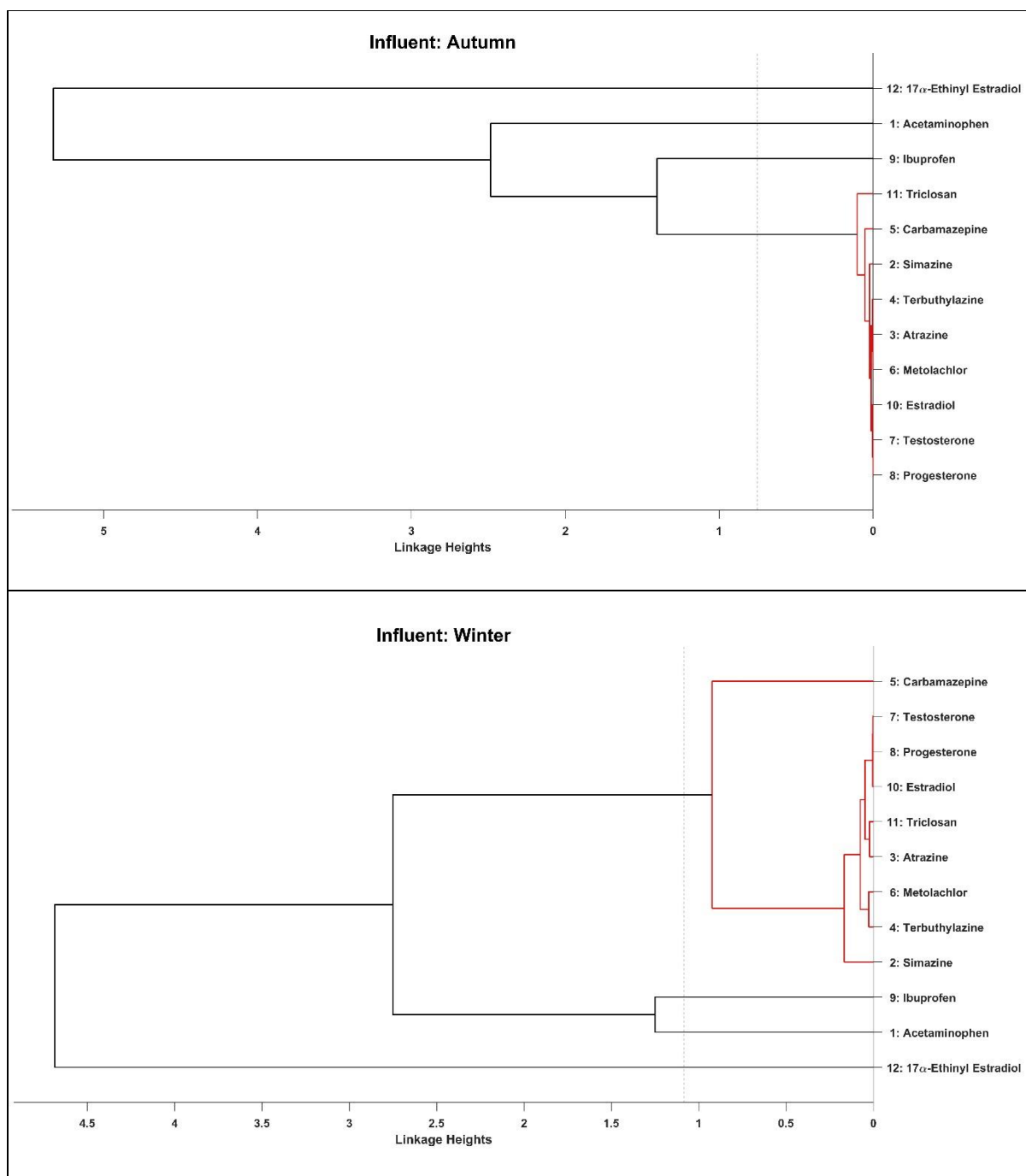


Figure 7.6 Cluster diagram showing similarities of emerging contaminants in wastewater influent during the dry season

Moreover, in wastewater effluent during the spring season, C1 contained nine contaminants (progesterone, acetaminophen, testosterone, metolachlor, terbutylazine, atrazine, estradiol, triclosan and simazine). C2 contained one contaminant (carbamazepine), C3 one contaminant (ibuprofen), and C4 also one contaminant (17-alpha-ethinyl-estradiol). In the summer season, C1 contained one contaminant (carbamazepine), C2 eight contaminants (simazine, terbutylazine, progesterone, estradiol, triclosan, metolachlor, atrazine and

testosterone), C3 two contaminants (acetaminophen and ibuprofen) and C4 one contaminant (17-alpha-ethinyl-estradiol). The occurrence of contaminants in one cluster is an indication of a similar source of origin (Figure 7.7 and Table 7.12). During the autumn season, C1 had one contaminant (17-alpha-ethinyl-estradiol), C2 (acetaminophen), C3 (17-alpha-ethinyl-estradiol), while C4 contained nine contaminants (carbamazepine, simazine, triclosan, metolachlor, atrazine, terbuthylazine, estradiol, testosterone and progesterone). Furthermore, in the winter season, C1 had one contaminant (17-alpha-ethinyl-estradiol), C2 (simazine), C3 (acetaminophen, progesterone, testosterone, estradiol, terbuthylazine, metolachlor, atrazine, triclosan and carbamazepine) and C4 (ibuprofen). Having contaminants in one cluster possibly suggests that they are emanating from the same source (Figure 7.8 and Table 7.12).

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

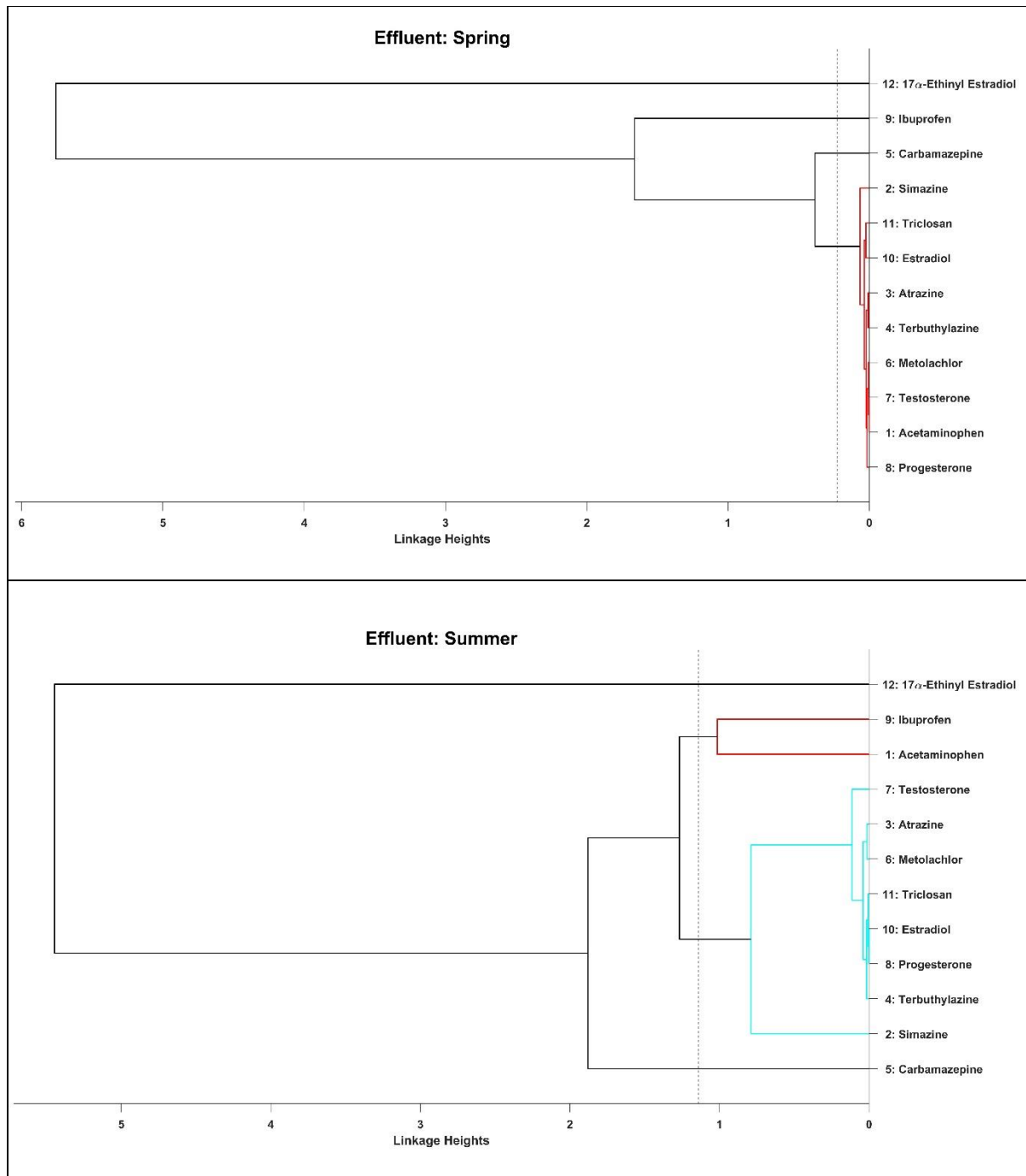


Figure 7.7 Cluster diagram showing similarities of emerging contaminants in wastewater effluent during the wet season

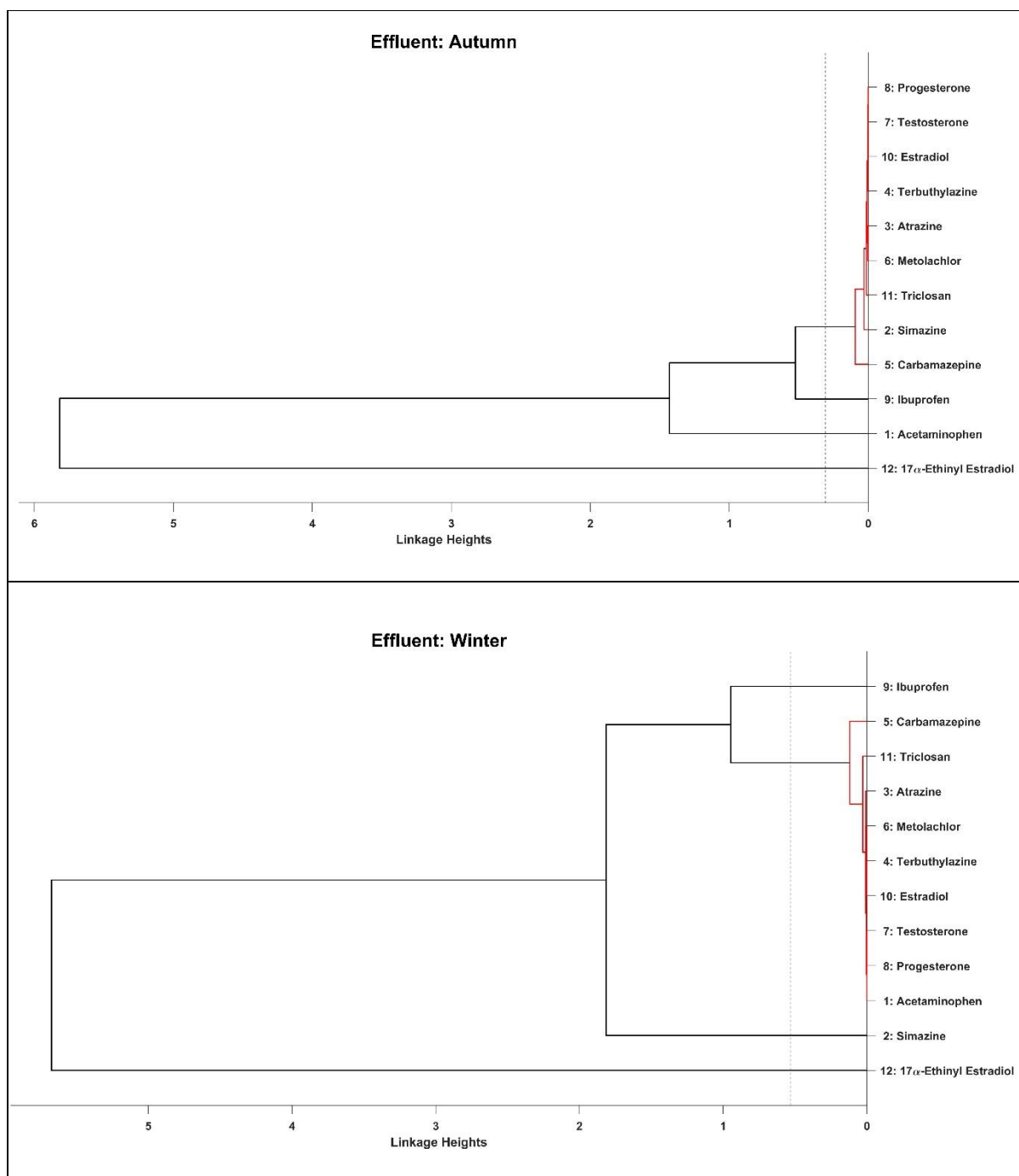


Figure 7.8 Cluster diagram showing similarities of emerging contaminants in wastewater effluent in the dry season

7.4.4 Identification of pollution source in treated drinking water

The hierarchical cluster analysis in treated drinking water also generated four clusters in all seasons as highlighted in Figure 7.9, Figure 7.10 and presented in Table 7.12. In the spring season, C1 was characterised by one contaminant (carbamazepine), C2 was characterised by seven contaminants (acetaminophen, terbutylazine, metolachlor, ibuprofen, simazine,

atrazine and terbuthylazine), C3 was characterised by three contaminants (estradiol, triclosan and progesterone), whereas C4 was characterised by only one contaminant (17-alpha-ethinyl-estradiol). In the summer season, C1 was characterised by six contaminants (acetaminophen, progesterone, testosterone, estradiol, carbamazepine and simazine), C2 was characterised by three contaminants (metolachlor, atrazine and terbuthylazine), C3 was characterised by two contaminants (triclosan and ibuprofen) and C4 was characterised by one contaminant (17-alpha-ethinyl-estradiol) as presented in Figure 7.9 and Table 7.12.

There were also four clusters in the autumn and winter seasons. During the autumn season, C1 was the host of seven contaminants (acetaminophen, testosterone, progesterone, simazine, estradiol, carbamazepine and terbuthylazine), C2 was the host of two contaminants (atrazine and metolachlor), C3 was the host of two contaminants (ibuprofen and triclosan) and C4 was the host of one contaminant (17-alpha-ethinyl-estradiol). In the winter season, C1 was the host of seven contaminants (acetaminophen, progesterone, testosterone, simazine, estradiol, carbamazepine and terbuthylazine), C2 was the host of two contaminants (metolachlor and atrazine), C3 was the host of two contaminants (triclosan and ibuprofen) and C4 was the host of 17-alpha-ethinyl-estradiol only (Figure 7.10; Table 7.12).

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

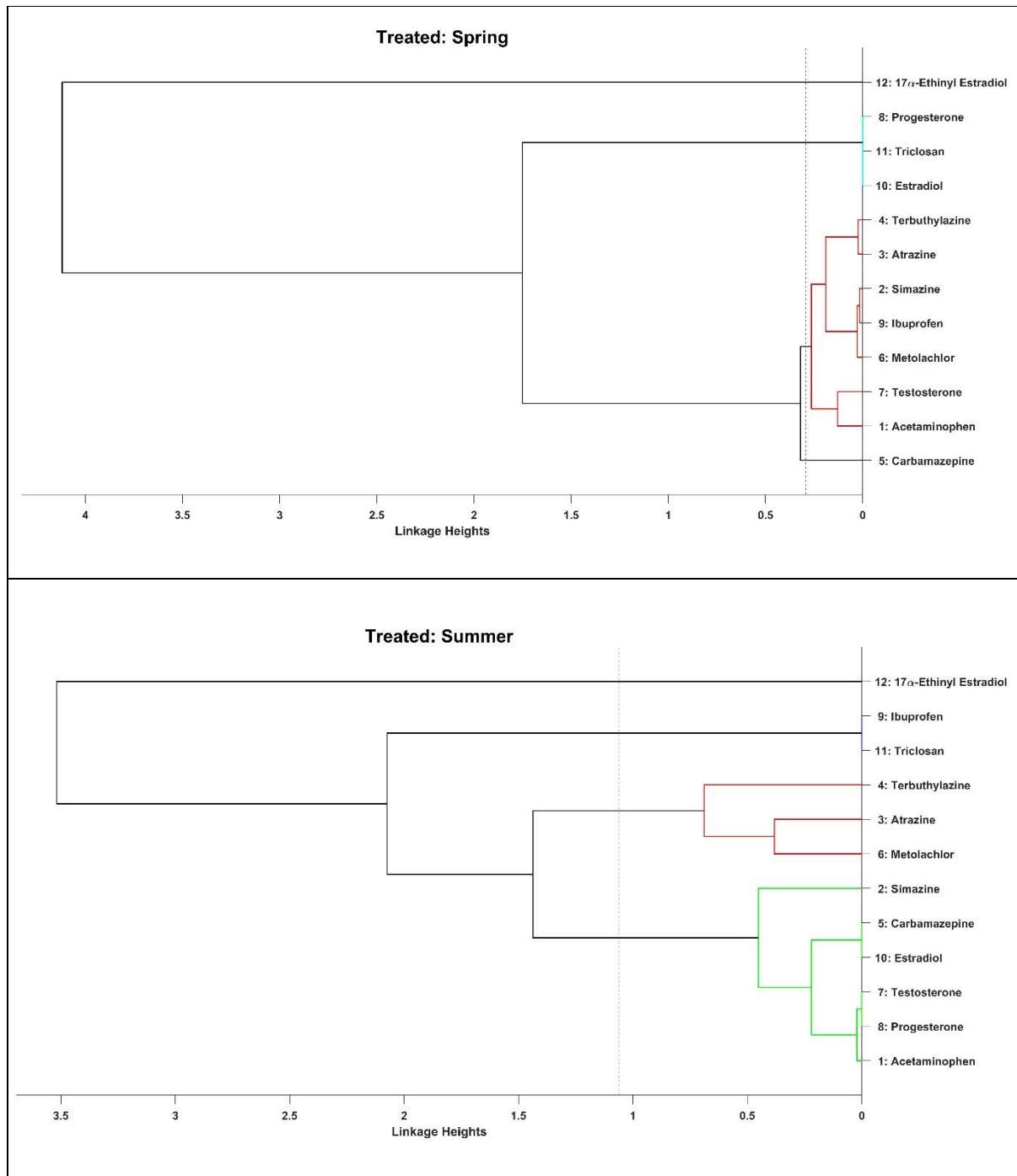


Figure 7.9 Cluster diagram showing similarities of emerging contaminants in treated drinking water during the wet season

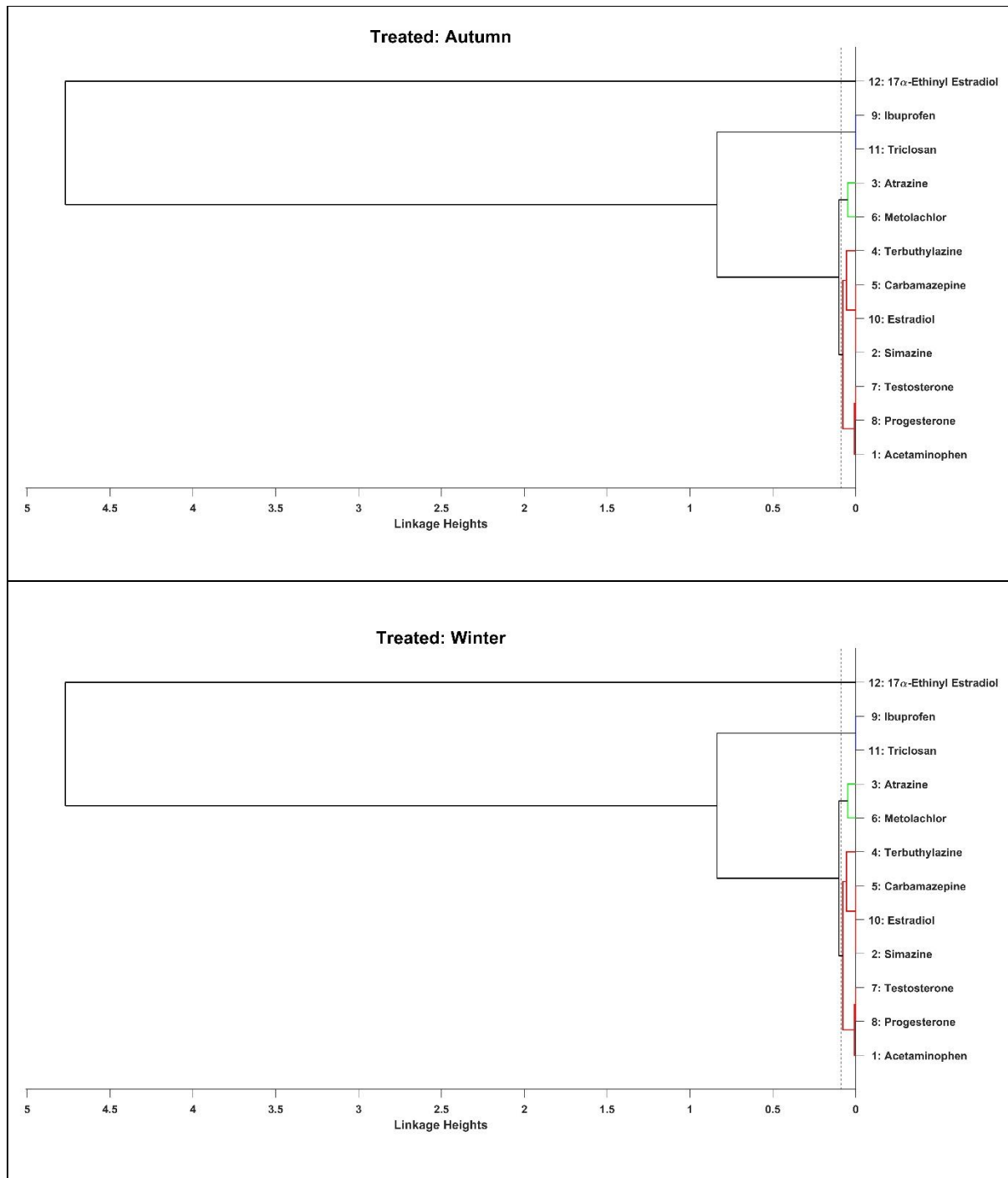


Figure 7.10 Cluster diagram showing similarities of emerging contaminants in treated drinking water during the dry season

Table 7.12 Simplified analysis of clusters identified for emerging contaminants in water sources around Bloemfontein

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

				sewage
	C2	7	Acetaminophen, progesterone, testosterone, estradiol, metolachlor, atrazine, and terbuthylazine	Wastewater effluent, illegal dumping, domestic sewage, agricultural runoff, and urban surface runoff
	C3	2	Triclosan, and ibuprofen	Wastewater effluent, illegal dumping, and domestic sewage
	C4	1	17-alpha-ethinyl-estradiol	Wastewater effluent, illegal dumping, and domestic sewage
Autumn	C1	9	Acetaminophen, testosterone, progesterone, atrazine, terbuthylazine, estradiol, metolachlor, ibuprofen, and carbamazepine	Wastewater effluent, illegal dumping, domestic sewage, and agricultural runoff
	C2	1	Simazine	Wastewater effluent, and agricultural runoff
	C3	1	Triclosan	Wastewater effluent
	C4	1	17-alpha-ethinyl-estradiol	Wastewater effluent, illegal dumping, and domestic sewage
Winter	C1	7	Simazine, acetaminophen, progesterone, testosterone, metolachlor, terbuthylazine, and estradiol	Wastewater effluent, illegal dumping, domestic sewage, and agricultural runoff
	C2	2	Carbamazepine, and atrazine	Wastewater effluent, illegal dumping and agricultural runoff
	C3	2	Triclosan, and ibuprofen.	Wastewater effluent, illegal dumping, and domestic sewage
	C4	1	17-alpha-ethinyl-estradiol.	Wastewater effluent, illegal dumping, and domestic sewage
Treated drinking water				
Spring	C1	1	Carbamazepine	Dams utilised as water sources for water treatment plants are polluted by wastewater effluent, agricultural runoff, illegal dumping, urban surface runoff and domestic sewage thus leading to detection of this contaminants in treated drinking water
	C2	7	Acetaminophen, testosterone, metolachlor, ibuprofen, simazine, atrazine, and terbuthylazine	
	C3	3	Estradiol, triclosan, and progesterone	
	C4	1	17-alpha-ethinyl-estradiol	
Summer	C1	6	Acetaminophen, progesterone, testosterone, estradiol, carbamazepine, and simazine	
	C2	3	Metolachlor, atrazine, and terbuthylazine	
	C3	2	Triclosan, and ibuprofen	
	C4	1	17-alpha-ethinyl-estradiol	
Autumn	C1	7	Acetaminophen, progesterone, testosterone, simazine, estradiol, carbamazepine, and terbuthylazine	
	C2	2	Atrazine, and metolachlor	
	C3	2	Ibuprofen, and triclosan	
	C4	1	17-alpha-ethinyl-estradiol	
Winter	C1	7	Acetaminophen, progesterone, testosterone, simazine, estradiol and terbuthylazine	
	C2	2	Metolachlor and atrazine	
	C3	2	Triclosan and ibuprofen	

	C4	1	17-alpha-ethynyl-estradiol	
Wastewater influent				
Spring	C1	9	Progesterone, testosterone, metolachlor, terbutylazine, atrazine, estradiol, triclosan, simazine and carbamazepine	Domestic, industrial, and hospital wastewater; urban stormwater
	C2	1	Acetaminophen	Domestic, industrial and hospital wastewater
	C3	1	Ibuprofen	Domestic, industrial and hospital wastewater
	C4	1	17-alpha-ethynyl-estradiol	Domestic, industrial and hospital wastewater
Summer	C1	9	Testosterone, atrazine, metolachlor, terbutylazine, estradiol, progesterone, triclosan, simazine and carbamazepine	Domestic, industrial, and hospital wastewater; urban stormwater
	C2	1	Ibuprofen	Domestic, industrial and hospital wastewater
	C3	1	Acetaminophen.	Domestic, industrial and hospital wastewater
	C4	1	17-alpha-ethynyl-estradiol	Domestic, industrial and hospital wastewater
Autumn	C1	9	Progesterone, testosterone, estradiol, metolachlor, atrazine, terbutylazine, simazine, carbamazepine, and triclosan	Domestic, industrial, and hospital wastewater; urban stormwater
	C2	1	Ibuprofen	Domestic, industrial and hospital wastewater
	C3	1	Acetaminophen	Domestic, industrial and hospital wastewater
	C4	1	17-alpha-ethynyl-estradiol	Domestic, industrial and hospital wastewater
Winter	C1	1	17-alpha-ethynyl-estradiol	Domestic, industrial and hospital wastewater
	C2	1	Acetaminophen	Domestic, industrial and hospital wastewater
	C3	1	Ibuprofen	Domestic, industrial and hospital wastewater
	C4	9	Simazine, terbutylazine, metolachlor, atrazine, triclosan, estradiol, progesterone, testosterone, and carbamazepine	Domestic, industrial, and hospital wastewater; urban stormwater
Wastewater effluent				
Spring	C1	9	Progesterone, acetaminophen, testosterone, metolachlor, terbutylazine, atrazine, estradiol, triclosan, and simazine	As a result of inefficient removal, contaminants end up in effluent. Thus they can be linked to received domestic, industrial, and hospital wastewater as well as urban stormwater
	C2	1	Carbamazepine	
	C3	1	Ibuprofen	
	C4	1	17-alpha-ethynyl-estradiol	
Summer	C1	1	Carbamazepine	As a result of inefficient removal, contaminants end up in effluent. Thus they can be linked to received domestic, industrial, and hospital wastewater as well as urban stormwater
	C2	8	Simazine, terbutylazine, progesterone, estradiol, triclosan, metolachlor, atrazine, and testosterone	
	C3	2	Acetaminophen, and Ibuprofen	
	C4	1	17-alpha-ethynyl-estradiol	
Autumn	C1	1	17-alpha-ethynyl-estradiol	

	C2	1	Acetaminophen
	C3	1	Ibuprofen
	C4	9	Carbamazepine, simazine, triclosan, metolachlor, atrazine, terbuthylazine, estradiol, testosterone and progesterone
	C1	1	17-alpha-ethinyl-estradiol
	C2	1	Simazine
Winter	C3	9	Acetaminophen, progesterone, testosterone, estradiol, terbuthylazine, metolachlor, atrazine, triclosan, and carbamazepine
	C4	1	Ibuprofen

7.5 Identification of pollution source using principal component analysis

The individual association of emerging contaminants in water sources around Bloemfontein was also determined by the PCA method. By using PCA, the unobserved pollution source can be identified (Hou et al., 2022). To identify the possible sources of origin in this study, the factor loadings are classified as strong (> 0.75), moderate ($0.75-0.50$) and weak ($0.50-0.30$) (Chen et al., 2016; Hou et al., 2022; Zhang et al., 2015).

7.5.1 Identification of pollution source in rivers

In the spring, summer, autumn and winter seasons, three principal components (PCs) were obtained in rivers (Table 7.13). The overall loading factors and the correlation between the first and second loading factors are also illustrated in Figures 7.11 and 7.12. In the spring season, the first principal component (PC1) had a weak positive loading of simazine, atrazine, terbuthylazine, carbamazepine and 17-alpha-ethinyl-estradiol, which explains 52.53% of the total variance. The loading in PC1 indicated that it may have originated from the same sources such as wastewater effluents, agricultural runoff, urban stormwater and illegal dumping. The second principal component (PC2), accounting for 30.79% of the total variance, showed a moderate positive loading of estradiol and a weak positive loading of metolachlor, triclosan, as well as 17-alpha-ethinyl-estradiol. These contaminants may be linked to agricultural runoff, urban stormwater, wastewater effluent and illegal dumping. PC3, accounting for 10.67% of the total variance, showed a moderate positive loading of acetaminophen and ibuprofen, together with a weak positive loading of carbamazepine. The contaminants in PC3 may be linked to wastewater effluent, illegal dumping and urban stormwater runoff. In the summer season, PC1 accounting for 67.55% of the total variance, showed a weak positive loading of simazine, atrazine, terbuthylazine, metolachlor and 17-alpha-ethinyl-estradiol. The sources of these contaminants may be interpreted as pollution

from agricultural runoff, urban stormwater and wastewater effluent. PC2 had 27.56% of total variance, with a moderate positive loading of carbamazepine and ibuprofen. Therefore, PC2 may be interpreted as pollution from wastewater effluent and illegal dumping. PC3 exhibited 4.67% of total variance, with a moderate positive loading of atrazine and terbuthylazine and a weak positive loading of simazine possibly from agricultural runoff and urban stormwater (Table 7.13 and Figure 7.11).

During the autumn season, PC1 had 75.56% of the total variance dominated by a weak positive loading of simazine, atrazine, terbuthylazine, carbamazepine and metolachlor. The loading in the first principal component may be associated with agricultural runoff, urban stormwater runoff, wastewater effluent and illegal dumping. PC2 had 13.03% of total variance with a strong positive loading of ibuprofen that may be linked to wastewater effluent and illegal dumping. PC3 had 8.71% of the total variance with a moderate positive loading of simazine and terbuthylazine, relating very well to agricultural runoff and urban stormwater. In the winter season, PC1 had 56.09% of the total variance, with a weak positive loading of simazine, atrazine, terbuthylazine, carbamazepine, metolachlor and ibuprofen. The introduction of these contaminants in rivers may be linked to wastewater effluent, agricultural runoff, urban stormwater and illegal dumping. In PC2, a weak positive loading of acetaminophen, simazine, atrazine, terbuthylazine and ibuprofen, which explains 22% of the total variance, was observed. These observations may be explained as a pollution from wastewater effluent, agricultural runoff, urban stormwater runoff and illegal dumping (Table 7.13 and Figure 7.12).

Table 7.13 Principal component analysis of emerging contaminants in rivers

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

Notation: PC = Principal component.

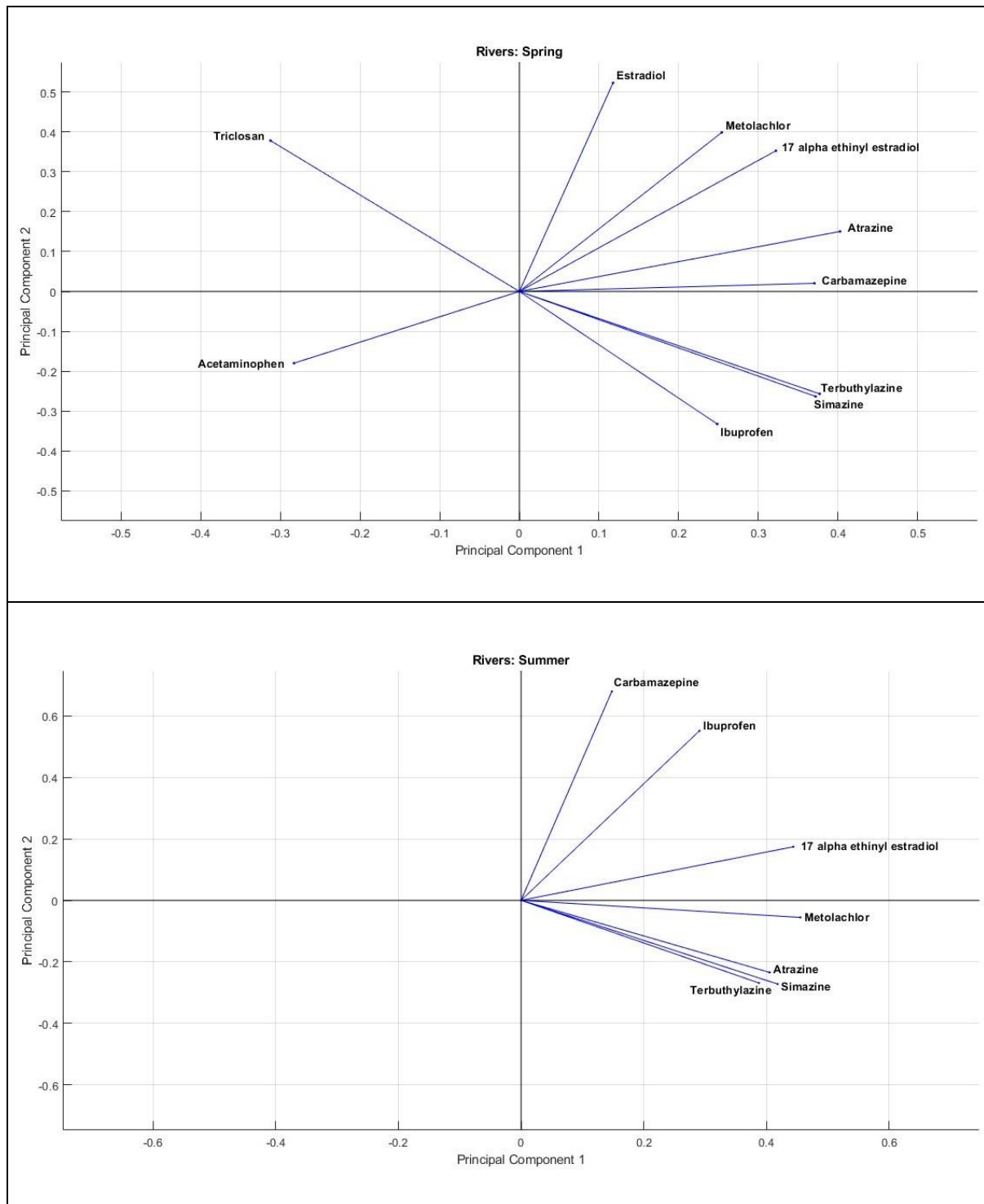


Figure 7.11 PCA results of the first two principal components in rivers during the wet season (spring and summer)

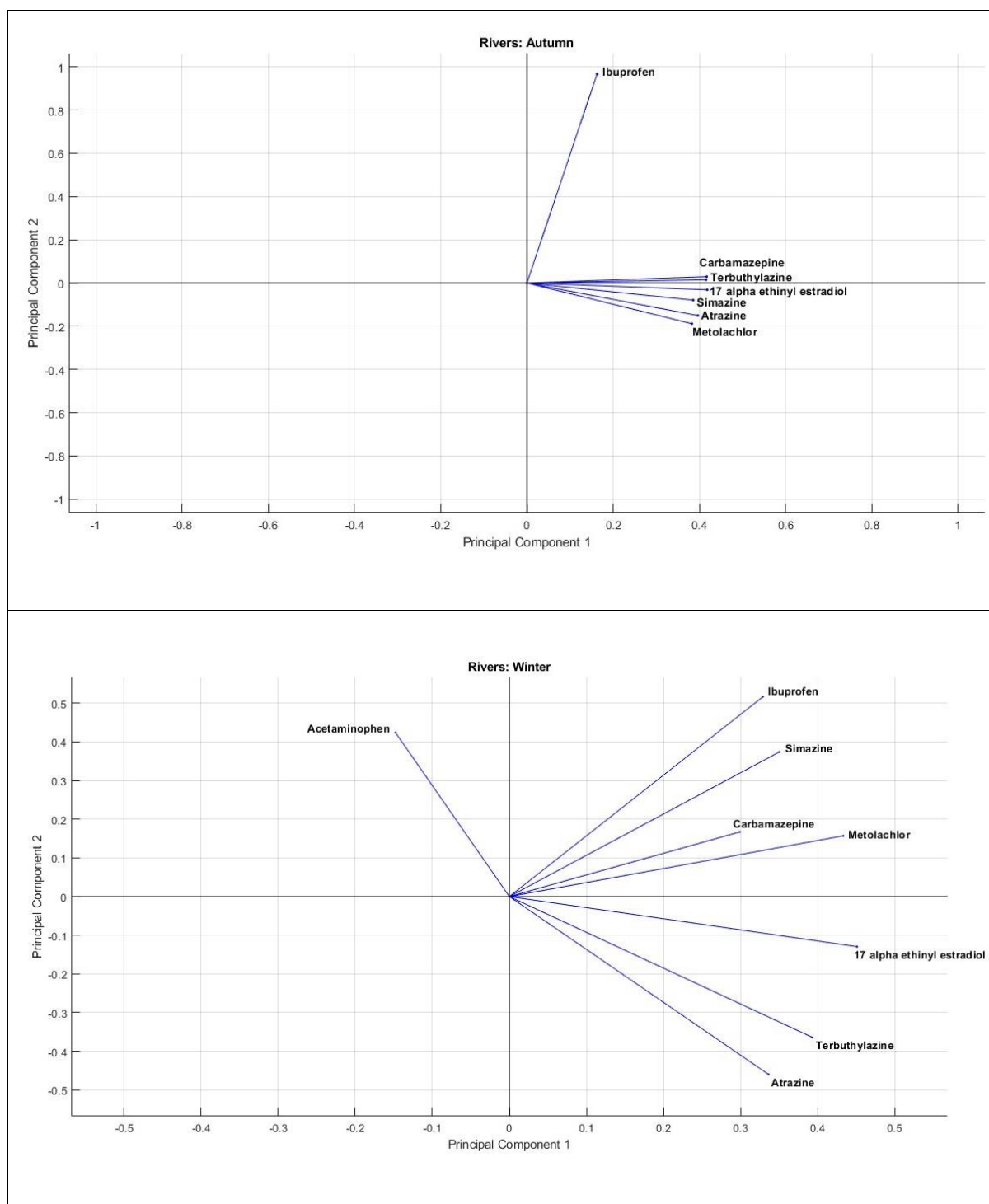


Figure 7.12 PCA results of the first two principal components in rivers during the dry season (autumn and winter)

The above results from the PCA indicate that the major pollution sources threatening the rivers around Bloemfontein are anthropogenic pollution from agricultural runoff, urban stormwater runoff, illegal dumping and wastewater effluent. Similarly, the contamination of rivers by agricultural runoff and wastewater effluent discharge was reported by other authors

in the Sinos River in Brazil (Alves et al., 2018); the Nag River in India (Dutta et al., 2018); the Kinta River in Malaysia (Isiyaka et al., 2018); the Jhelum River in Parkinstan (Mir et al., 2019); the Akaki River in Ethiopia (Yilma et al., 2018) and the Qinhuai River in China (Ma et al., 2020). In the study area, some of the rivers run through townships and cities; hence, improper waste disposal witnessed during the field visit may have introduced these contaminants in rivers. The selected WWTPs receive wastewater from households, industries and hospitals, which are the carriers of various organic chemicals. Consequently, their wastewater effluents discharged into these rivers may introduce traces of these emerging contaminants. Urban stormwater may also introduce these contaminants due to illegal dumping of unused or expired drugs (in residential areas) and application of sewage sludge to ensure soil fertility (in community gardens, recreational parks, golf courses and other public areas) in this study area (Čelić et al., 2019; Rodriguez-Mozaz et al., 2015).

7.5.2 Identification of pollution sources in dams and or reservoirs

As presented in Table 7.14, three PCs were obtained in samples collected from dams during the wet season (spring and summer) and dry season (autumn and winter). The overall loading factors and the correlation between the first and second loading factors are also described in Figures 7.13 and 7.14. In the spring season, PC1 accounting for 53.12% of the total variance, exhibited weak positive loadings for acetaminophen, simazine, terbuthylazine, ibuprofen and 17-alpha-ethinyl-estradiol, suggesting that they share a common source of origin such as domestic sewage, wastewater effluent, agricultural runoff and illegal dumping. PC2, with 39.36% of total variance, showed weak positive loadings for atrazine and metolachlor that are pesticides possibly originating from agricultural runoff and wastewater effluent. PC3, accounting for 7.44% of total variance, exhibits a weak positive loading of simazine and moderate positive loading of 17-alpha-ethinyl-estradiol derived from domestic sewage, wastewater effluent and agricultural runoff. In the summer season, PC1 showed 63.63% of total variance, with a weak positive loading of simazine, atrazine, terbuthylazine, carbamazepine, metolachlor and 17-alpha-ethinyl-estradiol, possibly from agricultural runoff, wastewater effluent, domestic sewage and illegal dumping. Accounting for 18.48% of the total variance, PC2 had a weak positive loading of carbamazepine and moderate loading of 17-alpha-ethinyl-estradiol. The loading of PC2 suggested that these contaminants shared a common source of origin such as domestic sewage, illegal dumping and wastewater effluent (Table 7.14 and Figure 7.13).

In the autumn season, PC1, accounting for 52.31% of the total variance, had weak positive loadings for simazine, atrazine, terbuthylazine, metolachlor and ibuprofen that may be linked

to wastewater effluent, domestic sewage, illegal dumping and agricultural runoff. PC2, with 34.07% of total variance, exhibited a moderate positive loading for carbamazepine and 17-alpha-ethinyl-estradiol, as well as a weak positive loading of ibuprofen. These contaminants in PC2 may have been introduced into dams by domestic sewage, illegal dumping and wastewater effluent. PC3, accounting for 9.1% of total variance, had a strong positive loading of acetaminophen, which may be linked to domestic sewage, illegal dumping and wastewater effluent. In the winter season, PC1 accounting for 53.04% of the total variance, had a weak positive loading of simazine, terbutylazine, carbamazepine, metolachlor and 17-alpha-ethinyl-estradiol that may have originated from agricultural runoff, wastewater effluent, domestic sewage and illegal dumping. PC2, accounting for 29.05% of total variance, had a positive loading of ibuprofen, possibly from domestic sewage, illegal dumping and wastewater effluent. PC3, accounting for 14.2% of the total variance, had a weak positive loading of atrazine, ibuprofen and 17-alpha-ethinyl-estradiol, and a moderate positive loading of carbamazepine. The loading in PC3 may be explained as pollution from domestic sewage, wastewater effluent, illegal dumping and agricultural runoff (Table 7.14 and Figure 7.14).

The main sources of emerging contaminants in dams are domestic sewage, illegal dumping, wastewater effluent and agricultural runoff. In many agricultural fields, pesticides are applied before and after planting to control broadleaf and grassy weeds (Wang et al., 2022). Considering that most of the dams are bordered by farming fields, runoff from those fields may introduce traces of pesticides in dams. Ma et al. (2020) also indicated agricultural activities as one of the sources of water pollution. During the field visit, clogged and running domestic sewage was channelled towards one of the dams, leading to the introduction of pollutants such as pharmaceuticals, steroid hormones and personal care products. Pollution of water sources by urban sewage overflow was also pin-pointed by other researchers (Hou et al., 2022; Zhang et al., 2015; Zhou et al., 2023). Moreover, some of the dams are open to the public for picnics and aquatic sports activities. Therefore, considering that some of the pharmaceuticals and personal care products are over the counter drugs administered to treat various ailments such as inflammatory diseases, arthritis, fever, dysmenorrhea, pains and headaches among many communities (Ekinci et al., 2020; Nannou et al., 2022). If care is not taken on, these activities may lead to their introduction in dams due to illegal dumping during aquatic sports activities, conferences and picnics.

Table 7.14 Principal component analysis of emerging contaminants in dams

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

Notation: PC = Principal component.

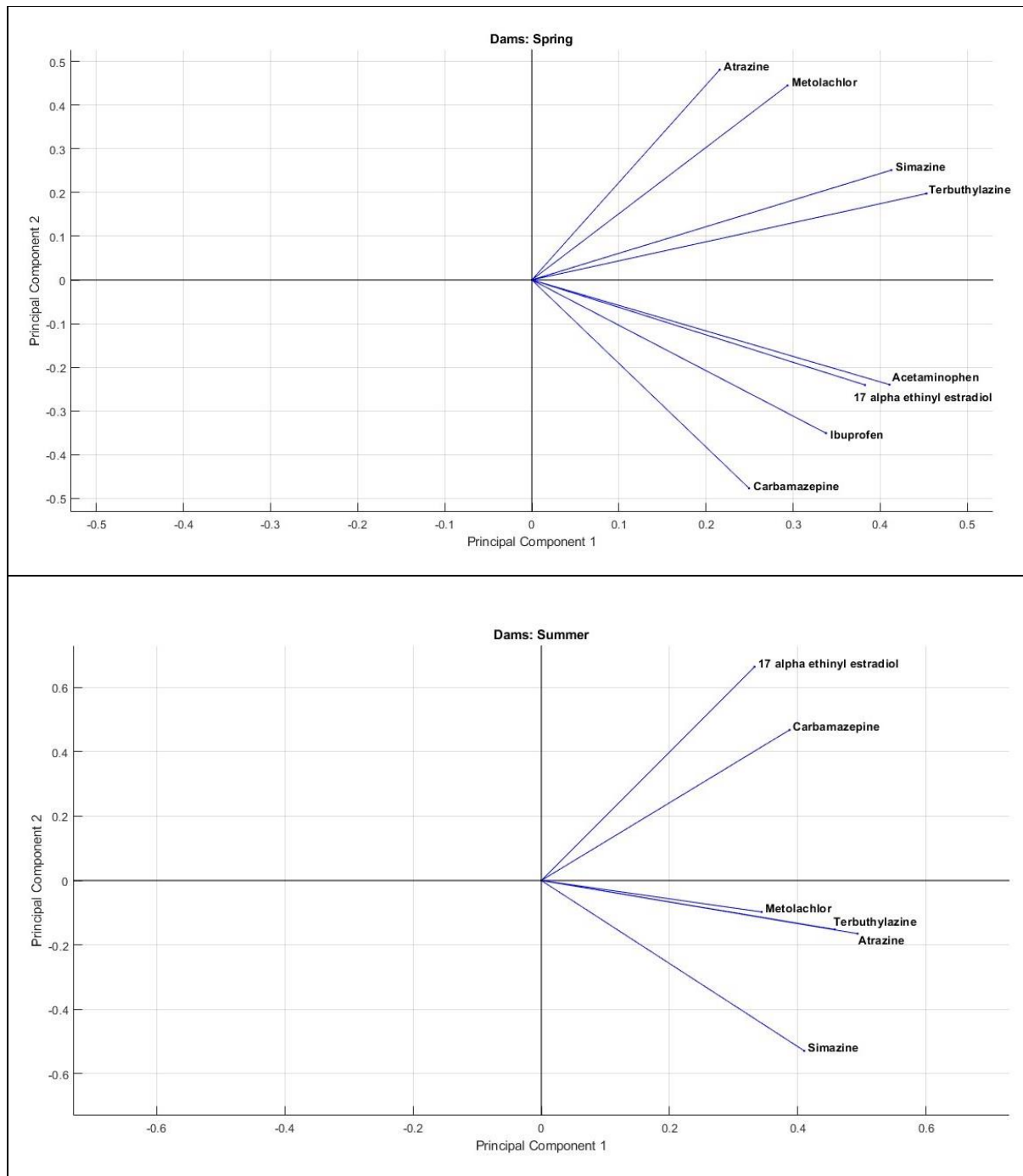


Figure 7.13 PCA results of the first two principal components in dams during the wet season (spring and summer)

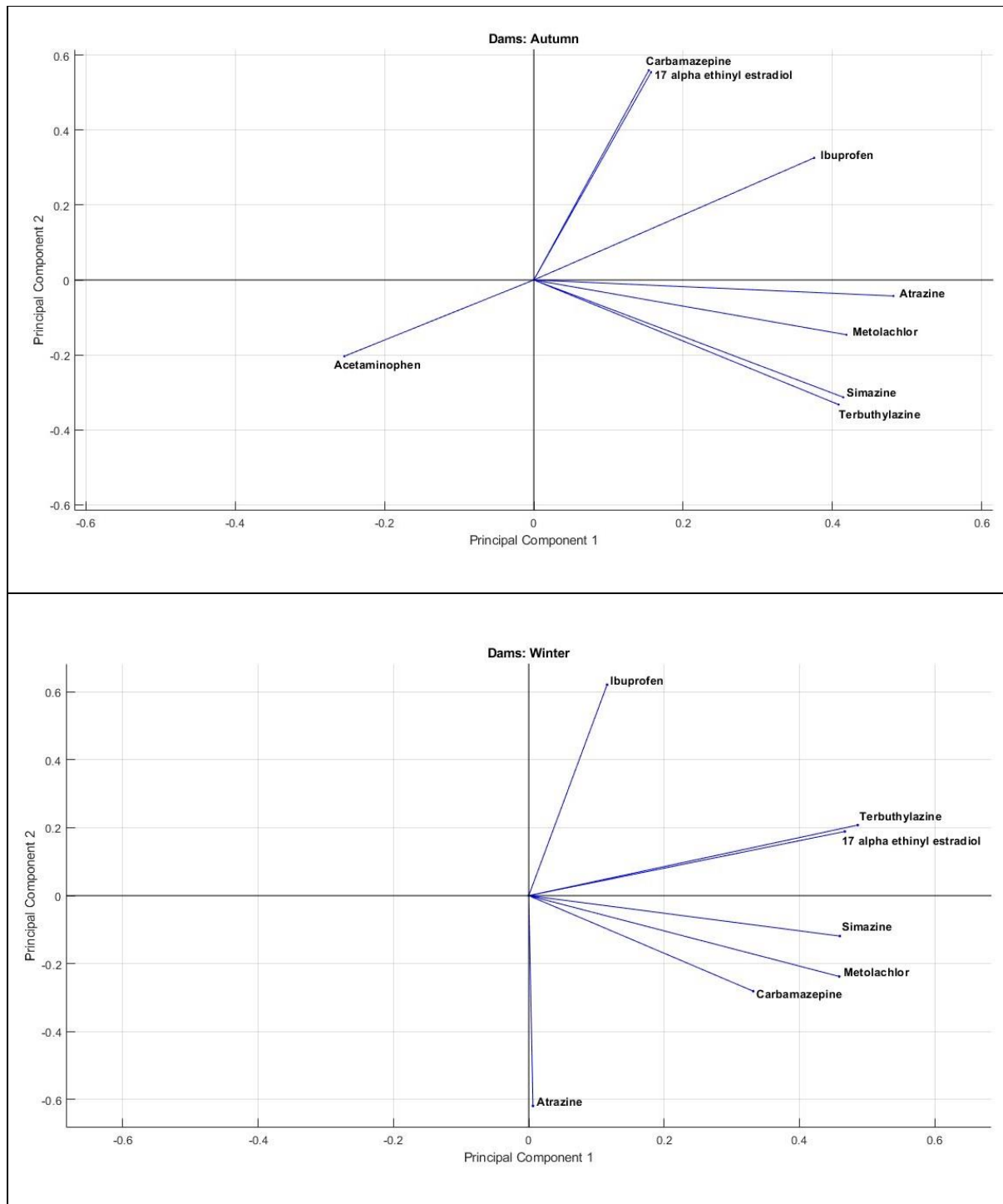


Figure 7.14 PCA results of the first two principal components in dams during the dry season (autumn and winter)

7.5.3 Identification of pollution sources in wastewater treatment plants

Table 7.15 shows the results of PCA in influents during the spring, summer, autumn and winter seasons. The overall loading factors and the correlation between the first and second loading factors are also described in Figures 7.15 and 7.16. In all seasons two principal

components were generated. During the spring season, the PC1 exhibits weak positive loading of simazine, terbuthylazine, carbamazepine and triclosan indicating that they may have originated from the same sources such as domestic, industrial and hospital wastewater as well as urban stormwater. Similarly, the weak positive loading of acetaminophen, metolachlor, testosterone and ibuprofen in PC2 may suggest that they share a common source of origin. The possible sources of this contaminants in PC2 may be linked to urban stormwater, industrial, domestic and hospital wastewater. In the summer season, PC1 exhibits weak positive loading of simazine, atrazine, terbuthylazine and metolachlor. The sources of these herbicides in PC1 may be urban stormwater received by these WWTPs. The PC2 shows moderate positive loading of acetaminophen and testosterone. Therefore, PC2 may be interpreted as pharmaceutical pollution from domestic, industrial and hospital wastewater (Table 7.15 and Figure 7.15).

In the autumn season, PC1 shows weak positive loading of acetaminophen, carbamazepine, testosterone, progesterone, ibuprofen, triclosan and 17-alpha-ethinyl-estradiol. The loading in PC1 may be linked to domestic, industrial and hospital wastewater received by these WWTPs. Similarly, the moderate positive loading of simazine in PC2 may be interpreted as organic pollution from urban stormwater. In winter season, the weak positive loading of simazine, atrazine, terbuthylazine and metolachlor in PC1 may be interpreted as pesticides pollution from urban stormwater. The moderate positive loading of carbamazepine and testosterone in PC2 suggests that they share a common source of origin which may be domestic, industrial and hospital wastewater received in these WWTPs (Table 7.15 and Figure 7.16).

From the PCA results in wastewater influents, the major pathways of emerging contaminants were stormwater runoff and domestic, industrial and hospital wastewater. Domestic wastewater, industrial wastewater and hospital wastewater have been reported as the major carriers of pharmaceuticals and personal care products in WWTPs (Khan et al., 2021; Tormo-Budowski et al., 2021; Ulvi et al., 2022). Considering that these WWTPs are located in the city and well established settlement with easy access to medicinal drugs, therefore, urination, flushing of expired drugs, improper handling of pharmaceutical products in households and release of hospital and industrial wastewater may definitely introduce these compounds into WWTPs. Urban stormwater may carry pharmaceuticals and personal care products as a result of illegal dumping of unused or expired drug in residential and industrial areas (Rodriguez-Mozaz et al., 2015). Therefore, illegal dumping of domestic wastes in the city centre and some residential settlement witnessed during field survey may also influence the occurrence of some medicinal drugs in WWTPs during rainy seasons. In some areas

sewage sludge, manures and pesticides are used to manage garden, public parks and golf course, which may introduce traces of emerging contaminants in nearby WWTPs due to urban stormwater runoff. Čelić et al. (2019) also indicated that urban stormwater may introduce organic pollutants in WWTPs as a result of the application of sewage sludge to ensure soil fertility in community garden, recreational parks and other public areas (Čelić et al., 2019).

Table 7.15 Principal component analysis of emerging contaminants in wastewater influents

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

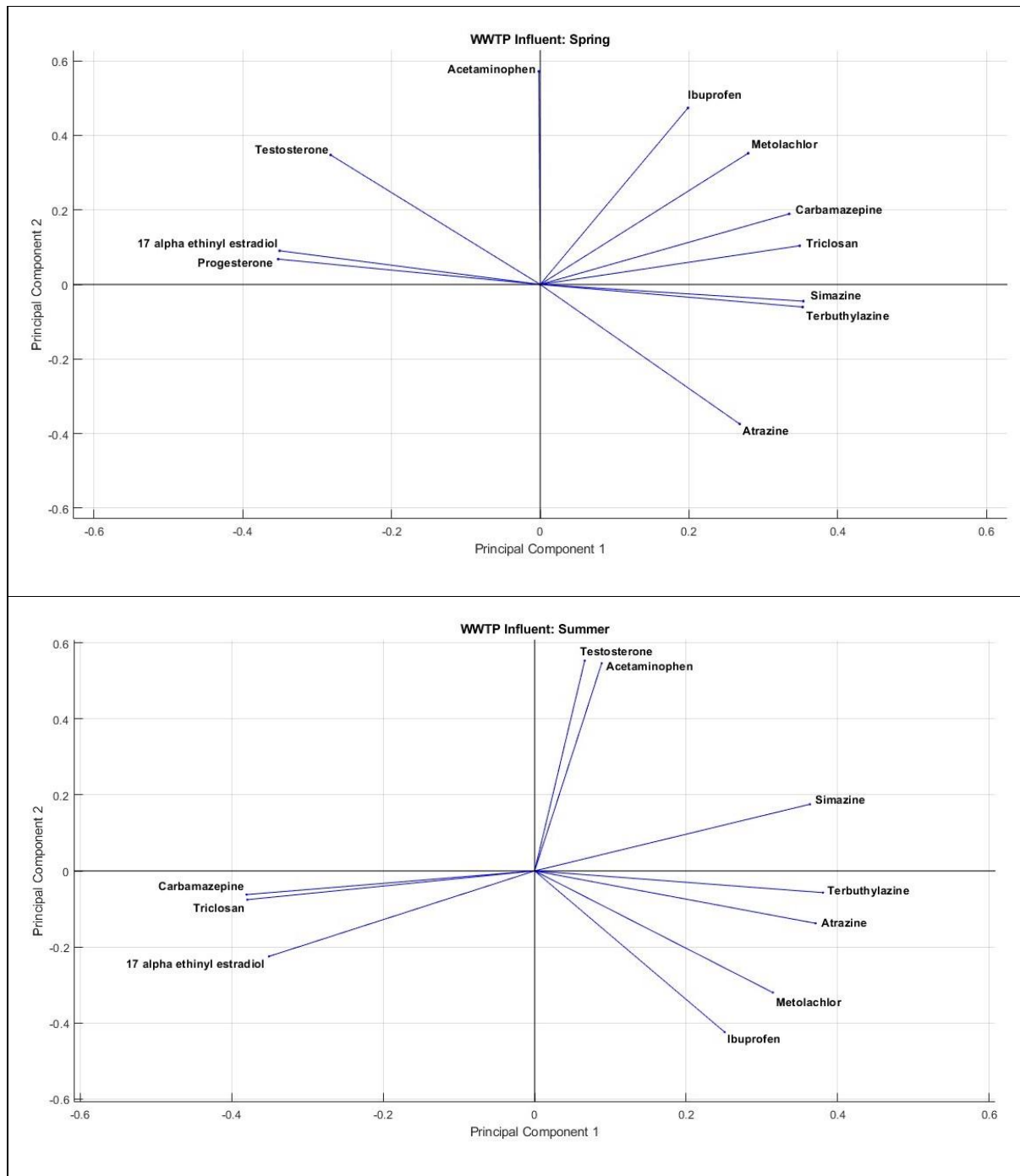


Figure 7.15 PCA results of the first two principal components in influents during the wet season (spring and summer)

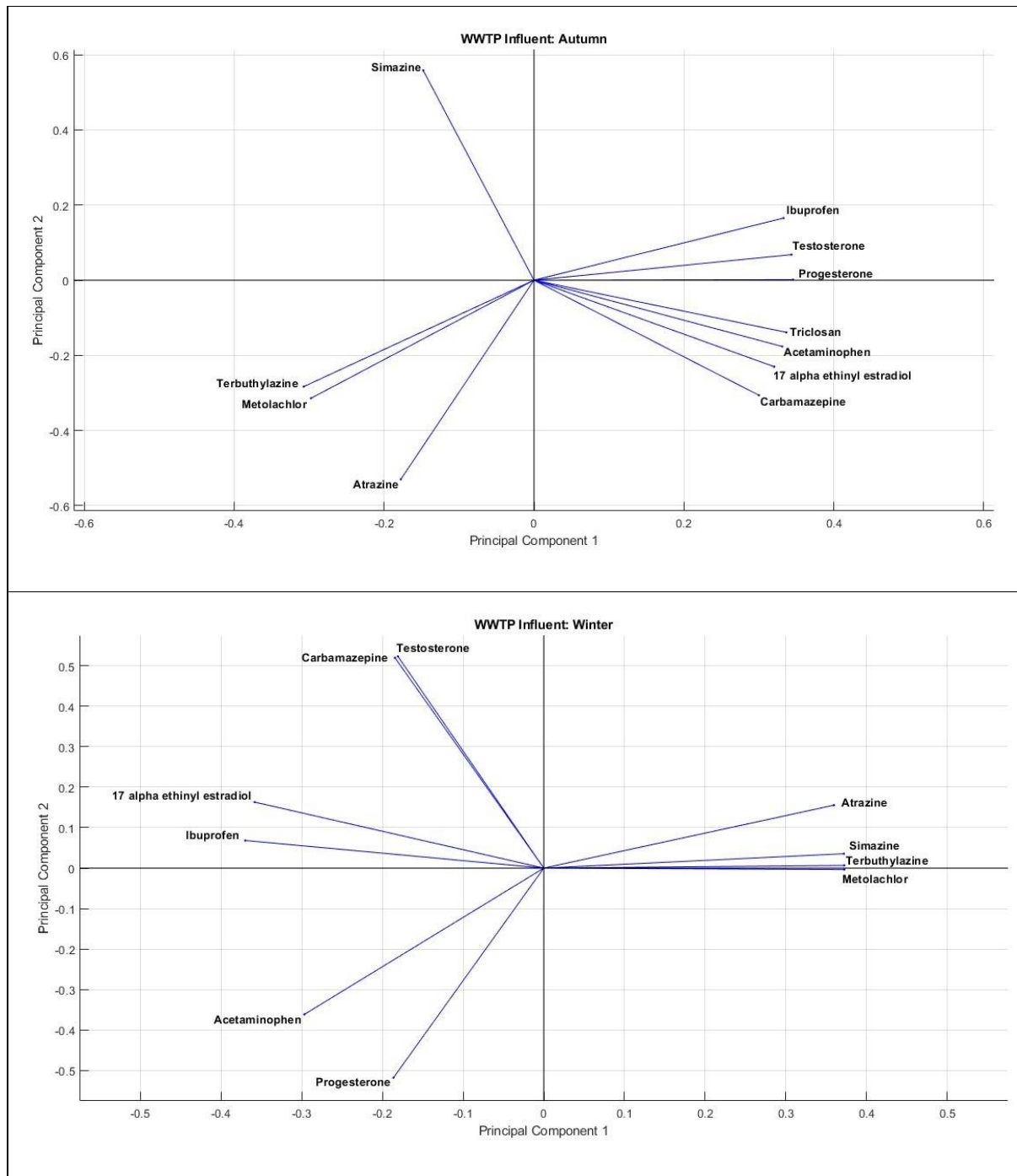


Figure 7.16 PCA results of the first two principal components in influent during the dry season (autumn and winter)

Moreover, PCA in wastewater effluent also generated two components in all seasons (Table 7.16). The overall loading factors and the correlation between the first and second loading factors are also described in Figures 7.17 and 7.18. In spring season, PC1 shows weak positive loading of atrazine, terbutylazine, testosterone and ibuprofen indicating that they may have originated from the same sources. Similarly, the weak positive loading of simazine, metolachlor, progesterone, triclosan and 17-alpha-ethinyl-estradiol may suggest

that they share a slight common source of origin. In the summer season, there was a weak positive loading of acetaminophen, testosterone, ibuprofen, triclosan and 17-alpha-ethinyl-estradiol in PC1 suggesting same source of origin. The PC2 has moderate loading of carbamazepine, metolachlor and weak loading of atrazine which is an indication of similar source of origin (Table 7.16 and Figure 7.17).

In the autumn season, PC1 shows a weak positive loading of simazine, atrazine, terbuthylazine, metolachlor and 17-alpha-ethinyl-estradiol. The PC2 shows a weak loading of atrazine, terbuthylazine, carbamazepine, metolachlor, ibuprofen and 17-alpha-ethinyl-estradiol. In winter season, the PC1 has weak positive loading of carbamazepine, ibuprofen and 17-alpha-ethinyl-estradiol while PC2 has moderate positive loading of simazine and terbuthylazine. The positive loading of contaminants in the same principal component indicates that they share a common source of origin (Table 7.16 and Figure 7.18).

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

Table 7.16 Principal component analysis of emerging contaminants in wastewater effluents

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

Notation: PC = Principal component.

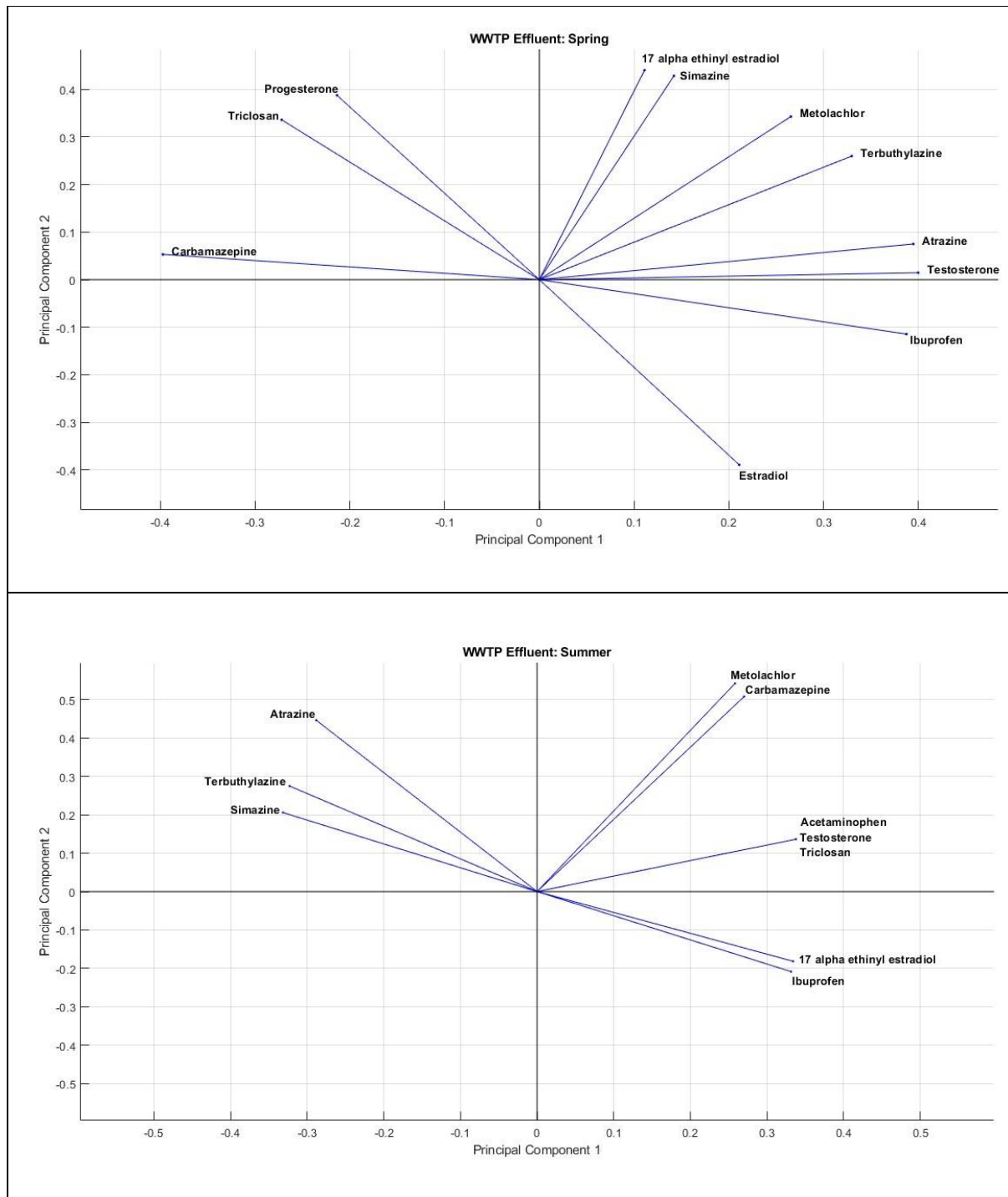


Figure 7.17 PCA results of the first two principal components in effluent during the wet season (spring and summer)

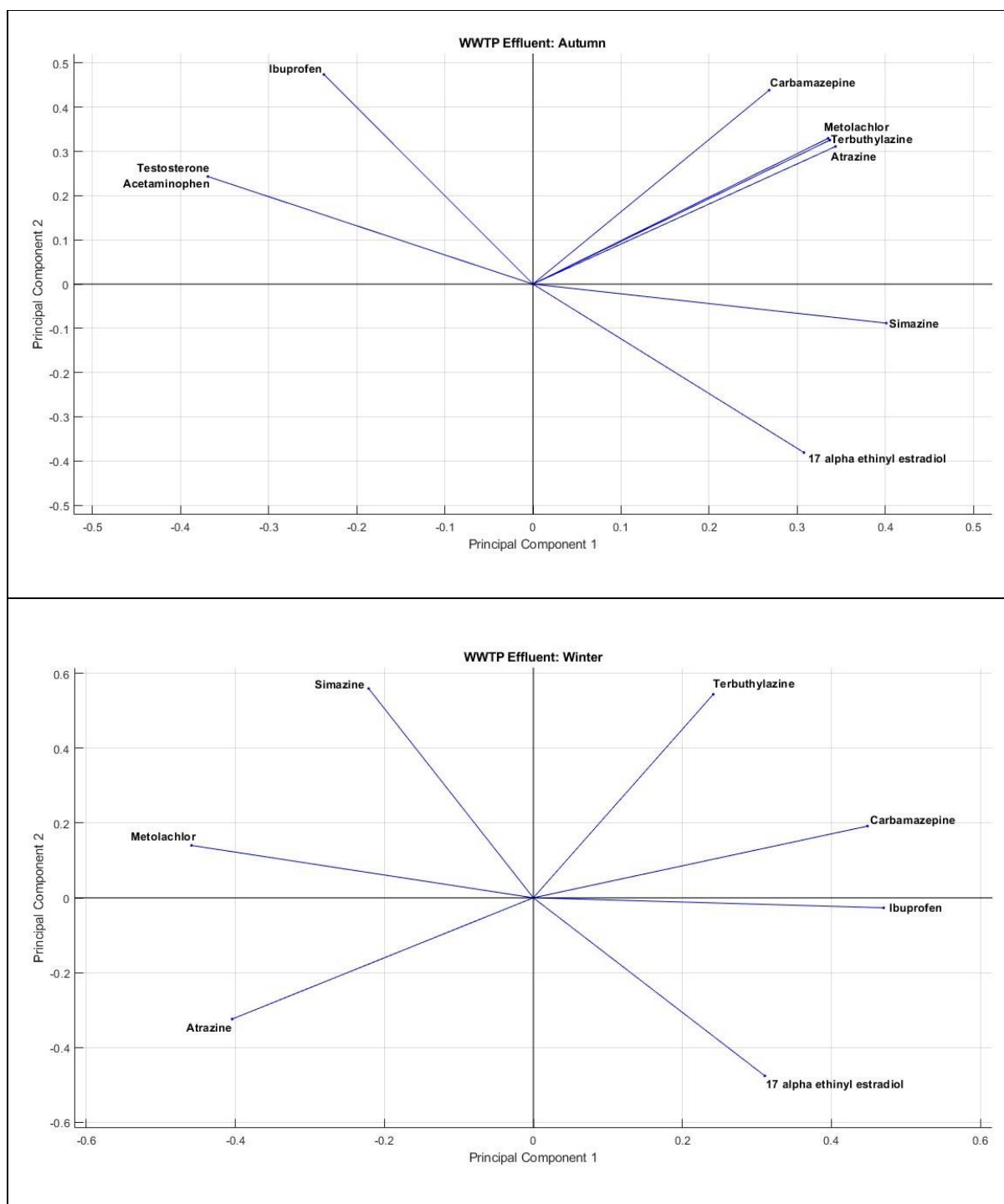


Figure 7.18 PCA results of the first two principal components in effluent during the dry season (autumn and winter)

7.5.4 Identification of pollution source in treated drinking water

As presented in Table 7.17, only one principal component (PC1) was generated in treated drinking water in all seasons. This may have been influenced by the low number of samples collected ($n=2$). The overall loading factors and the correlation between the first and second

loading factors are also described in Figures 7.19. In spring season, PC1 exhibited a weak positive loading of atrazine and terbuthylazine, suggesting that they share a slight common source of origin. In the summer season, PC1 exhibited a weak positive loading of simazine, atrazine, terbuthylazine, metolachlor and 17-alpha-ethinyl-estradiol. In the autumn and winter seasons, the results of PCA exhibited a weak positive loading of atrazine, terbuthylazine, metolachlor and 17-alpha-ethinyl-estradiol, connoting that they share a similar source of origin. This relative analysis in treated drinking water may be connected to the dams considered as water sources for water treatment plants in the area. The major pathways of pollution in dams were domestic sewage, wastewater effluent, agricultural runoff and illegal dumping. Therefore, the contamination of dams considered as a water source for water treatment plants could eventually lead to detection of emerging contaminants in treated drinking water as a result of inefficient removal by the treatment methods employed in water treatment plants. Most of the positive loadings in treated drinking water in all seasons were pesticides and steroid hormones. Therefore, their occurrence may be linked to wastewater effluent, domestic sewage and agricultural runoff. Agricultural activities are the major carriers of pesticides (Hou et al., 2022), while domestic sewage and wastewater effluents contain various emerging contaminants (Lim et al., 2017; Zhou et al., 2023).

Table 7.17 Principal component analysis of emerging contaminants in treated drinking waters

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

Notation: PC = Principal component.

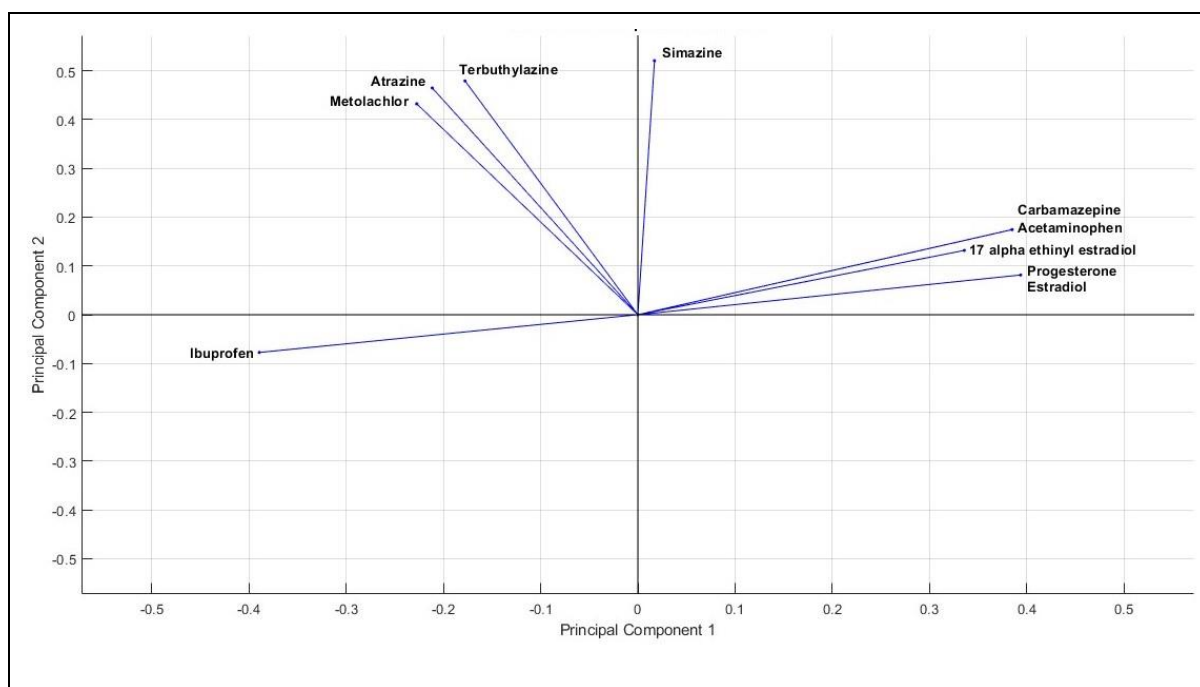


Figure 7.19 PCA results of the first two principal components in treated drinking water

7.6 Mitigation measures to prevent water pollution for sustainable management and environmental health protection

In order to inhibit or reduce the loads of emerging contaminant pollution in water sources for environmental health protection and sustainability of water resources around Bloemfontein, various types of interventions are necessary. Based on the source apportionment results in this study, emerging contaminants in water sources around Bloemfontein are generally released mainly as a result of anthropogenic activities. The established potential anthropogenic sources of pollution include wastewater effluents, domestic sewage, urban surface runoff, agricultural runoff and illegal dumping, as shown in Figure 7.20. It is worth noting that this study did not seek to implement any means of mitigation, but only to inform local inhabitants, WWTP managers, farmers and the relevant authorities about the sources of emerging contaminants to their water sources and also the possibilities around reducing the pollution of emerging contaminants through various mitigation actions. Therefore, the following mitigation measures are suggested to help manage or correct the situation.

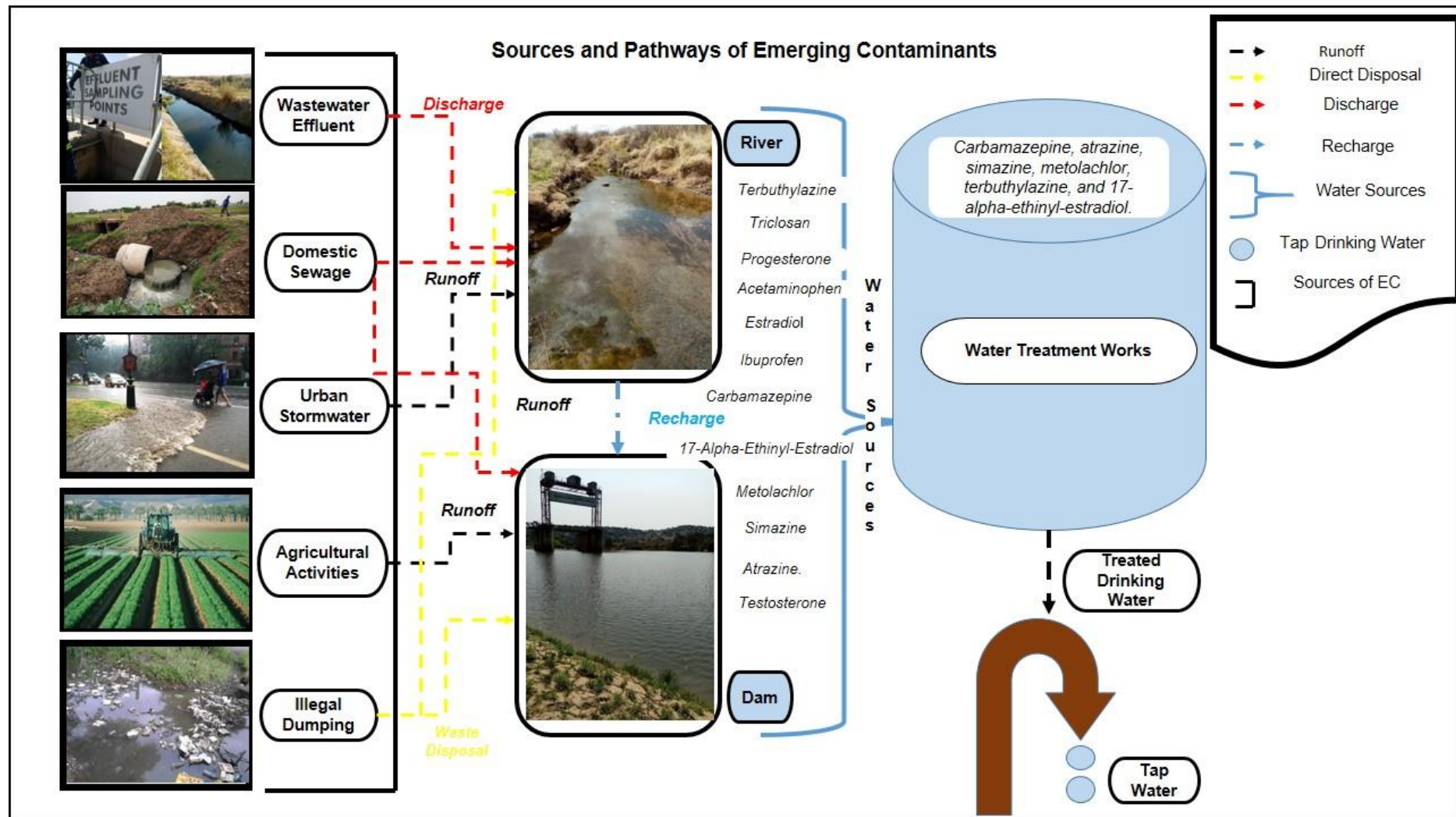


Figure 7.20 Exemplification of major routes of emerging contaminants in water sources around Bloemfontein

7.6.1 Wastewater effluent discharged in nearby streams

Most of the wastewater effluents in the study area are discharged into nearby streams, thus introducing traces of emerging contaminants in those water sources. According to Wang et al. (2015), conventional WWTPs were not constructed to eliminate emerging contaminants i.e. acetaminophen, ibuprofen, carbamazepine, triclosan, atrazine, metolachlor, terbuthilazine, simazine, 17-alpha-ethinyl-estradiol, progesterone, testosterone, and estradiol. The incompetence of WWTPs in the elimination of emerging contaminants makes them to be major points of release of emerging contaminants into the water environment. Therefore, relevant regulatory authorities should introduce proactive measures in the form of mandatory orders, and formulates proper guidelines for permissible limits for the discharge of effluents in streams to reduce emerging contaminant pollution (Caban and Stepnowski, 2021). Considering that WWTPs in this study receive industrial, domestic and hospital wastewater together, there should be implementation and application of monitoring schemes that are able to discriminate between the domestic, industrial and hospital wastewater in the area. Governments should also financially support current WWTPs in developing and implementing advanced treatment techniques such as powdered activated carbon treatment, ozonation, and peroxidation for the elimination of a broad spectrum of emerging contaminants with different properties (Gozzo et al., 2023). This should be followed by setting of performance indicators that assess the performance of WWTPs towards emerging contaminant removal. Moreover, WWTPs operators or managers should assess the overall mixture toxicity of emerging contaminants in effluents before discharge in order to protect aquatic life (Bourgin et al., 2018).

7.6.2 Illegal dumping of domestic waste near water bodies

During the sampling campaign, illegal dumping of domestic waste (likely to contain unused or expired medical drugs: acetaminophen, ibuprofen, or carbamazepine) near some of the dams and rivers was witnessed. This situation may be due to lack of knowledge about the impact that organic contaminants may have on the environment. Moreover, lack of proper disposal means may also have intensified illegal dumping around the area. Therefore, educating people to segregate wastes at the source and providing incentives to facilitate waste segregation may reduce illegal dumping in the area (Kihila et al., 2021). Taking back unused or expired medications may help to mitigate their quantities in the aqueous environment and their possible health risks. However, the effectiveness of this strategy rests on teaching people the possible environmental implications of unused or expired medicinal

drugs (Caban and Stepnowski, 2021). Therefore, local communities should be educated on the proper waste disposal methods and environmental implication of illegal dumping.

7.6.3 Emission from domestic sewage overflow

Domestic sewage overflows were also considered as the major sources for emerging contaminant emissions into water sources. From the field observation, some of the raw domestic sewage water overflows were channelled towards surface water. This situation makes the majority of contaminants (acetaminophen, ibuprofen, carbamazepine, triclosan, atrazine, metolachlor, terbuthilazine, simazine, 17-alpha-ethinyl-estradiol, progesterone, testosterone, or estradiol) to enter the water resources without the necessary treatment. Considering the increase in intensity and frequency of rainfall as a result of climate change, technical measures in the design of the sewer system are required in this area in order to reduce emission from these sources (Bourgin et al., 2018).

7.6.4 Emission from urban stormwater runoff

Stormwater is a cause of concern in urban areas due to the fact that urban areas are more polluted by a cocktail of anthropogenic emissions. The occurrence of emerging contaminants in stormwater may be a result of runoff; illegal dumping of wastewater and unsealed systems and overflow in combined sewer systems. Moreover, the pollution of surface runoff by emerging contaminants (acetaminophen, ibuprofen, carbamazepine, triclosan, atrazine, metolachlor, terbuthilazine, simazine, 17-alpha-ethinyl-estradiol, progesterone, testosterone, or estradiol) is related to various activities such as the utilisation of solid sludge from WWTPs for soil amendments; the use of reclaimed wastewater for soil irrigation; the use of slurry and liquid manure as fertilisers; and urination, defecation of grazing animals and pets. Rain water may carry pesticides from golf courses, parks and residential properties through stormwater drains and then into rivers and local water reservoirs. Priority should also be placed on enhancing nonpoint source pollution control measures around the study area, including the implementation of infrastructure improvements, such as rainwater and sewage separation systems. These measures can effectively impede the entry of land-based emerging contaminants into water sources around the city of Bloemfontein (Caban and Stepnowski, 2021).

7.6.5 Emission from agricultural activities

The city of Bloemfontein is surrounded by various agricultural activities such as crop production and animal husbandry. Crop production may necessitate the use of herbicides

(atrazine, simazine, metolachlor) for maintenance of various crops, while animal husbandry may require the use of medicinal drugs (fenbendazole, carprofen, or estradiol) for the health of livestock. Emission from these activities may introduce these compounds in nearby water bodies. According to Gozzo et al. (2023), one of the main causes of pharmaceutical pollution is intensive farming, excretion through faeces, urine during the free grazing of animals, manure spreading on land and contamination via runoff. Therefore, reducing both intensive farming and the use of livestock drugs could be crucial to warrant the quality of surface waters around Bloemfontein. Furthermore, improvements in agricultural practices may protect water bodies and also contribute to the reduction of risks connected with the occurrence of emerging contaminants. Changes in treatment timings and intensities, as well as manure application rates and timings may help to reduce discharges of emerging contaminants in the area (Topp et al., 2008).

7.7 Conclusion

Examining the potential sources of emerging contaminants for the first time in water sources around Bloemfontein brings to an end the dearth of data on the origin of emerging contaminant pollution. The present study suggests that water sources around Bloemfontein are vulnerable to pollution by emerging contaminants as a result of anthropogenic activities. From the results of multivariate statistical analysis, anthropogenic activities such as wastewater effluents, domestic sewage, urban surface runoff, agricultural runoff and illegal dumping were specified as the possible sources of these contaminants in water sources. Although this study did not seek to implement means of mitigation, but only to inform local inhabitants, WWTP managers, farmers and relevant authorities of the pathways of emerging contaminants to their water sources and also the possibilities around reducing the pollution of emerging contaminants through various mitigation actions, its outcomes may be relevant for the prioritisation of hazardous substances in order to address suitable monitoring campaigns and any necessary countermeasures to be adopted for environmental protection as well as sustainability of water resources. It may also facilitate the management of existing and future sources of emerging contaminant pollution around Bloemfontein.

Chapter 8

CONCLUSIONS AND RECOMMENDATIONS

The aim of the project was to assess the environmental health risks of potential emerging contaminants identified from water sources around Bloemfontein in the Free State province of South Africa. This was achieved by first conducting a non-targeted qualitative screening of emerging contaminants which was followed by quantification of targeted emerging contaminants in various water sources. The second part of the project was to assess the environmental health risks ensuing from exposure to emerging contaminants in water sources. The last segment of the study focused on identifying possible sources of targeted emerging contaminants as well as proposing possible control measures based on their sources identified. From the findings of this project, the following conclusions and recommendations were drawn.

8.1 Conclusions

8.1.1 Investigation and monitoring of potential emerging contaminants in water sources

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

The quantification of targeted emerging contaminants such as acetaminophen, carbamazepine, ibuprofen, triclosan, atrazine, simazine, metolachlor, terbutylazine, 17-alpha-ethinyl-estradiol, estradiol, progesterone and testosterone in selected water sources around Bloemfontein provided a much needed initial measurement of these contaminants. The majority of these contaminants have been found in quantifiable concentrations in all water sources. Among them, 17-alpha-ethinyl-estradiol, simazine and ibuprofen showed the highest concentrations in all water sources and should be listed as priority pollutants in

future pollution monitoring and waste management programmes within the area. Most remarkable was the concentration of 17-alpha-ethinyl-estradiol that was far higher than the one detected in most studies around South Africa. These findings will raise awareness on the presence of emerging contaminants in water sources and may facilitate the need to develop regulations aimed at plummeting the spread of emerging contaminants in the area and other parts of the country.

Moreover, WWTPs showed insufficient removal efficiency of compounds such as carbamazepine, atrazine, metolachlor, simazine and 17-alpha-ethinyl-estradiol. Most prominent was the inability of wastewater treatment work to get rid of pesticides. In South Africa, wastewater effluent is typically released into nearby streams introducing pollutants into the aqueous environment. Therefore, based on the findings of their removal efficiency, it can be concluded that the release of wastewater effluents to nearby watercourses will eventually cause pollution and adversely affect the aquatic species and human health.

8.1.2 Environmental risk assessment of emerging contaminants

To have a complete understanding of the environmental risks emanating from exposure to emerging contaminants, both individual and mixture risks were assessed. Individual environmental risk assessment results showed the possibility of some emerging contaminants to pose high risks on aquatic organisms. Moreover, the results of mixture risks assessment also confirmed that aquatic species were more sensitive to mixture of targeted compounds in this study. It can be concluded that water sources around Bloemfontein are not safe for aquatic species and public health. The high individual and mixture environmental risks reported in this study may seriously impair the ecosystem and adversely affect living organisms. Exposure to these contaminants in water sources may pose a variety of risks, including developmental, growth and reproductive effects. The outcomes of risk assessment will serve as a cornerstone in the Free State province for developing a more complete understanding of the environmental health risks linked to exposure to emerging contaminants. Furthermore, it will assist in establishing municipal contamination control and risk reduction approaches for organic chemicals.

8.1.3 Human health risk assessment of selected pesticides in water sources

The human health risk assessment results showed only atrazine to have the likelihood to impose high carcinogenic risks. The high carcinogenic risk of atrazine is a serious public health concern as its exposure is associated with reproductive and cancer risks. These outcomes suggest the need to use pesticides in a more sustainable manner and adoption of

less harmful pesticides. The findings of this work will fill in the lacuna on the knowledge of the public health risks linked to the exposure of pesticides in water sources around Bloemfontein. It may also help in the development of environmental quality standards for regulatory purposes as well as for environmental sustainability.

8.1.4 Sources of emerging contaminants in water sources and possible mitigation measures

The multivariate statistical analysis put forward that water sources around Bloemfontein are vulnerable to pollution by emerging contaminants as a result of anthropogenic activities such as wastewater effluents, domestic sewage, urban surface runoff, agricultural runoff and illegal dumping. Although this study did not seek to implement the means of mitigation, but only to inform local inhabitants, WWTP managers, farmers and relevant authorities of the sources of emerging contaminants to their water sources, its outcomes may be relevant for the prioritisation of hazardous substances in order to address suitable monitoring campaigns and any necessary countermeasures to be adopted for environmental protection and sustainability of water resources. Protecting raw water from emerging contaminant pollution is an indicative premise of the water environment and ecosystem health. This work may also facilitate the management of existing and future sources of emerging contaminant pollution within the city of Bloemfontein.

8.2 Recommendations

The following recommendations can be made:

- Additional groups of emerging contaminants should be targeted in water sources around Bloemfontein.
- Considering that WWTPs in this study receive industrial, domestic and hospital wastewater together, there should be implementation and application of monitoring schemes that are able to discriminate between the domestic, industrial and hospital wastewater in the area.
- Wastewater treatment managers should conduct individual and mixture risks assessment before discharging effluent into nearby streams.
- Development and implementation of advanced treatment technologies for the elimination of a broad spectrum of emerging contaminants with different properties is recommended.

- Residents in Bloemfontein and surrounding areas should be educated on segregating waste at the source.
- Taking back unused or expired medications may help to mitigate their quantities in the aqueous environment and their possible health risks.
- Reducing both intensive farming and the use of livestock drugs could be crucial to warranty the quality of surface water around Bloemfontein.
- Relevant organs of states should develop policies on the manufacturing, use, and release of ECs should be formulated.
- Future studies should assess the human health risk of pesticides exposure via vegetables irrigated by wastewater effluents.
- Future studies should monitor occurrence of emerging contaminants in groundwater sources around Bloemfontein.

REFERENCES

- Aalizadeh, R., Thomaidis, N.S., Bletsou, A.A., Gago-Ferrero, P. (2016). Quantitative structure-retention relationship models to support nontarget high-resolution mass spectrometric screening of emerging contaminants in environmental samples. *Journal of Chemical Information Modelling*, 56(7):1384-1398. <https://doi.org/10.1021/acs.jcim.5b00752>
- Abafe, O.A., Lawal, M.A., Chokwe, T.B. (2023). Non-targeted screening of emerging contaminants in South African surface and wastewater. *Emerging Contaminants*, 9(4), article 100246. <https://doi.org/10.1016/j.emcon.2023.100246>
- Abera, B., Van Echelpoel, W., De Cock, A., Tytgat, B., Kibret, M., Spanoghe, P., Mengistu, D., Adgo, E., Nyssen, J., Goethals, P.L.M., Verleyen, E. (2022). Environmental and human health risks of pesticide presence in the Lake Tana basin (Ethiopia). *Sustainability*, 14(21), article 14008. <https://doi.org/10.3390/su142114008>
- Adeleye, A.P. (2016). Perfluorinated compounds, bishenol and acetaminophen in selected waste water treatment plants in and around Cape Town, South Africa. Masters dissertation, Cape Peninsula University of Technology, South Africa. <http://hdl.handle.net/20.500.11838/2331>
- Ademoyegun, O.T (2017). Evaluation of some pharmaceutical and personal care products and pesticide residues in selected wastewater treatment plants and receiving watersheds in Eastern Cape, South Africa. Doctoral thesis, University of Fort Hare, South Africa. <http://hdl.handle.net/10353/2922>
- Adjei, J.K., Dayie, A.D., Addo, J.K., Asamoah A., Amoako, E.O., Egoh, B.Y., Bekoe, E., Ofori, N.O., Adjei, G.A., and Essumang, D.K. (2022). Occurrence, ecological risk assessment and source apportionment of pharmaceuticals, steroid hormones and xenoestrogens in the Ghanaian aquatic environments. *Toxicology Reports*, 9:1398-1409. <https://doi.org/10.1016/j.toxrep.2022.06.011>
- Agunbiade, F.O., Moodley, B. (2014). Pharmaceuticals as emerging organic contaminants in Umgeni River water system, KwaZulu-Natal, South Africa. *Environmental Monitoring and Assessment*, 186(11):7273-7291. <https://doi.org/10.1007/s10661-014-3926-z>
- Agunbiade, F.O., Moodley, B. (2016). Occurrence and distribution pattern of acidic pharmaceuticals in surface water, wastewater, and sediment of the Msunduzi River,

KwaZulu-Natal, South Africa. *Environmental Toxicology and Chemistry*, 35(1):36-46.
<https://doi.org/10.1002/etc.3144>

Alexovič, M., Horstkotte, B., Solich, P., Sabo, J. (2016). Automation of static and dynamic non-dispersive liquid phase microextraction. Part 1: Approaches based on extractant drop-, plug-, film- and microflow-formation. *Analytical Chemical Acta*, 4(906):22-40.
<https://doi.org/10.1016/j.aca.2015.11.038>

Al-Kaf, A.G., Naji, K.M., Abdullah, Q.Y.M., Edrees, W.H.A. (2017). Occurrence of paracetamol in aquatic environments and transformation by microorganisms: A review. *Chronicles of Pharmaceutical Science*, 1(6):341-355.
<https://www.researchgate.net/publication/32204110>

Almberg, K.S., Mary E., M.E., Jones, R.M., Rankin, K., Freels, S., Stayner, L.T. (2018). Atrazine Contamination of drinking water and adverse birth outcomes in community water systems with elevated atrazine in Ohio, 2006-2008. *International Journal of Environmental Research Public Health*, 15(9), article 1889. <https://doi.org/10.3390/ijerph15091889>

Almomani, F.A., Shawaqfah, M., Bhosale, R.R., Kumar, A. (2016). Removal of emerging pharmaceuticals from wastewater by ozone-based advanced oxidation processes. *Environmental Progress & Sustainable Energy*, 35(4):982-995.
<https://doi.org/10.1002/ep.12306>

Al-Tarawneh, I., El-Dosoky, M., Alawi, M., Batarseh, M., Widyasari, A., Kreuzig, R., Bahadir, M. (2014). Studies on human pharmaceuticals in Jordanian wastewater samples. *Clean: Soil, Air, Water*, 43(4):504-511. <https://doi.org/10.1002/clen.201300920>

Alves, D.D., Riegel, R.P., De Quevedo, D.M., Osório, D.M.M., Da Costa, G.M., Do Nascimento, C.A., Telöken, F. (2018). Seasonal assessment and apportionment of surface water pollution using multivariate statistical methods: Sinos River, southern Brazil. *Environmental Monitoring and Assessment*, 190(7), article 384.
<https://doi.org/10.1007/s10661-018-6759-3>

Archer, E., Wolfaardt, G.M., Van Wyk, J.H. (2017). Pharmaceutical and personal care products (PPCPs) as endocrine disrupting contaminants (EDCs) in South African surface waters. *Water SA*, 43(4):1-23. <https://doi.org/10.4314/wsa.v43i4.16>

Archer, E., Volschenk, M., Bocker, L., Wolfaardt, G.M. (2021). A two-year study of emerging micro-pollutants and drugs of abuse in two Western Cape wastewater treatment works (South Africa). *Chemosphere*, 285, article 131460.
<https://doi.org/10.1016/j.chemosphere.2021.131460>

Archer, E., Holtonb, E., Fidal, J., Kasprzyk-Hordern, B., Carstens, A., Brocker, L., Kjeldsen, T.R., Wolfaardt, G.M. (2023). Occurrence of contaminants of emerging concern in the Eerste River, South Africa: Towards the optimisation of an urban water profiling approach for public- and ecological health risk characterisation. *Science of the Total Environment*, 859, article 160254. <https://doi.org/10.1016/j.scitotenv.2022.160254>

Aydinalp, C., Monica, M., Porca, M.M. (2004). The effects of pesticides in water resources. *Journal of Central European Agriculture*, 5(1):5-12. <https://icea.agr.hr/en/issues/article/149>

Babuji, P., Thirumalaisamy, S., Duraisamy, K., Periyasamy, G. (2023). Human Health Risks due to Exposure to Water Pollution: A Review. *Water*, 15, 2532. doi: 10.3390/w15142532

Backhaus, T., Faust, M. (2012). Predictive environmental risk assessment of chemical mixtures: a conceptual framework. *Environmental Science and Technology*, 46:2564-2573. <https://doi.org/10.1021/es2034125>

Backhaus, T., Karlsson, M. (2014). Screening level mixture risk assessment of pharmaceuticals in STP effluents. *Water Research*, 49:157-165. <https://doi.org/10.1016/j.watres.2013.11.005>

Backhaus, T., Altenburger, R., Faust, M., Frein, D., Frische, T., Johansson, P., Kehrner, A., Porsbring, T. (2013). Proposal for environmental mixture risk assessment in the context of the biocidal product authorization in the EU. *Environmental Sciences Europe*, 25, article 4. <https://doi.org/10.1186/2190-4715-25-4>

Bagheri, M. (2021). Exposure assessment of emerging contaminants: Rapid screening and modeling of plant uptake. Doctoral thesis, Missouri University of Science and Technology. https://scholarsmine.mst.edu/doctoral_dissertations/2964

Bagnis, S., Boxall, A., Gachanja, A., Fitzsimons, M., Murigi, M., Snape, J., Tappin, A., Wilkinson, J., Comber, S. (2020). Characterization of the Nairobi River catchment impact zone and occurrence of pharmaceuticals: implications for an impact zone inclusive environmental risk assessment. *Science of the Total Environment*, 703, article 134925. <https://doi.org/10.1016/j.scitotenv.2019.134925>

Baker, D.R., Kasprzyk-Hordern, B. (2013). Spatial and temporal occurrence of pharmaceuticals and illicit drugs in the aqueous environment and during wastewater treatment: New developments. *Science of the Total Environment*, 454-455:442-456. <https://doi.org/10.1016/j.scitotenv.2013.03.043>

Banerjee, S., Mazumdar, S. (2012). Electrospray ionization mass spectrometry: A technique to access the information beyond the molecular weight of the analyte. *International Journal of Analytical Chemistry*, 2012, article 282574. <https://doi.org/10.1155/2012/282574>

Brack, W., Hollender, J., De Alda, M.L., Müller, C., Schulze, T., Schymanski, E., Slobodnik, J., Krauss, M. (2019). High-resolution mass spectrometry to complement monitoring and track emerging chemicals and pollution trends in European water resources. *Environmental Science Europe*, 31:62. <https://doi.org/10.1186/s12302-019-0230-0>

Barbosa, M.O, Ribeiro, A.R., Nuno Ratola, N., Hainc, E., Homemb, V., Pereira, M.F.R., Blaney, L., Silva, A.M.T. (2018). Spatial and seasonal occurrence of micro-pollutants in four Portuguese rivers and a case study for fluorescence excitation-emission matrices. *Science of the Total Environment*, 644:1128-1140. <https://doi.org/10.1016/j.scitotenv.2018.06.355>

Barceló, D., Petrovic, M. (2007). Pharmaceuticals and personal care products (PPCPs) in the environment. *Analytical and Bioanalytical Chemistry*, 387:1141-1142. <https://doi.org/10.1007/s00216-006-1012-2>

Barton-Maclaren, T.S., Wade, M., Basu, N., Bayen, S., Grundy, J., Marlatt, V., Moore, R., Parent, L., Parrott, J., Grigorova, P., Pinsonnault-Cooper, J., Langlois, V.S. (2022). Innovation in regulatory approaches for endocrine disrupting chemicals: The journey to risk assessment modernization in Canada. *Environmental Research*, 204, article 112225. <https://doi.org/10.1016/j.envres.2021.112225>

Bashingi, N., Hassan M.M., Das, D.K. (2018). Public transportation and land use impacts on accessibility for sustainable public transportation system in Bloemfontein. 37th Annual Southern African Transport Conference (SATC 2018). 769-780. ISBN: 978-1-920017-89-7

Bayen, S., Estrada, E.S., Juhel, G., Kit, L.W., Kelly, B.C. (2016). Pharmaceutically active compounds and endocrine disrupting chemicals in water, Sediments and mollusks in mangrove ecosystems from Singapore. *Maine Pollution Bulletin*, 109(2):716-722. <https://doi.org/10.1016/j.marpolbul.2016.06.105>

Beckie, R.D. (2013). Groundwater. In: *Reference module in earth systems and environmental sciences*, pp. 1-3. Elsevier Reference Collection in Earth Systems and Environmental Sciences. <https://doi.org/10.1016/B978-0-12-409548-9.05923-6>

Belden, J.B., Gilliom, R.J., Lydy, M.J. (2007) How well can we predict the toxicity of pesticide mixtures to aquatic life? *Integrated Environmental Assessment and Management*, 3:364-372. <https://pubmed.ncbi.nlm.nih.gov/17695109/>

Bella-Atangana, M.S., Dam-Ngoupayou, J.R., Deliege, J.F. (2023). Hydrogeochemistry and mercury contamination of surface water in the Lom Gold Basin (East Cameroon): Water quality index, multivariate statistical analysis and spatial interpolation. *Water*, 15, article 2502. <https://doi.org/10.3390/w15132502>

Benn, T.M., Westerhoff, P. (2008). Nanoparticle silver released into water from commercially available sock fabrics. *Environmental Science and Technology*, 42(11):4133-4139. <https://doi.org/10.1021/es7032718>

Benotti, M.J., Brownawell, B.J. (2009) Microbial degradation of pharmaceuticals in estuarine and coastal seawater. *Environmental Pollution*, 157(3):994-1002. <https://doi.org/10.1016/j.envpol.2008.10.009>

Bexfield, L.M., Toccalino, P.L., Belitz, K., Foreman, W.T., Furlong, E.T. (2019). Hormones and pharmaceuticals in groundwater used as a source of drinking water across the United States. *Environmental Science and Technology*, 53:2950-2960. <https://doi.org/10.1021/acs.est.8b05592>

Białk-Bielińska, A., Grabarczyk, L., Mulkiewicz, E., Puckowski, A., Stolte, S., Stepnowski, P. (2022). Mixture toxicity of six pharmaceuticals towards *Aliivibrio fischeri*, *Daphnia magna*, and *Lemna minor*. *Environmental Science and Pollution Research*, 29:26977-26991. <https://doi.org/10.1007/s11356-021-17928-y>

Birnbaum, L.S., Fenton, S.E. (2003). Cancer and development exposure to endocrine disruptors. *Environmental Health Perspectives*, 111(4):389-294. <https://doi.org/10.1289/ehp.5686>

Blackstock, K., Richards, C. (2007). Evaluating stakeholder involvement in river basin planning: A Scottish case study. *Water Policy*, 9(5):493-512. <https://doi.org/10.2166/wp.2007.018>

Bonecker, C.C., Diniz, L.P., De Braghin, L.S.M., Mantovano, T., Da Silva, J.V.F., Bomfim, F., De Fátima Bomfim, F., Moi, D.A., Deosti, S., Dos Santos, G.N.T., Das Candeias, D.A., Mota, A.J. de M.M., Velho, L.F.M., Tôha, F.A.L. (2020). Synergistic effects of natural and anthropogenic impacts on zooplankton diversity in a subtropical floodplain: A long-term study. *Oecologia Australis*, 24(2):524-537. <https://doi.org/10.4257/oeco.2020.2402.20>

Bourgin, M., Beck, B., Boehler, M., Borowska, E., Fleiner, J., Salhi, E., Teichler, R., Von Gunten, U., Siegrist, H., McArdell, C.S. (2018). Evaluation of a full-scale wastewater treatment plant upgraded with ozonation and biological post-treatments: Abatement of

micropollutants, formation of transformation products and oxidation by-products. *Water Research*, 129:486-498. <https://doi.org/10.1016/j.watres.2017.10.036>

Bouzas-Monroy, A., Wilkinson, A.L., Alistair, M., Boxall, A.B.A. (2022). Assessment of the potential ecotoxicological effects of pharmaceuticals in the world's rivers. *Environmental Toxicology and Chemistry*, 41(8):2008-2020. <https://doi.org/10.1002/etc.5355>

Boxall, A.B.A. (2012). New and emerging water pollutants arising from agriculture. OCED study (2012): *Water quality and agriculture: Meeting the policy challenge*. OECD Publishing. <https://www.oecd.org/greengrowth/sustainable-agriculture/49848768.pdf>

Brack, W., Hollender, J., de Alda, M.L., Müller, C., Schulze, T., Schymanski, E., Slobodnik, J., Krauss, M. (2019). High-resolution mass spectrometry to complement monitoring and track emerging chemicals and pollution trends in European water resources. *Environmental Science Europe*, 31, article 62. <https://doi.org/10.1186/s12302-019-0230-0>

Brausch, J.M., Rand, G.M. (2011). A review of personal care products in the aquatic environment: environmental concentrations and toxicity. *Chemosphere*, 82:1518-1532. <https://doi.org/10.1016/j.chemosphere.2010.11.018>

Brumovský, M., Becanova, J., Kohoutek, J., Borghini, M., Nizzetto, L., (2017). Contaminants of emerging concern in the open sea waters of the Western Mediterranean. *Environmental Pollution*, 229:976-983. <https://doi.org/10.1016/j.envpol.2017.07.082>

Brun, G.L., Bermer, M., Losier, R., Doe, K., Jackman, P., Lee, H.B. (2006). Pharmaceutically active compounds in Atlantic Canadian sewage treatment plant effluents and receiving water and potential for environmental effects as measured by acute and chronic aquatic toxicity. *Environmental Toxicology and Chemistry*, 25(8):2163-2176. <https://doi.org/10.1897/05-426R.1>

Bundschuh, M., Filser, J., Lüderwald, S., Mckee, M.S., Metreveli, G., Schaumann, G.E., Schulz, R., Wagner, S. (2018). Nanoparticles in the environment: where do we come from, where do go to? *Environmental Science Europe*, 30, article 6. <https://doi.org/10.1186/s12302-018-0132-6>

Bwapwa, J.K., Jaiyeola, A.T. (2019). Emerging contaminants in drinking water and wastewater, effects on environment and remediation. *International Journal of Applied Engineering Research*, 14(2):539-546. https://www.ripublication.com/ijaer19/ijaerv14n2_28.pdf

Bwire, G., Sack, D.A., Kagirita, A., Obala, T., Debes, A.M., Ram, M., Komakech, H., George, C.M., Orach, C.G. (2020). The quality of drinking and domestic water from the surface water sources (lakes, rivers, irrigation canals and ponds) and springs in cholera prone communities of Uganda: An analysis of vital physicochemical parameters. *BMC Public Health*, 20, article 1128. <https://doi.org/10.1186/s12889-020-09186-3>

Caban, M., Stepnowski, P. (2021). How to decrease pharmaceuticals in the environment? A review. *Environmental Chemistry Letters*, 19:3115-3138. <https://doi.org/10.1007/s10311-021-01194-y>

Cai, M.Q., Wang, R., Feng, L., Zhang, L.Q. (2015). Determination of selected pharmaceuticals in tap water and drinking water treatment plant by high-performance liquid chromatography-triple quadrupole mass spectrometer in Beijing, China. *Environmental Science and Pollution Research*, 22(3):1854-1867. <https://doi.org/10.1007/s11356-014-3473-8>

Campos, D., Gravato, C., Quintaneiro, C., Koba, O., Randak, T., Soares, A.M., Pestana, J.L. (2016). Are insect repellents toxic to freshwater insects? A case study using caddisflies exposed to DEET. *Chemosphere*, 49:177-182. <https://doi.org/10.1016/j.chemosphere.2016.01.098>

Cardini, A., Pellegrino, E., Ercoli, L. (2021). Predicted and measured concentration of pharmaceuticals in surface water of areas with increasing anthropic pressure: A case study in the coastal area of central Italy. *Water*, 13, article 2807. <https://doi.org/10.3390/w13202807>

Carrard, N., Foster, T., Willetts, J. (2019). Groundwater as a source of drinking water in southeast Asia and the Pacific: A multi-country review of current reliance and resource concerns. *Water*, 11(8), article 1605. <https://doi.org/10.3390/w11081605>

Casida, J.E. (2019). Pest toxicology: The primary mechanisms of pesticide actions. *Chemical Research in Toxicology*, 22:609-619. <https://doi.org/10.1021/tx8004949>

Castiglioni, S., Zuccato, E., Fattore, E., Riva, F., Terzaghi, E., Koenig, R., Principi, P., Di Guardo, A. (2020). Micropollutants in Lake Como water in the context of circular economy: a snapshot of water cycle contamination in a changing pollution scenario. *Journal of Hazardous Material*, 384, article 121441. <https://doi.org/10.1016/j.jhazmat.2019.121441>

Čelić, M., Gros, M., Farre, M., Barceló, D., Petrovic, M. (2019). Pharmaceuticals as chemical markers of wastewater contamination in the vulnerable area of the Ebro Delta (Spain).

Science of the Total Environment, 652:952-963.

<https://doi.org/10.1016/j.scitotenv.2018.10.290>

Čelić, M., Jaen-Gil, A., Briceno-Guevara, S., Rodríguez-Mozaz, S., Gros, M., Petrovic, M. (2021). Extended suspect screening to identify contaminants of emerging concern in riverine and coastal ecosystems and assessment of environmental risks Mira. *Journal of Hazardous Materials*, 404, article 124102. <https://doi.org/10.1016/j.jhazmat.2020.124102>

Chang, H., Wan, Y., Wu, S.M., Fan, Z.L., Hu, J.Y. (2011). Occurrence of androgens and progestogens in wastewater treatment plants and receiving river waters: Comparison to estrogens, *Water Research*, 45(2):732-740. <https://doi.org/10.1016/j.watres.2010.08.046>

Chauveau-Duriot, B., Doreau, M., Nozière, P., Graulet, B. (2010). Simultaneous quantification of carotenoids, retinol, and tocopherols in forages, bovine plasma, and milk: validation of a novel UPLC method. *Analytical and Bioanalytical Chemistry*, 397(2):777-790. <https://doi.org/10.1007/s00216-010-3594-y>

Chemical Safety Facts. (2021). *Flame retardants*.

<https://www.chemicalsafetyfacts.org/flame-retardants/>

Chen, C., Zou, W., Chen, S., Zhang, K., Ma, L. (2020). Ecological and health risk assessment of organochlorine pesticides in an urbanized river network of Shanghai, China. *Environmental Science Europe*, 32, article 42. <https://doi.org/10.1186/s12302-020-00322-9>

Chen, H.C., Wang, P.L., Ding, W.H. (2008). Using liquid chromatography ion trap mass spectrometry to determine pharmaceutical residues in Taiwanese rivers and wastewaters. *Chemosphere*, 72(6):863-869. <https://doi.org/10.1016/j.chemosphere.2008.04.005>

Chen, H.Y., Teng, Y.G., Wang, J.S., Song, L.T. (2012). Source apportionment of water pollution in the Jinjiang River (China) using factor analysis with nonnegative constraints and support vector machines. *Environmental Forensics*, 13(2):175-184. <https://doi.org/10.1080/15275922.2012.676597>

Chen, J., Li, F., Fan, Z., Wang, Y. (2016). Integrated application of multivariate statistical methods to source apportionment of watercourses in the Liao River basin, northeast China. *International Journal Environmental Research and Public Health*, 13, article 1035. <https://doi.org/10.3390/ijerph13101035>

Chen, X., Zhu, L., Pan, X., Fang, S., Zhang, Y., Yang, L. (2015). Isomeric specific partitioning behaviors of perfluoroalkyl substances in water dissolved phase, suspended

particulate matters and sediments in Liao River basin and Taihu Lake, China. *Water Research*, 80:235-244. <https://doi.org/10.1016/j.watres.2015.04.032>

Choi, K., Kim, Y., Park, J., Park, C.K., Kim, M., Kim, H.S., Kim, P. (2008). Seasonal variations of several pharmaceutical residues in surface water and sewage treatment plants of Han River, Korea. *Science of the Total Environment*, 405(1-3):120-128. <https://doi.org/10.1016/j.scitotenv.2008.06.038>

Cleuvers, M. (2004). Mixture toxicity of the anti-inflammatory drugs diclofenac, ibuprofen, naproxen, and acetylsalicylic acid. *Ecotoxicology, Environment and Safety*, 59(3):309-315. [https://doi.org/10.1016/S0147-6513\(03\)00141-6](https://doi.org/10.1016/S0147-6513(03)00141-6)

Cochran, K. (2018). Prediction of the degradation of emerging contaminants during oxidative treatment via analysis of reaction rate constants. Master dissertation, California Polytechnic State University, San Luis Obispo, United States. <https://doi.org/10.15368/theses.2018.51>

Collaborative on Health and the Environment. (2019). *Flame retardants*. <https://www.healthandenvironment.org/environmental-health/environmental-risks/chemical-environment-overview/flame-retardants> (Accessed on 03 March 2022).

Correia, N.M., Carbonari, C.A., Velini, E.D. (2020). Detection of herbicides in water bodies of the Samambaia River sub-basin in the federal district and eastern Goiás. *Journal of Environmental Science and Health, Part B*, 55(6):574-582. <https://doi.org/10.1080/03601234.2020.1742000>

Curchod, L., Oltramare, C., Junghans, M., Stamm, C., Dalvie, M.A., Rösli, M., Fuhrmann, S. (2020). Temporal variation of pesticide mixtures in rivers of three agricultural watersheds during a major drought in the Western Cape, South Africa. *Water Research*, 6(1), article 100039. <https://doi.org/10.1016/j.wroa.2019.100039>

Dabrowski, J.M., Peall, S.K.C., Reinecke, A.J., Liess, M., Schulz, R. (2002). Runoff-related pesticide input into the Lourens River, South Africa: Basic data for exposure assessment and risk mitigation at the catchment scale. *Water, Air, and Soil Pollution*, 135:265-283. <https://doi.org/10.1023/A:1014705931212>

Dalvie, M.A., Africa, A., London, L. (2009). Change in the quantity and acute toxicity of pesticides sold in South African crop sectors, 1994–1999. *Environment International*, 35(4):683-687. <https://doi.org/10.1016/j.envint.2008.12.004>

Darradi, Y., Saur, E., Laplana, R., Lescot, J.M., Kuentz, V., Meyer, B.C. (2012). Optimizing the environmental performance of agricultural activities: A case study in La Boulouze watershed. *Ecological Indicators*, 22:27-37. <https://doi.org/10.1016/j.ecolind.2011.10.011>

Das, A. (2022). Multivariate statistical approach for the assessment of water quality of Mahanadi basin, Odisha. *Materials Today: Proceedings*, 65:A1-A11. <https://doi.org/10.1016/j.matpr.2022.08.146>

Das, R., Sarkar, S., Chakraborty, S., Choi, H., Bhattacharjee, C. (2014). Remediation of antiseptic components in wastewater by photocatalysis using TiO₂ nanoparticles. *Industrial & Engineering Chemistry Research*, 53(8):3012-3020. <https://doi.org/10.1021/ie403817z>

Daughton, C.G., Ruhoy, I.S. (2009). Environmental footprint of pharmaceuticals: The significance of factors beyond direct excretion to sewers. *Environmental Toxicology and Chemistry*, 28(12):2495-2521. <http://doi.org/10.1897/08-382.1>

David, A., Pancharatna, K. (2009). Developmental anomalies induced by a non-selective Cox inhibitor (ibuprofen) in zebrafish (*Danio rerio*). *Environmental Toxicology and Pharmacology*, 27:390-395. <https://doi.org/10.1016/j.etap.2009.01.002>

De Jager, C., Aneck-hahn, N.H., Swart, P., Truebody, B., Van Zijl, M.C. (2013). *Estrogenic activity and endocrine disrupting chemical (EDC) status in water obtained from selected distribution points in Pretoria and Cape Town*. Report No. KV317/13, Water Research Commission, Pretoria, South Africa. <https://www.wrc.org.za/wp-content/uploads/mdocs/KV%20317-13.pdf>

Deeb, A.A., Stephan, S., Schmitz, O.J., Schmidt, T.C. (2017). Suspect screening of micro-pollutants and their transformation products in advanced wastewater treatment. *Science of the Total Environment*, 601-602:1247-1253. <https://doi.org/10.1016/j.scitotenv.2017.05.271>

Department of Water Affairs and Forestry. (1996). *South African water quality guidelines, Volume 1: Domestic Water Use* (Second edition). https://www.dws.gov.za/Groundwater/documents/Pol_saWQguideFRESHDomesticusevol1.pdf

Dimpe, K.M., Nomngongo, P.N. (2016). Current sample preparation methodologies for analysis of emerging pollutants in different environmental matrices. *TrAC Trends in Analytical Chemistry*, 82:199-207. <https://doi.org/10.1016/j.trac.2016.05.023>

Dong, W., Zhang, Y., Quan, X. (2023). Health risk assessment of heavy metals and pesticides: A case study in the main drinking water source in Dalian, China. *Chemosphere*, 242, article 125113. <https://doi.org/10.1016/j.chemosphere.2019.125113>

Duarte, D.J., Niebaum, G., Lämmchen, V., Van Heijnsbergen, E., Oldenkamp, R., Hernández-Leal, L., Schmitt, H., Ragas, A.M.J., Klasmeier, J. (2022). Ecological risk assessment of pharmaceuticals in the transboundary Vecht River (Germany and The Netherlands). *Environmental Toxicology and Chemistry*, 41:648-662.
<https://doi.org/10.1002/etc.5062>

Dutta, S., Dwivedi, A., Kumar, M.S. (2018). Use of water quality index and multivariate statistical techniques for the assessment of spatial variations in water quality of a small river. *Environmental Monitoring and Assessment*, 190(12), article 718.
<https://doi.org/10.1007/s10661-018-7100-x>

Ebele, A.J., Abdallah M.A., Harrad, S. (2017). Pharmaceuticals and personal care products (PPCPs) in the freshwater aquatic environment. *Emerging Contaminants*, 3:1-16.
<https://doi.org/10.1016/j.emcon.2016.12.004>

ECOTOX Knowledgebase (2018). *Ecotoxicology (ECOTOX) knowledgebase resource hub*.
<https://www.epa.gov/comptox-tools/ecotoxicology-ecotox-knowledgebase-resource-hub>
(Accessed on 26 July 2023)

Edokpayi, J.N., Odiyo, J.O., Durowoju, O.S. (2017). Impact of wastewater on surface water quality in developing countries: A case study of South Africa. In: Tutu, H. (Eds.), *Water Quality*, pp. 401-416. London: Intechopen. <http://dx.doi.org/10.5772/66561>

Edwards, M., Mostafa, A., Górecki, T. (2011). Modulation in comprehensive two-dimensional gas chromatography: 20 years of innovation. *Analytical and Bioanalytical Chemistry*, 401:2335-2349. <https://doi.org/10.1007/s00216-011-5100-6>

Edwards, Q.A., Kulikov, S.M., Garner-O'neale, L.D. (2015). Caffeine in surface and waste-waters in Barbados, West Indies. *SpringerPlus*, 4, article 57. <https://doi.org/10.1186/s40064-015-0809-x>

Ekinci, M., Ciftci, B., Celik, E.C., Köse, E.A., Karakaya, M.A., Ozdenkaya, Y. (2020). A randomized, placebo-controlled, double-blind study that evaluates efficacy of intravenous ibuprofen and acetaminophen for postoperative pain treatment following laparoscopic cholecystectomy surgery. *Journal of Gastrointestinal Surgery*, 24(4):780-785.
<https://doi.org/10.1007/s11605-019-04220-1>

Enyigwe, M.T., Onwuka, O.S., Egbueri, J.C. (2022). Geochemical distribution, statistical and health risk assessment of toxic elements in groundwater from a typical mining district in Nigeria. *Environmental Forensics*, 23(5-6):469-481.

<https://doi.org/10.1080/15275922.2021.1907822>

Escudero, J., Muñoz, J.L., Morera-Herreras, T., Hernandez, R., Medrano, J., Domingo-Echaburu, S., Barceló, D., Orive, G., Lertxundi, U. (2021). Antipsychotics as environmental pollutants: An underrated threat? *Science of the Total Environment*, 769, article 144634.

<https://doi.org/10.1016/j.scitotenv.2020.144634>

Esplugas, S., Bila, D.M., Krause, L.G.T., Dezotti, M. (2007). Ozonation and advanced oxidation technologies to remove endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) in water effluents. *Journal of Hazardous Materials*, 149(3):631-642. <https://doi.org/10.1016/j.jhazmat.2007.07.073>

Esterhuizen, L. (2014). Drinking water quality and farming practices on dairy farms in the greater Mangaung Metro, South Africa. Doctoral thesis, Central University of Technology, Free State, South Africa. <http://hdl.handle.net/11462/1157>

European Commission (2011). Recommendation on the definition of nanomaterial (2011/696/EU). https://ec.europa.eu/environment/chemicals/nanotech/faq/definition_en.htm (Accessed on 28 May 2022).

Fairbairn, D.J., Karpuzcu, E.M., Arnold, W.A., Barber, B.L., Kaufenberg, E.F., Koskinen, W.C., Novak, P.J., Rice, P.J., Swackhamer, D.L. (2014). Sediment-water distribution of contaminants of emerging concern in a mixed use watershed. *Science of the Total Environment*, 505:896-904. <https://doi.org/10.1016/j.scitotenv.2014.10.046>

Fang, T.H., Nan, F.H., Chin, T.S., Feng, H.M. (2012). The occurrence and distribution of pharmaceutical compounds in the effluents of a major sewage treatment plant in Northern Taiwan and the receiving coastal waters. *Marine Pollution Bulletin*, 64:1435-1444. <https://doi.org/10.1016/j.marpolbul.2012.04.008>

Fawell, J., Nieuwenhuijsen, M.J. (2003). Contaminants in drinking water: environmental pollution and health. *British Medical Bulletin*, 68(1):199-208. <https://doi.org/10.1093/bmb/ldq027>

Ferrari, B., Mons, R., Vollat, B., Frayssé, B., Paxéus, N., Giudice, R.L., Pollio, A., Garric, J. (2004). Environmental risk assessment of six human pharmaceuticals: are the current environmental risk assessment procedures sufficient for the protection of the aquatic

environment? *Environmental Toxicology and Chemistry*, 23(5):1344-1354.

<https://doi.org/10.1897/03-246>

Finckh, S., Beckers, L., Busch, W., Carmona, E., Dulio, V., Kramer, L., Krauss, M., Posthuma, L., Schulze, T., Slootweg, J., Von Der Ohe, P.C., Brack, W. (2022). A risk based assessment approach for chemical mixtures from wastewater treatment plant effluents. *Environment International*, 164, article 107234. <https://doi.org/10.1016/j.envint.2022.107234>

Food and Agriculture Organization of the United Nations (1996) *Chapter 4: Pesticides as water pollutants*. <https://www.fao.org/3/w2598e/w2598e07.htm> (Accessed on 09 May 2022).

Food and Agriculture Organization of the United Nations. (2013) *International code of conduct on the distribution and use of pesticides*. Annotated list of technical guidelines for the implementation of the International Code of Conduct on the Distribution and Use of Pesticides.

FAO Pesticide Risk Reduction Group, Rome. https://www.fao.org/fileadmin/templates/agphome/documents/Pests_Pesticides/Code/Annotated_Guidelines2013.pdf

Forghani, M., Sadeghi, G., Mazyar, M. (2018). The presence of 17 beta-estradiol in the environment: Health effects and increasing environmental concerns. *International journal of Epidemiology Research*, 5(4):151-158. <https://doi.org/10.15171/ijer.2018.31>

Free State Info (2022, 9 October). *Getting to know the Free State province*. <https://www.free-state-info.co.za/provinces/article/3526/getting-to-know-the-free-state-province> (Accessed on 22 June 2024).

Furuichi, T., Kannan, K., Suzuki, K., Tanaka, S., Giesy, J.P., Masunaga, S. (2006). Occurrence of estrogenic compounds in and removal by a swine farm waste treatment plant. *Environmental Science and Technology*, 40(24):7896-7902. <https://doi.org/10.1021/es0609598>

Galindo-Miranda, J.M., Guízar-González, C., Becerril-Bravo, E.J., Moeller-Chávez, G., León-Becerril, E., Vallejo-Rodríguez, R. (2019). Occurrence of emerging contaminants in environmental surface waters and their analytical methodology – A review. *Water Science and Technology: Water supply*, 19(7):1871-1884. <https://doi.org/10.1016/j.copbio.2007.03.005>

Galus, M., Kirischian, N., Higgins, S., Purdy, J., Chow, J., Rangaranjan, S., Hontgxia, L., Metcalfe, C., Wilson, J.Y. (2013a). Chronic, low concentration exposure to pharmaceuticals

impacts multiple organ systems in zebrafish. *Aquatic Toxicology*, 132-133:200-211. <https://doi.org/10.1016/j.aquatox.2012.12.021>

Galus, M., Jeyaranjaan, J., Smith, E., Li, H., Metcalfe, C. and Wilson, J.Y. (2013b) Chronic effects of exposure to a pharmaceutical mixture and municipal wastewater in zebrafish. *Aquatic Toxicology*, 132-133:212-222. <https://doi.org/10.1016/j.aquatox.2012.12.016>

Ganaie, M.I., Jan, I., Mayer, A.N., Dar, A.A., Mayer, I.A., Ahmed, P., Sofi J.A. (2023). Health risk assessment of pesticide residues in drinking water of upper Jhelum region in Kashmir Valley – India by GC-MS/MS. *International Journal of Analytical Chemistry*, 2023, article 6802782. <https://doi.org/10.1155/2023/6802782>

Garcia, A., Barbas, C. (2011). Gas chromatography–mass spectrometry (GC–MS)-based metabolomics. *Methods in Molecular Biology*, 708:191-204. doi: <https://doi.org/10.1007/978-1-61737-985-7-11>

Garcia, X., Pargament, D. (2015). Reusing wastewater to cope with water scarcity: Economic, social and environmental considerations for decision-making. *Resources, Conservation and Recycling*, 101:154-166. <https://doi.org/10.1016/j.resconrec.2015.05.015>

Gerber, E. (2019). Endocrine disrupting effects of HIV antiretrovirals in the South African aquatic environment. Master's dissertation, North-West University, South Africa. <http://hdl.handle.net/10394/33861>

Gheraout, D., Elboughdiri, N. (2019). Water reuse: Emerging contaminants elimination-progress and trends. *Open Access Library Journal*, 6, e5981. <https://doi.org/10.4236/oalib.1105981>

Ghlichloo, I, Gerriets, V. (2022). *Nonsteroidal anti-inflammatory drugs (NSAIDs)*. Treasure Island, Florida: StatPearls Publishing. <https://www.ncbi.nlm.nih.gov/books/NBK547742/> (Accessed 22 June 2022).

Glassmeyer, S.T., Furlong, E.T., Kolpin, D.W., Batt, A.L., Bensond, R., Boone, J.S., Conerly, O.C., Donohue, M.J., Kinga, D.N., Kostich, M.S., Mash, H.E., Pfaller, S.L.P., Schenck, K.M., Simmons, J.E., Varughese, E.A., Vesper, S.J., Villegas, E.N., Wilson, V.S. (2016). Nationwide reconnaissance of contaminants of emerging concern in source and treated drinking waters of the United States. *Science of the Total Environment*, 581-582:909-922. <http://dx.doi.org/10.1016/j.scitotenv.2016.12.004>

Gogoi, A., Mazumder, P., Tyagi, V.K., Chaminda, T.G.G., Kyoungjin A.N., Kumar, M. (2018). Occurrence and fate of emerging contaminants in water environment: A review.

Groundwater for Sustainable Development, 6:169-180.

<https://doi.org/10.1016/j.gsd.2017.12.009>

Gomez, M.J., Sirtori, C., Mezcuca, M., Fernandez-Alba, A.R., Aguera, A. (2008). Photodegradation study of three dipyrone metabolites in various water systems: Identification and toxicity of their photodegradation products. *Water Research*, 42(10-11):2698-2706. <https://doi.org/10.1016/j.watres.2008.01.022>

Gozzo, S., Moles, S., Kinska, K., Ormad, M.P., Mosteo, R., Gómez, J., Laborda, F., Szpunar, J. (2023). Screening for antibiotics and their degradation products in surface and wastewaters of the POCTEFA Territory by Solid-Phase Extraction–UPLC–Electrospray MS/MS. *Water*, 15, article 14. <https://doi.org/10.3390/w15010014>

Grandclément, C., Seyssiecq, I., Piram, A., Wong-Wah-Chung, P., Vanot, G., Tiliacos, T., Roche, N., Doumenq, P. (2017). From the conventional biological wastewater treatment to hybrid processes, the evaluation of organic micropollutant removal: A review. *Water Research*, 111:297-317. <https://doi.org/10.1016/j.watres.2017.01.005>

Grung, M., Kallqvist, T., Sakshaug, S., Skurtveit, S., Thomas, K.V. (2008). Environmental assessment of Norwegian priority pharmaceuticals based on the EMEA guideline. *Ecotoxicology and Environmental Safety*, 71:328-340. <https://doi.org/10.1016/j.ecoenv.2007.10.015>

Gunnarsson, L., Kristiansson, E., Rutgersson, C., Sturve, J., Fick, J., Förlin, L., Larsson, D. (2009). Pharmaceutical industry effluent diluted 1:500 affects global gene expression, Cytochrome P450 1a activity, and plasma phosphate in fish. *Environmental Toxicology and Chemistry*, 28(12):2639-2647. <https://doi.org/10.1897/09-120.1>

Guo, J., Chen, W., Wu, M., Qu, C., Sun, H., Guo, J. (2023). Distribution, sources, and risk assessment of organochlorine pesticides in water from Beiluo River, Loess Plateau, China. *Toxics*, 11(6), article 496. <https://doi.org/10.3390/toxics11060496>

Guruge, K., Goswami, P., Tanoue, R., Nomiya, K., Wijesekara, R.G.S., Dharmaratne, T.S. (2019). First nationwide investigation and environmental risk assessment of 72 pharmaceuticals and personal care products from Sri Lankan surface waterways. *Science of the Total Environment*, 690:683-695. <https://doi.org/10.1016/j.scitotenv.2019.07.042>

Hamilton, D., Dieterle, R., Felsot, A., Harris, C., Holland, P., Katayama, A., Kurihara, N., Linders, J., Unsworth, J., Wong, S.S. (2003). Regulatory limits for pesticides residues in water (IUPAC Technical Report). *Journal of Pure and Applied Chemistry*, 75:1123-1155. <https://doi.org/10.1351/pac200375081123>

Hapeshi, E., Gros, M., Lopez-Serna, R., Boleda, M.R., Ventura, F., Petrovic, M., Barceló, D., Kassinos, F.D. (2015). Licit and illicit drugs in urban wastewater in Cyprus. *Clean: Soil, Air, Water*, 43(9):1272-1278. <https://doi.org/10.1002/clen.201400483>

Hendricks, R., Pool, E.J. (2012). The effectiveness of sewage treatment processes to remove faecal pathogens and antibiotic residues. *Journal of Environmental Science and Health: Part A*, 47(2):289-297. <https://doi.org/10.1080/10934529.2012.637432>

Hermes, N., Jewell, K., Wick, A., Ternes, T. (2018). Quantification of more than 150 micro-pollutants including transformation products in aqueous samples by liquid chromatography tandem mass spectrometry using scheduled multiple reaction monitoring. *Journal of Chromatography A*, 1531:64-73. <https://doi.org/10.1016/j.chroma.2017.11.020>

Hernando, M.D., Mezcuca, M., Fernandez-Alba, A.R., Barcelo, D. (2006). Environmental risk assessment of pharmaceutical residues in wastewater effluents, surface waters and sediments. *Talanta*, 69:334-342. <https://doi.org/10.1016/j.talanta.2005.09.037>

Heys, K.A., Shore, R.F., Pereira, M.G., Kevin, C., Jones, J.C., Francis, L., Martin, F.L. (2016). Risk assessment of environmental mixture effects. *RSC Advances*, 6:47844-47853. <https://doi.org/10.1039/c6ra05406d>

Ho, C.S., Lam, C.W.K., Chan, M.H.M., Cheung, R.C.K., Law, L.K., Lit, L.C.W., Ng, K.F., Suen, M.W.M., Tai, H.L (2003). Electrospray ionisation mass spectrometry: Principles and clinical applications. *Clinical Biochemist Reviews*, 24(1):3-12. <https://www.ncbi.nlm.nih.gov/pmc/articles/PMC1853331/> (Accessed 28 June 2024).

Hollender, J., Schymanski, E.L., Singer, H.P., Ferguson, L.P. (2017). Nontarget screening with high resolution mass spectrometry in the environment: Ready to go? *Environmental Science and Technology*, 51:11505-11512. <https://doi.org/10.1021/acs.est.7b02184>

Hong, L., Meng, X., Bao, T., Liu, B., Wang, Q., Jin, J., Wu, K. (2023). Spatial-temporal distribution and ecological risk assessment of microplastics in the Shiwuli River. *Water*, 15, article 2330. <https://doi.org/10.3390/w15132330>

Horak, I., Horn, S., Pieters, R. (2021). Agrochemicals in freshwater systems and their potential as endocrine disrupting chemicals: A South African context. *Environmental Pollution*, 268, article 115718. <https://doi.org/10.1016/j.envpol.2020.115718>

Horn, S., Pieters, R., Bøhn, T. (2019). A first assessment of glyphosate, 2,4-D and Cry proteins in surface water of South Africa. *South African Journal of Science*, 115(9/10):1-7. <https://doi.org/10.17159/sajs.2019/5988>

Hossain, A., Nakamichi, S., Habibullah-Al-Mamun, M., Tani, K., Masunaga, S., Matsuda, H. (2018). Occurrence and ecological risk of pharmaceuticals in river surface water of Bangladesh. *Environmental Research*, 165:258-266.

<https://doi.org/10.1016/j.envres.2018.04.030>

Hou, X., Gao, W., Zhang, M., Xia, R., Zhang, Y., Zhang, K., Wang, X., Yang, K., Chen, X., Deng, Y. (2022). Source apportionment of water pollutants in Poyang Lake Basin in China using absolute principal component score-multiple linear regression model combined with landuse parameters. *Frontier Environmental Science*, 10, article 924350.

<https://doi.org/10.3389/fenvs.2022.924350>

Hu, J., Zhang, Z., Shen, W.-J., Azhar, S. (2010). Cellular cholesterol delivery, intracellular processing and utilization for biosynthesis of steroid hormones. *Nutrition and Metabolism*, 7, article 47. <https://doi.org/10.1186/1743-7075-7-47>

Huang T., Guo Q., Tian H., Mao X., Ding Z., Zhang G., Li, J., Ma, J., Gao, H. (2014). Assessing spatial distribution, sources, and human health risk of organochlorine pesticide residues in the soils of arid and semiarid areas of northwest China. *Environmental Science and Pollution Research*, 21:6124-6135. <https://doi.org/10.1007/s11356-014-2505-8>

Huang, W., Lv, W., Yuan, Q., Zhou, W., Li, T., Dong, B. (2023). Effects of long-term exposure of pharmaceuticals and personal care products on algogenic organic matter characteristics. *Water*, 15(13), article 2447. <https://doi.org/10.3390/w15132447>

Hunt, P.A., Sathyanarayana, S., Fowler, P.A., Trasande, L. (2016). Female reproductive disorders, diseases, and costs of exposure to endocrine disrupting chemicals in the European Union. *Journal of Clinical Endocrinology and Metabolism*, 101:1562-1570. <https://doi.org/10.1210/jc.2015-2873>

Iancu, V.I., Puiu, D., Radu, G.L. (2020). Determination of some beta-blockers in surface water samples. *University Politehnica Bucharest Scientific Bulletin, Series B*, 82(2):121-130. https://www.scientificbulletin.upb.ro/rev_docs_arhiva/full6cb_150864.pdf

Inyinbor, A.A., Adebisin, B.O., Oluyori, A.P., Adelani-Akande, T.A., Dada, A.O., Oreofe, T.A. (2018). Water pollution: Effects, prevention, and climatic impact. In: Glavan, M. (Ed.), *Water challenges of an urbanizing world*. Intechopen, pp. 34-53. <https://doi.org/10.5772/intechopen.72018>

Isah, A., Abdullahi, U., Ndamitso M.M. (2013). Application of multivariate methods for assessment of variations in rivers/streams water quality in Niger state, Nigeria. *American*

Journal of Theoretical and Applied Statistics, 2(6):176-183.

<https://doi.org/10.11648/j.ajtas.20130206.14>

Isiyaka, H.A., Mustapha, A., Juahir, H., Phil-Eze, P. (2018). Water quality modelling using artificial neural network and multivariate statistical techniques. *Model. Earth System and Environment*, 5:583-593. <https://doi.org/10.1007/s40808-018-0551-9>

Janna, H. (2011). Occurrence and removal of emerging contaminants in wastewaters. Doctoral thesis, Brunel University, London, United Kingdom.

<http://bura.brunel.ac.uk/handle/2438/6097>

Ji, K., Choi, K., Lee, S., Park, S., Seong, J., Jo, E., Choi, K., Zhang, X. and Giesy, J.P. (2010) Effects of sulfathiazole, oxytetracycline and chlortetracycline on steroidogenesis in the human adrenocarcinoma (H295R) cell line and freshwater fish *Oryzias latipes*. *Journal of Hazardous Materials*, 182:494-502. <https://doi.org/10.1016/j.jhazmat.2010.06.059>

Jiang, J.Q., Zhou, Z., Sharma, V.K. (2013). Occurrence, transportation, monitoring and treatment of emerging micro-pollutants in waste water – A review from global views. *Microchemical Journal*, 110:292-300. <https://doi.org/10.1016/j.microc.2013.04.014>

Jin, Y., Wang, L., Chen, G., Lin, X., Miao, W., Fu, Z. (2014). Exposure of mice to atrazine and its metabolite diaminochlorotriazine elicits oxidative stress and endocrine disruption. *Environmental Toxicology and Pharmacology*, 37:782-790.

<https://doi.org/10.1016/j.etap.2014.02.014>

Jonsson, A. (2005). Public participation in water resources management: Stakeholder voices on degree, scale, potential, and methods in future water management. *Ambio – A Journal of the Human Environment*, 34(7):495-500. <http://dx.doi.org/10.1579/0044-7447-34.7.495>

Jover, E., Matamoros, V. and Bayona, J. (2009). Characterization of benzothiazoles, benzotriazoles and benzosulfonamides in aqueous matrixes by solid-phase extraction followed by comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry. *Journal of Chromatography A* 1216(18):4013-4019.

<https://doi.org/10.1016/j.chroma.2029.02.052>

Kairigo, P., Ngumba, E., Sundberg, L., Gachanja, A., Tuhkanen, T. (2020). Contamination of surface water and river sediments by antibiotic and antiretroviral drug cocktails in low and middle-income countries: Occurrence, risk and mitigation strategies. *Water*, 12(5), article 1376. <https://doi.org/10.3390/w12051376>

Kamunda, C., Mathuthu, M., Madhuku, M. (2018). Potential human risk of dissolved heavy metals in gold mine waters of Gauteng Province, South Africa. *Journal of Toxicology and Environmental Health Sciences*, 10(6):56-63. <https://doi.org/10.5897/JTEHS2018.0422>

Kanama, K.M., Daso, A.P., Mpenyana-Monyatsi, L., Coetzee, M.A. (2018). Assessment of pharmaceuticals, personal care products, and hormones in wastewater treatment plants receiving inflows from health facilities in North West Province, South Africa. *Journal of Toxicology*, article 3751930. <https://doi.org/10.1155/2018/3751930>

Karelid, V., Larsson, G., Bjorlenius, B. (2017). Pilot-scale removal of pharmaceuticals in municipal wastewater: Comparison of granular and powdered activated carbon treatment at three wastewater treatment plants. *Journal of Environmental Management*, 193:491-502. <https://doi.org/10.1016/j.jenvman.2017.02.042>

Karpinska, J., Kotowska, U. (2021). New aspects of occurrence and removal of emerging pollutants. *Water*, 13(17), article 2418. <https://doi.org/10.3390/w13172418>

Kasprzyk-Hordern, B., Dinsdale, R.M., Guwy, A.J. (2008). The effect of signal suppression and mobile phase composition on the simultaneous analysis of multiple classes of acidic/neutral pharmaceuticals and personal care products in surface water by solid-phase extraction and ultra-performance liquid chromatogra. *Talanta*, 74(5):1299-1312. <https://doi.org/10.1016/j.talanta.2007.08.037>

Kasprzyk-Hordern, B., Proctor, K., Jagadeesan, K., Watkins, S., Standerwick, R., Barden, R., Barnett, J. (2021). Diagnosing down-the-drain disposal of unused pharmaceuticals at a river catchment level: unrecognized sources of environmental contamination that require nontechnological solutions. *Environmental Science and Technology*, 55:11657-11666. <https://doi.org/10.1021/acs.est.1c01274>

Khan, M.A., Wen, J. (2021). Evaluation of physicochemical and heavy metals characteristics in surface water under anthropogenic activities using multivariate statistical methods, Garra River, Ganges Basin, India. *Environmental Engineering Research*, 26(6), article 200280. <https://doi.org/10.4491/eer.2020.280>

Khan, N.A., Vambol, V., Vambol, S., Bolibrukh, B., Sillanpaa, M., Changani, F., Esraflı, A., Yousefi, M. (2021). Hospital effluent guidelines and legislation scenario around the globe: A critical review. *Journal of Environmental Chemical Engineering*, 9(5). Article 105874. <https://doi.org/10.1016/j.jece.2021.105874>

Kidd, K.A., Blanchfield, P.J., Mills, K.H., Palace, V.P., Evans, R.E., Lazorchak, J.M., Flick, R.W. (2007). Collapse of a fish population after exposure to a synthetic estrogen.

Proceedings of the National Academy of Sciences, 104 (21):8897-8901. doi: 10.1073/pnas.0609568104

Kienzler, A., Bopp, S., Halder, M., Embry, M., Worth, A. (2019). Application of new statistical distribution approaches for environmental mixture risk assessment: A case study. *Science of the Total Environment*, 693, article 133510. <https://doi.org/10.1016/j.scitotenv.2019.07.316>

Kihila, J.M., Wernsted, K., Kasev, M. (2021). Waste segregation and potential for recycling - A case study in Dar es Salaam City. *Tanzania. Sustainable Environment*, 7(1):1-13. <https://doi.org/10.1080/27658511.2021.1935532>

Kim, J.W., Ishibashi, H., Yamauchi, R., Ichikawa, N., Takao, Y., Hirano, M., Koga, M., Arizono, K. (2009a). Acute toxicity of pharmaceutical and personal care products on fresh water crustacean (*Thamnocephalus platyurus*) and fish (*Oryzias latipes*). *Journal of Toxicological Science* 34:227-232. <https://doi.org/10.2131/jts.34.227>

Kim, J.W., Jang, H.S., Kim, J.G., Ishibashi, H., Hirano, M., Nasu, K., Ichikawa, N., Takao, Y., Shinohara, R., Arizono, K. (2009b). Occurrence of pharmaceutical and personal care products (PPCPs) in surface water from Mankyung River, South Korea. *Journal of Health Sciences*, 55(2):249-258. <https://doi.org/10.1248/jhs.55.249>

Knopp, G., Prasse, C., Ternes, T.A., Cornel, P. (2016). Elimination of micropollutants and transformation products from a wastewater treatment plant effluent through pilot scale ozonation followed by various activated carbon and biological filters. *Water Research*, 100:580-592. <https://doi.org/10.1016/j.watres.2016.04.069>

Köck-Schulmeyer, M., Ginebreda, A., Gonzalez, S., Cortina, J.C., Alda, M.L., Barcel, D. (2012). Analysis of the occurrence and risk assessment of polar pesticides in the Llobregat River Basin (NE Spain). *Chemosphere*, 86(1):8-16. <https://doi.org/10.1016/j.chemosphere.2011.08.034>

Kortesmäki, E., Östman, J.R., Meierjohann, A., Brozinski, J.M., Eklund, P., Kronberg, L. (2020). Occurrence of antibiotics in influent and effluent from 3 major wastewater-treatment plants in Finland. *Environmental Toxicology and Chemistry*, 39(9):1774-1789. <https://doi.org/10.1002/etc.4805>

Kosma, C.I., Lambropoulou, D.A., Alnanis, T.A. (2014). Investigation of PPCPs in wastewater treatment plants in Greece: Occurrence, removal and environmental risk assessment. *Science of the Total Environment*, 466-467:421-438. <https://doi.org/10.1016/j.scitotenv.2013.07.044>

- Kumar, S., Sharma, A.K., Rawat, S., Jain, D., Ghosh, S. (2013). Use of pesticides in agriculture and livestock animals and its impact on environment of India. *Asian Journal of Environmental Sciences*, 8:51-57. <https://www.researchgate.net/publication/257311156>
- Kümmerer, K. (2010). Pharmaceuticals in the environment. *Annual Review of Environment and Resources*, 35:57-75. <https://doi.org/10.1146/annurev-environ-052809-161223>
- Kunene, P.N. (2019). Method development and application: Solid phase extraction (SPE), Ultrasonic extraction (UE) and Soxhlet extraction (SE) for the analysis of pesticides in water, soil, sediment and sludge. Master's dissertation, University of KwaZulu Natal, South Africa. <https://researchspace.ukzn.ac.za/handle/10413/17795> (Accessed on 03 April 2022).
- Kuroda, K., Li, C., Dhangar, K., Kumar, M. (2021). Predicted occurrence, ecotoxicological risk and environmentally acquired resistance of antiviral drugs associated with COVID-19 in environmental waters. *Science of the Total Environment*, 776, article 145740. <https://doi.org/10.1016/j.scitotenv.2021.145740>
- Kuzmanovic, M., Ginebreda, P.M., Barcelo, D. (2015). Risk assessment based prioritisation of 200 organic micropollutants in iberian rivers. *Science for the Total Environment* 503-504:289-299. <https://doi.org/10.1016/j.scitotenv.2014.06.056>
- La Merrill, M.A., Vandenberg, L.N., Smith, M.T., Goodson, W., Browne, P., Patisaul, H.B., Guyton, K.Z., Kortenkamp, A., Coglian, V.J., Woodruff, T.J., Rieswijk, L., Sone, H., Korach, K.S., Gore, A.C., Zeise, L., Zoeller, R.T. (2020). Consensus on the key characteristics of endocrine- disrupting chemicals as a basis for hazard identification. *Nature Reviews*, 16:45-57. <https://doi.org/10.1038/s41574-019-0273-8>
- Langford, K.H., Lester, J.N. (2003). Fate and behavior of endocrine disrupters in wastewater treatment processes. In: Birkett, J.W. and Lester, J.N. (Eds.), *Endocrine disrupters in wastewater and sludge treatment processes*. Boca Raton: Lewis Pub, pp. 103-134.
- Lapworth, D.J., Baran, N., Stuart, M.E., Ward, R.S. (2012). Emerging organic contaminants in groundwater: A review of sources, fate and occurrence. *Environmental Pollution*, 163:287-303. <https://doi.org/10.1016/j.envpol.2011.12.034>
- Lee, Y., Von Gunten, U. (2010). Oxidative transformation of micropollutants during municipal wastewater treatment: Comparison of kinetic aspects of selective (chlorine, chlorine dioxide, ferrateVI, and ozone) and non-selective oxidants (hydroxyl radical). *Water Research*, 44(2):555-566. <https://doi.org/10.1016/j.watres.2009.11.045>

Li, C., Wang, X., Xiao, S., Wang, H. (2023b). The source apportionment of heavy metals in surface dust in the main district bus stops of Tianshui City based on the positive matrix factorization model and geo-statistics. *Atmosphere*, 14(3), article 591.

<https://doi.org/10.3390/atmos14030591>

Li, H., Dong, Z., Weng, Q., Chang, C.C., Liu, B. (2015). Emerging Pollutants - Part I: Occurrence, fate and transport. *Water Environment Research*, 87(10):1849-

1872. <https://doi.org/10.2175/106143015X14338845156425>

Li, P., Sabarathinam, C., Elumalai, V. (2023a). Groundwater pollution and its remediation for sustainable water management. *Chemosphere*, 329, article 138621. <https://doi.org/10.1016/j.chemosphere.2023.138621>

Lim, F.Y., Ong, S.L., Hu, J. (2017). Recent advances in the use of chemical markers for tracing wastewater contamination in aquatic environment: A review. *Water*, 9, article 143.

<https://doi.org/10.3390/w9020143>

Lin, D., Tian, X., Wu, F., Xing, B. (2010). Fate and transport of engineered nanomaterials in the environment. *Journal of Environmental Quality*, 39(6):1896-1908.

<https://doi.org/10.2134/jeq2009.0423>

Lin, X., Xua, J., Keller, A.A., Hea, L., Gua, Y., Zheng, W., Sun, D., Lu, Z., Huang, J., Huang, X., Li, G. (2020). Occurrence and risk assessment of emerging contaminants in a water reclamation and ecological reuse project. *Science of the Total Environment*, 744, article 140977. <https://doi.org/10.1016/j.scitotenv.2020.140977>

Lin, Y.C., Lai, W.W.P., Tung, H.H., Lin, A.Y.C. (2015). Occurrence of pharmaceuticals, hormones, and perfluorinated compounds in groundwater in Taiwan. *Environmental Monitoring and Assessment*, 187, article 256. <https://doi.org/10.1007/s10661-015-4497-3>

Lindberg, R.H., Bjorklund, K., Rendahl, P., Johansson, M.I., Tysklind, M., Andersson, B.A.V. (2007). Environmental risk assessment of antibiotics in the Swedish environment with emphasis on sewage treatment plants. *Water Research*, 41(3):613-619.

<https://doi.org/10.1016/j.watres.2006.11.014>

Liu, N., Jin, X., Feng, C., Wang, Z., Wu, F., Johnson, A.C., Xiao, H., Hollert, H., Giesy, J.P. (2020a). Ecological risk assessment of fifty pharmaceuticals and personal care products (PPCPs) in Chinese surface water: A proposed multiple level system. *Environmental International*, 136, article 105454. <https://doi.org/10.1016/j.envint.2019.105454>

Liu, N., Jin, X., Yan, Z., Luo, Y., Feng, C., Fu, Z., Tan, Z., Wu, F., Giesy, J.P. (2020b). Occurrence and multiple-level ecological risk assessment of pharmaceuticals and personal care products (PPCPs) in two shallow lakes of China. *Environmental Science Europe*, 32, article 69. <https://doi.org/10.1186/s12302-020-00346-1>

Liu, Q., Zhough, Q., Jiang G. (2014). Nanomaterials for analysis and monitoring of emerging chemical pollutants. *Trends in Analytical Chemistry*, 58:10-22.
<https://doi.org/10.1016/j.trac.2014.02.014>

Liu, Y., Shi, X., Chen, X., Ding, P., Zhang, L., Yang, J., Pan, J., Yu, Y., Wu, J., Hu, G. (2023). Spatial distribution and risk assessment of antibiotics in 15 pharmaceutical plants in the Pearl River Delta. *Toxics*, 11, article 382. <https://doi.org/10.3390/toxics11040382>

Liu, Z.H., Kanjo, Y., Mizutani, S. (2009). Removal mechanisms for endocrine disrupting compounds (EDCs) in wastewater treatment-physical means, biodegradation, and chemical advanced oxidation: A review. *Science of the Total Environment*, 407(2):731-748.
<https://doi.org/10.1016/j.scitotenv.2008.08.039>

Llamas, M., Vadillo-Pérez, I., Candela, L., Jiménez-Gavilán, P., Corada-Fernández, C., Castro-Gámez, A.F. (2020). Screening and distribution of contaminants of emerging concern and regulated organic pollutants in the heavily modified Guadalhorce River Basin, Southern Spain. *Water*, 12(11), article 3012. <https://doi.org/10.3390/w12113012>

Lodeiro, C., Capelo, J.L., Oliveira, E., Lodeiro, J.F. (2019). New toxic emerging contaminants: beyond the toxicological effects, *Environmental Science and Pollution Research*, 26:1-4, <https://doi.org/10.1007/s11356-018-3003-1>

London, L., Dalvie, M.A., Cairncross, E., Solomons, A. (2000). *The quality of surface and groundwater in the rural Western Cape with regards to pesticides*. Report No. 795/1/00, Water Research Commission, Pretoria, South Africa. <https://www.wrc.org.za/wp-content/uploads/mdocs/795-1-00.pdf>

Ma, X., Wang, L., Yang, H., Li, N., Gong, C. (2020). Spatiotemporal analysis of water quality using multivariate statistical techniques and the water quality identification index for the Qinhuai River Basin, East China. *Water*, 12(10), article 2764.
<https://doi.org/10.3390/w12102764>

Maasz, G., Mayer, M., Zrinyi, Z., Molnar, E., Kuzma, M., Fodor, I., Pirger, Z., Takacs, P. (2019). Spatiotemporal variations of pharmacologically active compounds in surface waters of a summer holiday destination. *Science of the Total Environment*, 10:545-555.
<https://doi.org/10.1016/j.scitotenv.2019.04.286>

Machado, K.C., Grassi, M.T., Vidal, C., Pescara, I.C., Jardim, W.F., Fernandes, A.N., Sodré, F.F., Almeida, F.V., Santana, J.S., Canela, C.C., Nunes, C.R.O., Bichinho, K.M., Severo, F.J.R. (2016). A preliminary nationwide survey of the presence of emerging contaminants in drinking and source waters in Brazil. *Science of the Total Environment*, 572:138-146. <https://doi.org/10.1016/j.scitotenv.2016.07.210>

Madikizela, L.M., Chimuka, L. (2017). Occurrence of naproxen, ibuprofen, and diclofenac residues in wastewater and river water of KwaZulu-Natal Province in South Africa. *Environmental Monitoring and Assessment*, 189(7), article 348. <https://doi.org/10.1007/s10661-017-6069-1>

Madikizela, L.M., Ncube, S. (2021). Occurrence and ecotoxicological risk assessment of non-steroidal anti-inflammatory drugs in South African aquatic environment: What is known and the missing information? *Chemosphere* 280, article 130688. <https://doi.org/10.1016/j.chemosphere.2021.130688>

Madikizela, L.M., Muthwa, S.F., Chimuka, L. (2014). Determination of triclosan and ketoprofen in river water and wastewater by solid phase extraction and high performance liquid chromatography. *South African Journal of Chemistry*, 67:143-150. <http://journals.sabinet.co.za/sajchem/>

Madikizela, L.M., Ncube, S., Chimuka, L. (2020). Analysis, Occurrence and Removal of Pharmaceuticals in African Water Resources: A Current Status. *Journal of Environmental Management*, 253, article 109741. <https://doi.org/10.1016/j.jenvman.2019.109741>

Madikizela, L.M., Nuapia, Y.B., Chimuka, L., Ncube, S., Etale, A. (2022). Target and suspect screening of pharmaceuticals and their transformation products in the Klip River, South Africa, using ultra-high-performance liquid chromatography-mass spectrometry. *Environmental Toxicology and Chemistry*, 41:437-447. <https://doi.org/10.1002/etc.5265>

Makhadi, R., Oke, S.A., Ololade, O.O. (2020). The influence of non-engineered municipal landfills on groundwater chemistry and quality in Bloemfontein, South Africa. *Molecules*, 25(23), article 5599. <https://doi.org/10.3390/molecules25235599>

Malaj, E., Von der Ohe, P.C., Grote, M., Kühne, R., Mondy, C.P., Usseglio-Polatera, P., Brack, W. and Schafer, R.B. (2014). Organic chemicals jeopardize the health of freshwater ecosystems on the continental scale. *Proceedings of the National Academy of Sciences of the United States of America* 111(26):9549-9554. <https://doi.org/10.1073/pnas.1321082111>

Malewandja, A.M. (2018). The impact of environmental pollution on the water quality in Johannesburg. Master's dissertation, University of Johannesburg, South Africa.
<http://hdl.handle.net/102000/0002>

Malisa, R., Schwella, E., Kidd, M. (2019). From 'government' to 'governance': A quantitative transition analysis of urban wastewater management principles in Stellenbosch Municipality. *Science of the Total Environment*, 674:494-511.
<https://doi.org/10.1016/j.scitotenv.2019.04.194>

Manahil, M. (2017). Endocrine-disrupting properties of pharmaceuticals and personal care products (PPCPS): An evaluation using aquatic model organisms. Master's dissertation, Wayne State University, United States of America.
https://digitalcommons.wayne.edu/oa_theses/578 (Accessed on 17 February 2022).

Mandarić, L. (2018). Transport, distribution, and the fate of emerging contaminants in wastewater-receiving rivers under multiple stress conditions. Doctoral thesis, University of Girona, Spain. <http://hdl.handle.net/10803/666341>

Mangaung Metropolitan Municipality (2022) *Final Integrated Development Plan 2022/2027*.
<http://www.mangaung.co.za/wp-content/uploads/2022/05/2-Final-IDP-2022-2027-24.05.2022-Signed.pdf>

Manickum, T., John, W. (2014). Occurrence, fate and environmental risk assessment of endocrine disrupting compounds at the wastewater treatment works in Pietermaritzburg (South Africa). *Science of the Total Environment*, 468-469:584-597.
<https://doi.org/10.1016/j.scitotenv.2013.08.041>

Markert, N., Rhiem, S., Trimborn, M., Guhl, B. (2020). Mixture toxicity in the Erft River: assessment of ecological risks and toxicity drivers. *Environmental Science Europe*, 32, article 51. <https://doi.org/10.1186/s12302-020-00326-5>

Mas, L.I., Aparicio, V.C., De Gerónimo, E., Costa, J.L. (2020). Pesticides in water sources used for human consumption in the semi-arid region of Argentina. *SN Applied Sciences*, 2, article 691. <https://doi.org/10.1007/s42452-020-2513-x>

Mashile, G.P., Mpupa, A., Nomngongo, P.N. (2021). Magnetic mesoporous carbon/ β -cyclodextrin-chitosan nanocomposite for extraction and preconcentration of multi-class emerging contaminant residues in environmental samples. *Nanomaterials*, 11, article 540.
<https://doi.org/10.3390/nano11020540>

Matongo, S., Birungi, G., Moodley, B., Ndungu, P. (2015). Pharmaceutical residues in water and sediment of Msunduzi River, KwaZulu Natal, South Africa. *Chemosphere*, 134:133-140. <https://doi.org/10.1016/j.chemosphere.2015.03.093>

Mawussi, G., Sanda, K., Merlina, G., Pinelli, E. (2009). Assessment of average exposure to organochlorine pesticides in southern Togo from water, maize (*Zea mays*) and cowpea (*Vigna unguiculata*). *Food Additives and Contaminants: Part A*, 26(3):348-354. <https://doi.org/10.1080/02652030802528343>

Mcdonnell, G., Russell, A.D. (1999). Antiseptics and disinfectants: activity, action, and resistance. *Microbiology Review*, 12(1):147-179. <https://doi.org/10.1128/CMR.12.1.147>

Medkova, D., Hollerova, A., Riesova, B., Blahova, J., Hodkovicova, N., Marsalek, P., Doubkova, V., Weiserova, Z., Mares, J., Faldyna, M., Tichy, F., Svobodova, Z., Lakdawala, P. (2023). Pesticides and parabens contaminating aquatic environment: acute and sub-chronic toxicity towards early-life stages of freshwater fish and amphibians. *Toxics*, 11, article 333. <https://doi.org/10.3390/toxics11040333>

Mercanti, T., El Hachmi, M., Falcinelli, S., Sebastiani, B. (2023). Occurrence of persistent organochlorine pollutants in sediments from lake Piediluco, Italy. *Environments*, 10, article 120. <https://doi.org/10.3390/environments10070120>

Meride, Y., Ayenew, B. (2016). Drinking water quality assessment and its effects on residents' health in Wondo genet campus, Ethiopia. *Environmental System Research*, 5(1). <https://doi.org/10.1186/s40068-016-0053-6>

Mhuka, V., Dube, S., Nindi, M.M. (2020). Occurrence of pharmaceutical and personal care products (PPCPs) in wastewater and receiving waters in South Africa using LC-Orbitrap™ MS. *Emerging Contaminants*, 6:250-258. <https://doi.org/10.1016/j.emcon.2020.07.002>

Miller, K.K.J., Meek, J. (2006). *Helena Valley ground water: Pharmaceuticals, personal care products, endocrine disruptors (PPCPs), and microbial indicators of faecal contamination*. Report no. 532, Montana Bureau of Mines and Geology Open-file, Montana, United States. <http://www.mbmgs.mtech.edu/pdf-open-files/mbmg532-helenavalley.pdf>

Mir, R.A., Gani, K.M. (2019). Water quality evaluation of the upper stretch of the river Jhelum using multivariate statistical techniques. *Arabian Journal of Geoscience*, 12(14), article 445. <https://doi.org/10.1007/s12517-019-4578-7>

Miraji, H., Mureithi, E.W., Othman, O.C., Ngassapa, F. (2020). 1-D transport behaviour of emerging contaminants in the unidirectional flowing surface waters of the Msimbazi River.

Tanzania Journal of Science, 46(2):371-382.

<https://www.ajol.info/index.php/tjs/article/view/196320/185310>

Miraji, H., Othman, O.C., Ngassapa, F.N., Mureithi, E.W., (2016). Research trends in emerging contaminants on the aquatic environments of Tanzania. *Scientifica*, 9:1-6.

<http://doi.org/10.1155/2016/3769690>

Montagner, C.C., Sodré, F.F., Acayaba, R.D., Vidal, C., Campestrini, I., Locatelli, M.A.F., Pescara, I.C., Albuquerque, A.F., Umbuzeiro, G.A., Jardim, W.F. (2019). Ten years-snapshot of the occurrence of emerging contaminants in drinking, surface and ground waters and wastewaters from São Paulo State Brazil. *Journal of Brazilian Chemical Society*, 30:614-632. <https://doi.org/10.21577/0103-5053.20180232>

Montes, R., Méndez, S., Carro, N., Cobas, J., Alves, N., Neuparth, T., Santos, M.M., Quintana, J.B., Rodil, R. (2022). Screening of contaminants of emerging concern in surface water and wastewater effluents, assisted by the persistency–mobility–toxicity criteria. *Molecules*, 27(12), article 3915. <https://doi.org/10.3390/molecules27123915>

Moodley, B., Birungi, G., Ndungu, P. (2016). Detection and quantification of emerging organic pollutants in the Umgeni and Msunduzi Rivers. Report no. 2215/1/16. Water Research Commission, Pretoria, South Africa. <https://www.wrc.org.za/wp-content/uploads/mdocs/2215-1-16.pdf>

Moon, H.B., Kannan, K., Choi, M., Choi, H.G. (2007). Polybrominated diphenyl ethers (PBDEs) in marine sediments from industrialized bays of Korea. *Marine Pollution Bulletin*, 54(9):1402-1412. <https://doi.org/10.1016/j.marpolbul.2007.05.024>

Morin-Crini, N., Lichtfouse, E., Fourmentin, M., Ribeiro, A.R., Noutsopoulos, C., Mapelli, F., Fenyvesi, É., Vieira, M.G., Picos-Corrales, L.A., Moreno-Piraján, J.C., Giraldo, L., Sohajda, T., Huq M.M., Soltan, J., Torri, G., Magureanu, M., Bradu, C., Crini, G. (2022). Removal of emerging contaminants from wastewater using advanced treatments. A review. *Environmental Chemistry Letters*, 20(2):1333-75. <https://doi.org/10.1007/s10311-021-01379-5>

Moritz, S. (2014). Emerging pollutants in surface water developments in society and pollution of tomorrow. Master's dissertation, University of Tübingen, Germany.

<https://www.oeko.de/fileadmin/oekodoc/Emerging-pollutants-in-surface-water.pdf>

Moses M. (2005). An investigation into the negative external impact of water pollution, public policy options and coping Strategies – with specific reference to the Lotus River catchment area. Master' dissertation, University of the Western Cape, South Africa.

<http://hdl.handle.net/11394/1595>

Mugudamani, I., Oke, S.A., Gumede, T.P. (2022). Influence of urban informal settlements on trace element accumulation in road dust and their possible health implications in Ekurhuleni Metropolitan Municipality, South Africa. *Toxics*, 10(5), article 253.

<https://doi.org/10.3390/toxics10050253>

Mugudamani, I., Oke, S.A., Gumede, T.P., Senbore, S. (2023). Herbicides in water sources: Communicating potential risks to the population of Mangaung Metropolitan Municipality, South Africa. *Toxics*, 11, article 538. <https://doi.org/10.3390/toxics11060538>

Mutiyar, P.K., Mittal, A.K. (2014). Occurrences and fate of selected human antibiotics in influents and effluents of sewage treatment plant and effluent-receiving river Yamuna in Delhi (India). *Environmental Monitoring and Assessment*, 186(1):541–557.

<https://doi.org/10.1007/s10661-013-3398-6>

Naik, A.Q., Zafar, T., Shrivastava, V.K. (2021). Environmental impact of the presence, distribution, and use of artificial sweeteners as emerging sources of pollution. *Journal of Environmental and Public Health*, 2021(1): article 6624569.

<https://doi.org/10.1155/2021/6624569>

Nannou, C.I., Kosma, C.I., Albanis, T.A. (2015). Occurrence of pharmaceuticals in surface waters: analytical method development and environmental risk assessment. *International Journal of Environmental Analytical Chemistry*, 95 (13), 1242-1262.

<https://doi.org/10.1080/03067319.2015.1085520>

Nannou, C., Ofrydopoulou, A., Evgenidou, E., Heath, D., Heath, E., Lambropoulou, D. (2020). Antiviral drugs in aquatic environment and wastewater treatment plants: A review on occurrence, fate, removal and ecotoxicity. *Science of the Total Environment*, 10(699), article 134322. <https://doi.org/10.1016/j.scitotenv.2019.134322>

Nannou, C., Kaprara, E., Psaltou, S., Salapasidou, M., Palasantza, P.A., Diamantopoulos, P., Lambropoulou, D.A., Mitrakas, M., Zouboulis, A. (2022). Monitoring of a broad set of pharmaceuticals in wastewaters by high-resolution mass spectrometry and evaluation of heterogenous catalytic ozonation for their removal in a pre-industrial level unit. *Analytica*, 3:195-212. <https://doi.org/10.3390/analytica3020014>

Natasha, Shahid, M., Khalid, S., Murtaza B., Anwar, H., Shah, A.H., Sarder, A., Shabbir, Z., Niazi, N.K. (2020). A critical analysis of wastewater use in agriculture and associated health risks in Pakistan. *Environmental Geochemistry and Health*, 45:5599-5618.

<https://doi.org/10.1007/s10653-020-00702-3>

Ncube, E.J. (2009) Selection and prioritization of organic contaminants for monitoring in the drinking water value chain. Doctoral thesis, University of Pretoria, South Africa.

<http://hdl.handle.net/2263/28574>

Ncube, S., Nuapia, Y.B., Chimuka, L., Madikizela, L.M., Etale, A. (2021). Trace detection and quantitation of antibiotics in a South African Stream receiving wastewater effluents and municipal dumpsite leachates. *Frontiers Environmental Science*, 9, article 733065.

<https://doi.org/10.3389/fenvs.2021.733065>

Neamtu, M., Frimmel, F.H. (2006). Photodegradation of endocrine disrupting chemical nonylphenol by simulated solar UV-irradiation. *Science of the Total Environment*, 369(1-3): 295-306. <https://doi.org/10.1016/j.scitotenv.2006.05.002>

Nesbitt, R. (2011). Effects of chronic exposure to ibuprofen and naproxen on Florida flagfish (*Jordanella floridae*) over one complete life-cycle. Master's dissertation, University of Ontario Institute of Technology, Canada. https://ir.library.utoronto.ca/bitstream/10155/176/1/Nesbitt_Richard.pdf

Newbold, R. (1995). Cellular and molecular effects of developmental exposure to diethylstilbestrol: Implications for other environmental estrogens. *Environmental Health Perspectives*, 103(7):83-87. <https://doi.org/10.1289/ehp.95103s783>

Ngqwala, N.P, Muchesa, P. (2020). Occurrence of pharmaceuticals in aquatic environments: A review and potential impacts in South Africa. *South African Journal Science*, 116(7/8), article 5730. <https://doi.org/10.17159/sajs.2020/5730>

Ngumba E, Gachanja A, Tuhkanen, T. (2016). Occurrence of selected antibiotics and antiretroviral drugs in Nairobi River Basin, Kenya. *Science of the Total Environment*, 539:206-213. <https://doi.org/10.1016/j.scitotenv.2015.08.139>

Ngumba, E., Gachanja, A., Nyirenda, J., Maldonado, J., Tuhkanen, T. (2020). Occurrence of antibiotics and antiretroviral drugs in source-separated urine, groundwater, surface water and wastewater in the peri-urban area of Chunga in Lusaka, Zambia. *Water South African*, 46(2):278-284. <https://doi.org/10.17159/wsa/2020.v46.i2.8243>

Nicolopoulou-Stamati, P., Maipas, S., Kotampasi, C., Stamatis, P., Hens, L. (2016). Chemical pesticides and human health: The urgent need for a new concept in agriculture. *Frontier Public Health*, 4, article 148. <https://doi.org/10.3389/fpubh.2016.00148>

Nkadile, L. (2022). Improving the performance of high occupancy vehicle infrastructure to alleviate city congestion. Master Dissertation, Central University of Technology, South Africa.

Oaks, J. L., Gilbert, M., Virani, M.Z., Watson, R.T., Meteyer, C.U., Rideout, B.A., Shivaprasad, H., Shakeel, A., Chaudhry, M., Arshad, M., Mahmood, S., Ali, A., Khan, A. (2004). Diclofenac residues as the cause of vulture population decline in Pakistan. *Nature*, 427:630-633. <https://doi.org/10.1038/nature02317>

Odendaal, C., Seaman, M.T., Kemp, G., Patterson, H.E., Patterson, H.-G. (2015). An LC-MS/MS based survey of contaminants of emerging concern in drinking water in South Africa. *South African Journal of Science*, 111(9-10), art. 6. <https://doi.org/10.17159/sajs.2015/20140401>

Ofrydopoulou, A., Nannou, C., Evgenidou, E., Christodoulou, A., Lambropoulou, D. (2021). Assessment of a wide array of organic micropollutants of emerging concern in wastewater treatment plants in Greece: Occurrence, removals, mass loading and potential risks. *Science for the Total Environment*, 802, article 149860. <https://doi.org/10.1016/j.scitotenv.2021.149860>

Ogah, C.O., Adetifa, I.O., Basheeru, K.A. (2020). Pharmaceuticals in the Environment: Levels of Selected Drugs in Water in Lagos, Nigeria. *Nigerian Journal of Pharmaceutical and Applied Science Research*, 9(2):13-18. <https://nijophasr.net/index.php/nijophasr/article/view/338>

Ogunbanwo, O.M., Kay, P., Boxall, A.B., Wilkinson, J., Sinclair, C.J., Shabi, R.A., Fasasi, A.E., Lewis, G.A., Amoda, O.A., Brown, L.E. (2022). High concentrations of pharmaceuticals in a Nigerian river catchment. *Environmental Toxicology and Chemistry*, 41:551-558. <https://doi.org/10.1002/etc.4879>

Ojemaye, C.Y. (2020). Identification and quantification of chemicals of emerging concern (persistent organic and inorganic pollutants) in some selected marine environments of Cape Town, South Africa. Doctoral thesis, University of the Western Cape, South Africa. <http://hdl.handle.net/11394/7877>

Ojemaye, C.Y., Pampanin, D.M., Sydnes, M.O., Green, L., Petrik, L. (2022). The burden of emerging contaminants upon an Atlantic Ocean marine protected reserve adjacent to Camps Bay, Cape Town, South Africa. *Heliyon*, 8(12), e12625. <https://doi.org/10.1016/j.heliyon.2022.e12625>

Oke, S.A., Alowo, R. (2021). Groundwater of the Modder River catchment of South Africa: A sustainability prediction. *Water*, 13(7), article 936. <https://doi.org/10.3390/w13070936>

Okoye, C.O., Okeke, E.S., Okoye, K.C., Echude, D., Andong, F.A., Chukwudozie, K.I., Okoye, H.U., Ezeonyejiaku, C.D. (2022). Occurrence and fate of pharmaceuticals, personal

care products (PPCPs) and pesticides in African water systems: a need for timely intervention. *Heliyon*, 8, e09143. <https://doi.org/10.1016/j.heliyon.2022.e09143>

Olarinmoye, O., Bakare, A., Ugwumba, O., Hein, A. (2016). Quantification of pharmaceutical residues in wastewater impacted surface waters and sewage sludge from Lagos, Nigeria. *Journal of Environmental Chemistry and Ecotoxicology*, 8(3):14-24.
<https://doi.org/10.5897/JECE2015.0364>

Olujimi, O.O., Fatoki, O.S., Odendaal, J.P., Okonkwo, J.O. (2010). Endocrine disrupting chemicals (phenol and phthalates) in the South African environment: A need for more monitoring. Review. *Water South Africa*, 36(5):671-682.
<https://doi.org/10.4314/wsa.v36i5.62001>

Oluwole, A.O., Omotola, E.O., Olatunji, O.S. (2020). Pharmaceuticals and personal care products in water and wastewater: a review of treatment processes and use of photocatalyst immobilized on functionalized carbon in AOP degradation. *BMC Chemistry*, 14, article 62.
<https://doi.org/10.1186/s13065-020-00714-1>

Ort, C., Lawrence, M.G., Rieckermann, J.R., Joss, A. (2010). Sampling for Pharmaceuticals and Personal Care Products (PPCPs) and Illicit Drugs in Wastewater Systems: Are Your Conclusions Valid? A Critical Review. *Environmental Science Technology*, 44(16):6024–6035. <https://doi.org/10.1021/es100779n>

Osunmakinde, C.S., Tshabalala, O.S., Dube, S., Nindi, M.M. (2013). *Verification and validation of analytical methods for testing the levels of PPHCPs (pharmaceutical & personal health care products) in treated drinking water and sewage*. Report no. 2094/1/13, Water Research Commission (WRC), Pretoria, South Africa. <https://www.wrc.org.za/wp-content/uploads/mdocs/2094-1-13.pdf>

Oulton, K.T., Cwiertny, D.M. (2010). Pharmaceuticals and personal care products in effluent matrices: A survey of transformation and removal during wastewater treatment and implications for wastewater management. *Journal of Environmental Monitoring*, 12(11):1929-2188. <https://doi.org/10.1039/C0EM00068J>

Paciuszkiewicz, K., Ryan, M., Wright, I.A., Reynolds, J.K. (2019). Variations in illicit compounds discharged from treated wastewater. *Water*, 11(5), article1071.
<https://doi.org/10.3390/w11051071>

Pal, A., Gin, K.Y.H., Lin, A.Y.C., Reinhard, M. (2010). Impacts of emerging organic contaminants on freshwater resources: Review of recent occurrences, sources, fate and

effects. *Science of the Total Environment*, 408(24):6062-6069.

<https://doi.org/10.1016/j.scitotenv.2010.09.026>

Pandey, P., Caudill, J., Lesmeister, S., Zheng, Y., Wang, Y., Stillway, M., Hoffmann, K., Gilbert, P., Kwong, M., Conrad, L., The, S. (2019). Assessing glyphosate and fluridone concentrations in water column and sediment leachate. *Frontier Environmental Science*, 7, article 22. <https://doi.org/10.3389/fenvs.2019.00022>

Patel, M., Kumar, R., Kishor, K., Mlsna, T., Charles, U., Pittman, J.C.U., Mohan, D. (2019). Pharmaceuticals of emerging concern in aquatic systems: Chemistry, occurrence, effects, and removal methods. *Chemical Reviews*, 119:3510-3673.

<https://doi.org/10.1021/acs.chemrev.8b00299>

Patterson, H.G. (2013). *Scoping study and research strategy development on currently known and emerging contaminants influencing drinking water quality*. Report no. 2093/1/13. Water Research Commission, Pretoria, South Africa. <https://www.wrc.org.za/wp-content/uploads/mdocs/2093-1-13.pdf>

Paun, I., Pirvu, F., Iancu, V.I., Chiriac, F.L. (2022). Occurrence and transport of isothiazolinone-type biocides from commercial products to aquatic environment and environmental risk assessment. *International Journal of environmental Research and Public Health*, 19, article 7777. <https://doi.org/10.3390/ijerph19137777>

Pei, S., Li, B., Wang, B., Liu, J., Song, X. (2022). Distribution and ecological risk assessment of pharmaceuticals and personal care products in sediments of North Canal, China. *Water*, 14, article 1999. <https://doi.org/10.3390/w14131999>

Peng, X., Tang, C., Yu, Y., Tan, J., Huang, Q., Wu, J., Chen, S., Mai, B. (2009). Concentrations, transport, fate, and releases of polybrominated diphenyl ethers in sewage treatment plants in the Pearl River Delta, South China. *Environment International*, 35(2):303-309. <https://doi.org/10.1016/j.envint.2008.07.021>

Petersen, F. (2016). Prioritisation of emerging contaminants in South African water resources. Master's dissertation, University of Pretoria, South Africa.

<http://hdl.handle.net/2263/57282>

Petrović, M., Gonzalez, S., Barceló, D. (2003). Analysis and removal of emerging contaminants in wastewater and drinking water. *Trends in Analytical Chemistry*, 22(10):685-696. [https://doi.org/10.1016/S0165-9936\(03\)01105-1](https://doi.org/10.1016/S0165-9936(03)01105-1)

Pitarch, E., Cervera, M., Portolés, T., Ibañez, M., Barreda, M., Renau-Pruñonosa, A., Morell, I., López, F., Albarrán, F., Hernández, F. (2016). Comprehensive monitoring of organic micro-pollutants in surface and groundwater in the surrounding of a solid-waste treatment plant of Castellón, Spain. *Science of the Total Environment*, 548-549:211-220.

<https://doi.org/10.1016/j.scitotenv.2015.12.166>

Pivetta, G.G., Gastaldini, M.C.C. (2019). Presence of emerging contaminants in urban water bodies in southern Brazil. *Journal of Water and Health*, 17(2):329-337.

<https://doi.org/10.2166/wh.2019.092>

Pope, L., Boxall, A., Corsing, C., Halling-Sorensen, B., Tait, A., Topp, E. (2009). Exposure assessment of veterinary medicines in terrestrial systems. In: Crane, M., Boxall, A.B.A., Barrett, K. (Eds.), *Veterinary medicines in the environment*. CRC Press, pp. 129-153.

Prasse, C., Schlusener, M.P., Schulz, R., Ternes, T.A. (2010). Antiviral drugs in wastewater and surface waters: A new pharmaceutical class of environmental relevance? *Environmental Science and Technology*, 44(5):1728-1735. <https://doi.org/10.1021/es903216p>

Pretorius, E., Gericke, O.J., Slabbert, S.W., Dent, M. (2005). Catchment hydrology management using GIS: Case study of the Modder River Basin, South Africa. *WIT Transactions on Ecology and the Environment*, 83:305-314.

<https://doi.org/10.2495/RM050301>

Prior, J.C. (2019). Progesterone is important for transgender women therapy-applying evidence for the benefits of progesterone in ciswoman. *Journal of Clinical Endocrinology and Metabolism*, 104(4):1181-1186. <https://doi.org/10.1210/jc.2018-01777>

Ramírez-Malule, H., Quinones-Murillo, D.H., Manotas-Duque, D. (2020). Emerging contaminants as global environmental hazards. A bibliometric analysis. *Emerging Contaminants*, 6:179-193. <https://doi.org/10.1016/j.emcon.2020.05.001>

Rapp-Write, H., Regan, F., White, B., Barron, L.P. (2023). A year-long study of the occurrence and risk of over 140 contaminants of emerging concern in wastewater influent, effluent and receiving waters in the Republic of Ireland. *Science of the Total Environment*, 860, article 160379. <https://doi.org/10.1016/j.scitotenv.2022.160379>

Rashid, A., Ayub, M., Ullah, Z., Ali, A., Khattak, S.A., Ali, L., Gao, X., Li, C., Khan, S., El-Serehy, H.A., Kaushik, P. (2022). Geochemical Modeling source provenance, public health exposure, and evaluating potentially harmful elements in groundwater: Statistical and human health risk assessment (HHRA). *International Journal of Environmental Research and Public Health*, 19, article 6472. <https://doi.org/10.3390/ijerph19116472>

Rashid, A., Khan, S., Ayub, M., Sardar, T., Jehan, S., Zahir, S., Khan, M.S., Muhammad, J., Khan, R., Ali, A., Ullah, H. (2019). Mapping human health risk from exposure to potential toxic metal contamination in groundwater of Lower Dir, Pakistan: Application of multivariate and geographical information system. *Chemosphere*, 225,:785-795.

<https://doi.org/10.1016/j.chemosphere.2019.03.066>

Reemtsma, T., Quintana, J. (2006). Analytical methods for polar pollutants. In: Reemtsma, T. and Jekel, M. (Eds.), *Organic pollutants in the water cycle*. Weinheim, Germany: Wiley, pp. 1-40. <https://doi.org/10.1002/352760877X.ch1>

Reyes, N.J.D.G., Geronimo, F.K.F., Yano, K.A.V., Guerra, H.B., Kim, L.H. (2021). Pharmaceutical and personal care products in different matrices: Occurrence, pathways, and treatment processes. *Water*, 13, article 1159. <https://doi.org/10.3390/w13091159>

Rezka, P., Balcerzak, W., Kwaśny, J. (2015). Carbamazepine and other anti-epileptic drugs in the aquatic environment. *Technical Transactions Environment Engineering*, 1-Ś(18):111-118. <https://doi.org/10.4467/2353737XCT.15.189.4394>

Rimayi, C., Odusanya, D., Weiss, J.M., De Boer, J., Chimuka, L. (2018). Contaminants of emerging concern in the Hartbeespoort Dam catchment and the uMngeni River estuary 2016 pollution incident, South Africa. *Science of the Total Environment*, 627, 1008-1017. <https://doi.org/10.1016/j.scitotenv.2018.01.263>

Rimayi, C., Chimuka, L., Gravell, A., Fones, G.R., Mills, G.A. (2019). Use of the Chemcatcher® passive sampler and time-of-flight mass spectrometry to screen for emerging pollutants in rivers in Gauteng Province of South Africa. *Environmental Monitoring and Assessment*, 191, article 388. <https://doi.org/10.1007/s10661-019-7515-z>

Rivera-Jaimes, J., Postigo, C., Melgoza-Alemán, R., Aceña, J., Barceló, D., De Alda, M. (2018). Study of pharmaceuticals in surface and wastewater from Cuernavaca, Morelos, Mexico: Occurrence and environmental risk assessment. *Science of the Total Environment*, 613-614:1263-1274. <https://doi.org/10.1016/j.scitotenv.2017.09.134>

Robles-Molina, J., Gilbert-López, B., García-Reyes, J.F., Molina-Díaz, A. (2013). Gas chromatography triple quadrupole mass spectrometry method for monitoring multiclass organic pollutants in Spanish sewage treatment plants effluents. *Talanta*, 111:196-205. <https://doi.org/10.1016/j.talanta.2013.03.006>

Roca, R.A. (2016). Determination of emerging contaminants in environmental matrices. Doctoral thesis, Universida, Politecnica Madrid, Spain.

https://oa.upm.es/43058/1/RAMON_AZNAR_ROCA.pdf

Rodriguez-Mozaz, S., Chamorro, S., Marti, E., Huerta, B., Gros, M., Sanchez-Melsio, A., Borrego, C.M., Barcelo, D., Balcazar, J.L. (2015). Occurrence of antibiotics and antibiotic resistance genes in hospital and urban wastewaters and their impacts on the receiving river. *Water Research*, 69(2015):234-242. <https://doi.org/10.1016/j.waters.2014.11.021>

Rogers, H.R. (1996). Sources, behaviour and fate of organic contaminants during sewage treatment and in sewage sludge. *Science of the Total Environment*, 185(1-3):3-26. [https://doi.org/10.1016/0048-9697\(96\)05039-5](https://doi.org/10.1016/0048-9697(96)05039-5)

Rosal, R., Rodea-Palomares, I., Boltes, K., Fernández-Piñas, F., Leganés, F., Gonzalo, S., Petre, A. (2010). Ecotoxicity assessment of lipid regulators in water and biologically treated wastewater using three aquatic organisms. *Environmental Science Pollution Research*, 17:135-144. <https://doi.org/10.1007/s11356-009-0137-1>

Sanchez, W., Egea, E. (2018). Health and environmental risks associated with emerging pollutants and novel green processes. *Environmental Science and Pollution Research*, 25:6085-6086. <https://doi.org/10.1007/s11356-018-1372-0>

Santos, J.L., Aparicio, I., Alonso, E. (2007). Occurrence and risk assessment of pharmaceutically active compounds in wastewater treatment plants. A case study: Seville city (Spain). *Environment International Journal*, 33:596-601. <https://doi.org/10.1016/j.envint.2006.09.014>

Sathiakumar, N., MacLennan, P.A., Mandel, J., Delzell, E. (2011). A review of epidemiologic studies of triazine herbicides and cancer. *Critical Review in Toxicology*, 41:1-34. <https://doi.org/10.3109/10408444.2011.554793>

Schaar, H., Clara, M., Gans, O., Kreuzinger, N. (2010). Micropollutant removal during biological wastewater treatment and a subsequent ozonation step. *Environmental Pollution*, 158(5):1399-1404. <https://doi.org/10.1016/j.envpol.2009.12.038>

Schaider, L.A., Rudel, R.A., Ackerman, J.M., Dunagan, S.C., Brody, J.G. (2014). Pharmaceuticals, perfluorosurfactants, and other organic wastewater compounds in public drinking water wells in a shallow sand and gravel aquifer. *Science of the Total Environment*, 468-469:384-393. <https://doi.org/10.1016/j.scitotenv.2013.08.067>

Schönherr, J., Buchheim, J., Scholz, P., Stelter, M. (2017). Oxidation of carbon nanotubes with ozone and hydroxyl radicals. *Carbon*, 111:631-640. <https://doi.org/10.1016/j.carbon.2016.10.013>

Selvaraju, N., Pushpavanam, S., Anu, N. (2013). A holistic approach combining factor analysis, positive matrix factorization, and chemical mass balance applied to receptor modeling. *Environmental Monitoring and Assessment*, 185(12):10115-10129.

<https://doi.org/10.1007/s10661-013-3317-x>

Selvaraju, V., Baskaran, S., Agarwal, A., Henkel, R. (2021). Environmental contaminants and male infertility: Effects and mechanisms. *Andrologia*, 53, article 13646.

<https://doi.org/10.1111/and.13646>

Selwe, K.P., Thorn, J.P.R., Desrousseaux, A.O.S., Dessent, C.E.H., Sallach J.B. (2022). Emerging contaminant exposure to aquatic systems in the Southern African Development Community. *Environmental Toxicology and Chemistry*, 41(2):382-395.

<https://doi.org/10.1002/etc.5284>

Sereda, B.L., Meinhardt, H.R. (2005). Contamination of the water environment in malaria endemic areas of KwaZulu-Natal, South Africa, by agricultural insecticides. *Bulletin of Environmental Contamination and Toxicology*, 75(3):530-537.

<https://doi.org/10.1007/s00128-005-0784-y>

Shah, Z.U., Parveen, S. (2023). Distribution and risk assessment of pesticide residues in sediment samples from river Ganga, India. *PLoS One*, 18(2), e0279993.

<https://doi.org/10.1371/journal.pone.0279993>

Shao, Y., Chen, Z., Hollert, H., Zhou, S., Deutschmann, B., Seiler, T.B. (2019). Toxicity of 10 organic micro pollutants and their mixture: implications for aquatic risk assessment. *Science of the Total Environment*, 666:1273-1282.

<https://doi.org/10.1016/j.scitotenv.2019.02.047>

Sharma, B.M., Bečanová, J., Scheringer, M., Sharma, A., Bharat, G.K., Whitehead, P.G., Klánová, J., Nizzetto, L. (2018). Health and ecological risk assessment to emerging contaminants (pharmaceuticals, personal care products, and artificial sweeteners) in surface and groundwater (drinking water) in the Ganges River Basin, India. *Science of the Total Environment*, 646:1459-1467. <https://doi.org/10.1016/j.scitotenv.2018.07.235>

Shipingana, L.N.N, Shivaraju, H.P., Yashas, S.R. (2022). Quantitative assessment of pharmaceutical drugs in a municipal wastewater and overview of associated risks. *Applied Water Science*, 12, article 16. <https://doi.org/10.1007/s13201-022-01570-1>

Shore, R.F., Taggart, M.A., Smits, J., Mateo, R., Richards, N.L., Fryday, S. (2014). Detection and drivers of exposure and effects of pharmaceuticals in higher vertebrates. *Philosophical*

Transactions of Royal Society B, 369, article 20130570.

<https://doi.org/10.1098/rstb.2013.0570>

Shrestha, S., Kazama, F. (2007). Assessment of surface water quality using multivariate statistical techniques: A case study of the Fuji river basin, Japan. *Environmental Modelling and Software*, 22:464-475. <https://doi.org/10.1016/j.envsoft.2006.02.001>

Sibeko, P.A, Naicker, D., Mdluli, P.S., Madikizela, L.M. (2019). Naproxen, ibuprofen, and diclofenac residues in river water, sediments and *Eichhornia crassipes* of Mbokodweni River in South Africa: An initial screening. *Environmental Forensics*, 1-10.

<https://doi.org/10.1080/15275922.2019.1597780>

Sililo, O.T.N., Saayman, I.C., Fey, M.V. (2001). Groundwater vulnerability to pollution in urban catchments, Report No. 1008/1/01, Water Research Commission: Pretoria, South Africa. <https://www.wrc.org.za/wp-content/uploads/mdocs/1008-1-011.pdf>

Slabbert, N. (2007). The potential impact of an inter-basin water transfer on the Modder and Caledon river systems. Doctoral thesis, University of Free State, South Africa.

Stevanovic M, Gašić, S. (2019). Herbicides in surface water bodies-behaviour, effects on aquatic organisms and risk assessment. *Pesticide and Phytomedicine / Pesticidi i Fitomedicina* (Belgrade), 34(3-4):157-172.

<https://aseestant.ceon.rs/index.php/pif/article/view/PIF1904157S>

Snow, D.D., Bartelt-Hunt, S.L., Brown, D.L., Sangster, J., Cassada, D.A. (2010). Detection, occurrence and fate of pharmaceuticals and steroid hormones in agricultural environments. *Water Environment Research*, 82(10):869-882.

<https://doi.org/10.2175/106143010X12756668800618>

Sorensen, J.P.R., Lapworth, D.J., Nkhuwa, D.C.W., Stuart, M.E., Gooddy, D.C., Bell, R.A., Chirwa, M., Kabika, J., Liemisa, M., Chibesa, M., Pedley, S. (2015). Emerging contaminants in urban groundwater sources in Africa. *Water Research*, 72:51-63.

<https://doi.org/10.1016/j.watres.2014.08.002>

Späth, J., Arumugam, P., Lindberg, R.H., Afafe, O.A., Jansson, S., Fick, J., Buckley, C.A. (2021). Biochar for the removal of detected micropollutants in South African domestic wastewater: a case study from a demonstration-scale decentralised wastewater treatment system in eThekweni. *Water SA*, 47(4):396-416.

<https://doi.org/10.17159/wsa/2021.v47.i4.3861>

Stats SA (Statistics South Africa) (2019). *Statistical release (P0302): Mid-year population estimates*. <https://www.statssa.gov.za/publications/P0302/P03022019.pdf>

Stefanakis, A.I., Becker, J.A. (2016). A review of emerging contaminants in water: Classification, sources, and potential risks. In: Mckeown, A.E. (Ed.), *Impact of water pollution on human health and environmental sustainability*, IGI Global, Hershey, Pennsylvania, pp. 55-80. <https://doi.org/10.4018/978-1-4666-9559-7.ch003>

Sturm, R., Ahrens, L. (2010). Trends of polyfluoroalkyl compounds in marine biota and in humans. *Environmental Chemistry*, 7(6):457-484. <https://doi.org/10.1071/EN10072>

Styszko, K., Proctor, K., Castrignano, E., Kasprzyk-Hordern, B. (2021). Occurrence of pharmaceutical residues, personal care products, lifestyle chemicals, illicit drugs and metabolites in wastewater and receiving surface waters of Krakow agglomeration in South Poland. *Science of the Total Environment*, 768, article 144360. <https://doi.org/10.1016/j.scitotenv.2020.144360>

Suárez, S., Carballa, M., Omil, F., Lema, J.M. (2008). How are pharmaceutical and personal care products (PPCPs) removed from urban wastewaters? *Reviews in Environmental Science and Bio/Technology*, 7(2):125-138. <https://doi.org/10.1007/s11157-008-9130-2>

Subedi, B., Balakrishna, K., Joshua, D.I., Kannan, K. (2017). Mass loading and removal of pharmaceuticals and personal care products including psychoactives, antihypertensives, and antibiotics in two sewage treatment plants in Southern India. *Chemosphere*, 167:429-437. <https://doi.org/10.1016/j.chemosphere.2016.10.026>

Subedi, B., Codru, N., Dziewulski, D.M., Wilson, L.R., Xue, J., Yun, S., Braun-Howland, E., Minihane, C., Kannan, K. (2015). A pilot study on the assessment of trace organic contaminants including pharmaceuticals and personal care products from on-site wastewater treatment systems along Skaneateles Lake in New York State, USA. *Water Research*, 72:28-39. <https://doi.org/10.1016/j.watres.2014.10.049>

Sun, J., Luo, Q., Wang, D., Wang, Z. (2015). Occurrences of pharmaceuticals in drinking water sources of major river watersheds, China. *Ecotoxicology and Environmental Safety*, 117:132-140. <https://doi.org/10.1016/j.ecoenv.2015.03.032>

Swartz, C.D., Genthe, B., Chamier, J., Petrik, L.F., Tijani, J.O., Adeleye, A., Coomans, C.J., Ohlin, A., Falk, D., Menge, J.G. (2018). *Volume II: A prioritization framework for monitoring contaminants of emerging concern in reclaimed water for potable use*. Report No. TT 742/2/17, Water Research Commission, Pretoria, South Africa. <https://www.wrc.org.za/wp-content/uploads/mdocs/TT%20742%20Vol%202%20web.pdf>

Syafrudin, M., Kristanti, R.A., Yuniarto, A., Hadibarata, T., Rhee, J., Al-Onazi, W.A., Algarni, T.S., Almarri, A.H. and Al-Mohaimeed, A.M. (2021). Pesticides in drinking water – A review. *International Journal of Environmental Research and Public Health*, 18(2), article 468. <https://doi.org/10.3390/ijerph18020468>

Székács, A., Mörtl, M., Darvas, B. (2015). Monitoring pesticide residues in surface and ground water in Hungary: Surveys in 1990-2015. *Journal of Chemistry*, 2015, article 717948. <https://dx.doi.org/10.1155/2015/717948>

Ternes, T.A. (2006). Emerging substances in water. A new challenge for water management. *Stresa*, 19 June. https://www.norman-network.net/sites/default/files/files/Events/2006-2008/2006Jun19-20-Stresa-EmEnvPollutants-KeyIssuesChallenges/03-sess1_ternes.pdf

Ternes, T.A., Herrmann, N., Bonerz, M., Knacker, T., Siegrist, H., Joss, A. (2004). A rapid method to measure the solid-water distribution coefficient (K_d) for pharmaceuticals and musk fragrances in sewage sludge. *Water Research*, 38(19):4075-4084. <https://doi.org/10.1016/j.watres.2004.07.015>

Thomaidis, N.S., Asimakopoulos, A.G., Bletsou, A.A. (2012). Emerging contaminants: A tutorial mini-review. *Global NEST Journal*, 14:72-79. <https://doi.org/10.30955/gnj.000823>

Thomas, K.V., Dye, C., Schlabach, M., Langford, K.H. (2007). Source to sink tracking of selected human pharmaceuticals from two Oslo city hospitals and a wastewater treatment works. *Journal of Environmental Monitoring*, 9(12):1410-1418. <https://doi.org/10.1039/b709745j>

Thrupp, T.J., Runnalls, T.J., Scholze, M., Kugathas, S., Kortenkamp, A., Sumpter, J.P. (2018). The consequences of exposure to mixtures of chemicals: Something from ‘nothing’ and ‘a lot from a little’ when fish are exposed to steroid hormones. *Science of the Total Environment*, 619-620:1482-1492. <https://doi.org/10.1016/j.scitotenv.2017.11.081>

Tijani, J.O., Fatoba, O.O., Petrik, L.F. (2013). A review of pharmaceuticals and endocrine-disrupting compounds: sources, effects, removal, and detections. *Water, Air & Soil Pollution*, 224, article 1770. <https://doi.org/10.1007/s11270-013-1770-3>

Topp, E., Monteiro, S.C., Beck, A., Coehlo, B., Boxall, A.B., Duenk, P.W., Kleywegt, S., Lapen, D.R., Payne, M., Sabourin, L., Li, H., Metcalfe, C.D. (2008). Runoff of pharmaceuticals and personal care products following application of biosolids to an agricultural field. *Science of the Total Environment*, 396(1):52-59. <https://doi.org/10.1016/j.scitotenv.2008.02.011>

Tormo-Budowski, R., Cambronero-Heinrichs, J.C., Jej, D., Masís-Mora, M., Ramírez-Morales, D., Quirós-Fournier, J.P., Rodríguez-Rodríguez, C.E. (2021). Removal of pharmaceuticals and ecotoxicological changes in wastewater using *Trametes versicolor*: a comparison of fungal stirred tank and trickle-bed bioreactors. *Chemical Engineering Science*, 410(15), article 128210. <https://hdl.handle.net/10669/84523>

Torres-Padrón, M.E., Montesdeoca-Esponda, S., Santana-Viera, S., Guedes-Alonso, R., Herrera-Melián, J.A., Sosa-Ferrera, Z., Santana-Rodríguez, J.J. (2020). An update of the occurrence of organic contaminants of emerging concern in the Canary Islands (Spain). *Water*, 2548. <https://doi.org/10.3390/w12092548>

Tran, N.H, Urase, T., Ta, T.T. (2014). A preliminary study on the occurrence of pharmaceutically active compounds in hospital wastewater and surface water in Hanoi, Vietnam. *Clean: Soil, Air & Water*, 42:267-275. <https://doi.org/10.1002/clen.201300021>

Trenberth, K.E., Smith, L., Qian, T., Dai, A., Fasullo, J. (2007). Estimates of the global water budget and its annual cycle using observational and model data. *Journal of Hydrometeorology*, 8(4):758-769. <https://doi.org/10.1175/JHM600.1>

Tufenkji, N., Ryan, J.N., Elimelech, M. (2002). The promise of bank filtration. A simple technology may inexpensively clean up poor-quality raw surface water. *Environmental Science & Technology*, 36:422A-428A. <https://doi.org/10.1021/es022441j>

Ulvi, A., Aydin, S., Aydin, M.E. (2022). Fate of selected pharmaceuticals in hospital and municipal wastewater effluent: occurrence, removal, and environmental risk assessment. *Environmental Science and Pollution Research*, 29:75609-75625. <https://doi.org/10.1007/s11356-022-21131-y>

USEPA (United States Environmental Protection Agency) (2002). *Supplemental guidance for developing soil screening levels for superfund sites*. Office of Emergency and Remedial Response: Washington, DC, USA. <https://epa.gov/superfund/superfund-soil-screening-guidance> (Accessed on 13 July 2023).

USEPA (United States Environmental Protection Agency) (2004). *Risk assessment guidance for Superfund (RAGS): Part E, Supplemental guidance for dermal risk assessment*. Washington, DC. <https://www.epa.gov/risk/risk-assessment-guidance-superfund-rags-part-e> (Accessed on 10 July 2023)

USEPA (United States Environmental Protection Agency) (2008). *Nanotechnology for site remediation fact sheet. Solid waste and emergency response*. EPA 542-F-08-009.

Washington, DC, USA. <http://www.clu-in.org/download/remed/542-f-08-009.pdf> (Accessed on 04 March 2022).

USEPA (United States Environmental Protection Agency) (2016). *Chemical Search (IRIS)*. Washington, DC, USA. <https://cfpub.epa.gov/ncea/iris/search/index.cfm?keyword=atrazine> (Accessed on 13 July 2023).

USEPA (United State Environmental Protection Agency) (2021). Regional screening levels (RSLs). Washington, DC, USA. <https://www.epa.gov/risk/regional-screening-levels-rsls-generic-tables> (Accessed on 27 July 2023).

Usher, B.H., Pretorius, J.A., Van Tonder, G.J. (2007). Management of a Karoo fractured-rock aquifer system-Kalkveld Water User Association (WUA). *Water South Africa*, 32(1):9-19. <https://doi.org/10.4314/wsa.v32i1.5234>

Van Wyk, J.H., Archer, E., Babalola, O., Truter, C., Van Rensburg, E.J., Dabrowski, J. (2014). *Pesticides as endocrine disruptors in South Africa: Laboratory and field studies*. Report no. K5/1932, Water Research Commission, Pretoria, South Africa. <https://www.wrc.org.za/wp-content/uploads/mdocs/1932-1-141.pdf>

Van Wyk, M. (2019). *Geohydrological investigation and hydro-census for outspan 1960, Bloemfontein district, Free State*. MVW Geohydrologist <https://sahris.sahra.org.za/sites/default/files/additionaldocs/Musket%20Geohydrological%20Report%20-%20M.%20Van%20Wyk.pdf>

Van Zijl, M.C., Aneck-Hahn, N.H., Swart, P., Hayward, S., Genthe, B., De Jager, C. (2017). Estrogenic activity, chemical levels and health risk assessment of municipal distribution point water from Pretoria and Cape Town, South Africa. *Chemosphere*, 186:305-313. <https://doi.org/10.1016/j.chemosphere.2017.07.130>

Vasilachi, I.C., Asiminicesei, D.M., Fertu, D.I., Gavrilescu, M. (2021). Occurrence and Fate of Emerging Pollutants in Water Environment and Options for Their Removal. *Water*, 13(2), article 181. <https://doi.org/10.3390/w13020181>

Veldhoen, N., Skirrow, R.C., Brown, L.L.Y., Aggelen, G., Van Helbing, C.C. (2014). Effects of acute exposure to the non-steroidal anti-infl ammatory drug ibuprofen on the developing North American bullfrog (*Rana catesbeiana*) tadpole. *Environmental Science & Technology*, 48 (17), 10439-10447. <https://doi.org/10.1021/es502539g>

Vermeulen, P.D. (2012). A South African perspective on shale gas hydraulic fracturing. Proceedings of the International Mine Water Association Annual Conference, 2012, 146-149. http://www.mwen.info/docs/imwa_2012/IMWA2012_Vermeulen_149.pdf

Viana, P., Meisel, L., Lopes, A., De Jesus, R., Sarmento, G., Duarte, S., Sepodes, B., Fernandes, A., Dos Santos, M.M.C., Almeida, A., Oliveira, M.C. (2021). Identification of antibiotics in surface-groundwater. A tool towards the ecopharmacovigilance approach: A Portuguese case-study. *Antibiotics (Basel)*, 10(8), article 888. <https://doi.org/10.3390/antibiotics10080888>

Visca, A., Barra Caracciolo, A., Grenni, P., Rolando, L., Mariani, L., Rauseo, J., Spataro, F., Monostory, K., Sperlagh, B., Patrolecco, L. (2021). Legacy and emerging pollutants in an urban river stretch and effects on the bacterioplankton community. *Water*, 13, article 3402. <https://doi.org/10.3390/w13233402>

Völker, J., Stapf, M., Miehe, U., Wagner, M. (2019). Systematic review of toxicity removal by advanced wastewater treatment technologies via ozonation and activated carbon. *Environmental Science & Technology*, 53:7215-7233. <https://doi.org/10.1021/acs.est.9b00570>

Vumazonke, S., Khamanga, S.M., Ngqwala, N.P. (2020). Detection of pharmaceutical residues in surface waters of the Eastern Cape Province. *International Journal of Environmental Research and Public Health*, 17(11), article 4067. <https://doi.org/10.3390/ijerph17114067>

Wanda, E., Nyoni, H., Mamba, B., Msagati, T. (2017). Occurrence of emerging micropollutants in water systems in Gauteng, Mpumalanga and North West provinces, South Africa. *International Journal of Environmental Research and Public Health*, 14(1), article 79. <https://doi.org/10.3390/ijerph14010079>

Wang, M., Lv, J., Deng, H., Liu, Q., Liang, S. (2022). Occurrence and removal of triazine herbicides during wastewater treatment processes and their environmental impact on aquatic life. *International Journal of Environmental Research and Public Health*, 19, article 4557. <https://doi.org/10.3390/ijerph19084557>

Wang, Q., Wu, X., Zhao, B., Qin, J., Peng, T. (2015). Combined multivariate statistical techniques, water pollution index (WPI) and Daniel trend test methods to evaluate temporal and spatial variations and trends of water quality at Shanchong River in the Northwest basin of Lake Fuxian, China. *PLoS ONE*, 10(4), e0118590. <https://doi.org/10.1371/journal.pone.0118590>

Wang, Y., Li, N., Jiang, S., Chen, X. (2022). Application of extraction and determination based on deep eutectic solvents in different types of environmental samples. *Water*, 14(1), article 46. <https://doi.org/10.3390/w14010046>

Wang, Y., Zhang, S., Cui, W., Meng, X., Tang, X. (2018). Polycyclic aromatic hydrocarbons and organochlorine pesticides in surface water from the Yongding River basin, China: Seasonal distribution, source apportionment, and potential risk assessment. *Science of the Total Environment*, 618:419-429. <https://doi.org/10.1016/j.scitotenv.2017.11.066>

Wani, A.A., Dar, A.A., Jan, I., Sofi, K.A., Sofi, J.A., Dar, I.H. (2019). Method validation and simultaneous quantification of eight organochlorines/organophosphates in apple by gas chromatography. *Journal of the Science of Food and Agriculture*, 99(7):3687-3692. <https://doi.org/10.1002/jsfa.9599>

Warwick, C., Guerreiro, A., Soares, A. (2013). Sensing and analysis of soluble phosphates in environmental samples: A review. *Biosensors and Bioelectronics*, 41(15):1-11. <https://doi.org/10.1016/j.bios.2012.07.012>

Wee, S.Y., Aris, A.Z. (2019). Occurrence and public-perceived risk of endocrine disrupting compounds in drinking water. *Clean Water*, 2, article 4. <https://doi.org/10.1038/s41545-018-0029-3>

WHO and UNICEF (World Health Organization and the United Nations Children's Fund). (2019). *Progress on drinking water, sanitation and hygiene 2002-2017: Special focus on inequalities*. New York: UNICEF. <https://www.who.int/publications/i/item/97892415162355> (Accessed on 26 August 2023)

Wilkinson, J.L., Hooda, P.S., Swinden, J.S., Barker, J.B., Barton, S. (2017). Spatial distribution of organic contaminants in three rivers of Southern England bound to suspended particulate material and dissolved in water. *Science of the Total Environment*, 593-594:487-497. <http://dx.doi.org/10.1016/j.scitotenv.2017.03.167>

Wilkinson, J.L., Boxall, A.B.A., Kolpin, D.W., Leung, K.M.Y., Lai, R.W.S., Galban-Malagon, C., Adell, A.D., Mondon, J., Metian, M., Marchant, R.A., Bouzas-Monroy, A. et al. (2022). Pharmaceutical pollution of the world's rivers. *Proceedings of the National Academy of Sciences of the United States of America*, 119(8), e2113947119. <https://doi.org/10.1073/pnas.2113947119>

Wilm, M. (2011). Principles of electrospray ionization. *Molecular & Cellular Proteomics*, 10(7):M111.009407. <https://doi.org/10.1074/mcp.M111.009407>

- Wilson, N. (2018). Nanoparticle: Environmental problems or problem solvers? *Bioscience*, 68(4):241-246. <https://doi.org/10.1093/biosci/biy015>
- Wood, T.P., Duvenage, C.S.J., Rohwer, E. (2015). The occurrence of anti-retroviral compounds used for HIV treatment in South African surface water. *Environmental Pollution*, 199:235-243. <https://doi.org/10.1016/j.envpol.2015.01.030>
- Wu, J., Liu, J., Pan, Z., Wang, B., Zhang, D. (2020). Spatiotemporal distributions and ecological risk assessment of pharmaceuticals and personal care products in groundwater in North China. *Hydrology Research*, 51(5):911-924. <https://doi.org/10.2166/nh.2020.001>
- Wu, Y., Chen, J. (2013). Investigating the effects of point source and nonpoint source pollution on the water quality of the East River (Dongjiang) in South China. *Ecological Indicators*, 32, 294-304. <https://doi.org/10.1016/j.ecolind.2013.04.002>
- Yamamoto, H., Nakamura, Y., Moriguchi, S., Nakamura, Y., Honda, Y., Tamura, I., Hirata, Y., Hayashi, A., Sekizawa, J. (2009). Persistence and partitioning of eight selected pharmaceuticals in the aquatic environment: Laboratory photolysis, biodegradation, and sorption experiments. *Water Research*, 43(2):351-362.
<https://doi.org/10.1016/j.watres.2008.10.039>
- Yan, Q., Zhang, Y.X., Kang, J., Gan, X.M., Xu, Y.P., Guo, J.S., Gao, X. (2015). A Preliminary Study on the occurrence of pharmaceutically active compounds in the river basins and their removal in two conventional drinking water treatment plants in Chongqing, China. *Clean: Soil, Air & Water*, 43(6):794-803. <https://doi.org/10.1002/clen.201400039>
- Yang, G., Fan, M., Zhang, G. (2014). Emerging contaminants in surface waters in China – A short review. *Environmental Research Letters*, 9, article 074018.
<https://doi.org/10.1088/1748-9326/9/7/074018>
- Yang, Z., Zhang, M., Hao, C., Hou, X., Wang, L., Xia, R., Yin, J., Ma, C., Wang, Q., Zhang, Y. (2020). Source apportionment of total phosphorus pollution in Poyang lake basin based on source sink process modeling. *The Research of Environmental Sciences*, 33(11):2493-2506. <http://dx.doi.org/10.13198/j.issn.1001-6929.2020.09.11>
- Yilma, M., Kiflie, Z., Windsperger, A., Gessese, N. (2018). Assessment and interpretation of river water quality in Little Akaki River using multivariate statistical techniques. *International Journal of Environmental Science and Technology*, 16(17):3707-3720.
<https://doi.org/10.1007/s13762-018-2000-8>

Ying, G.G., Kookana, R.S., Kolpin, D.W. (2009). Occurrence and removal of pharmaceutically active compounds in sewage treatment plants with different technologies. *Journal of Environmental Monitoring and Assessment*, 11, 1498-1505.

<https://doi.org/10.1039/B904548A>

Ying, G.G., Zhao, J.L., Zhou, L.J., Liu, S. (2013). Chapter 14 – Fate and occurrence of pharmaceuticals in the aquatic environment (surface water and sediment). *Comprehensive Analytical Chemistry*, 62:453-557. <https://doi.org/10.1016/B978-0-444-62657-8.00014-8>

You, L., Nguyen, V.T., Pal, A., Chen, H., He, Y., Reinhard, M., Gin, K.Y.H. (2015). Investigation of pharmaceuticals, personal care products and endocrine disrupting chemicals in a tropical urban catchment and the influence of environmental factors. *Science of the Total Environment*, 536:955–963. <https://doi.org/10.1016/j.scitotenv.2015.06.041>

Yazdan, M.M.S., Kumar, R., Leung, S.W. (2022). The environmental and health impacts of steroids and hormones in wastewater effluent, as well as existing removal technologies: A review. *Ecologies*, 3:206-224. <https://doi.org/10.3390/ecologies3020016>

Zektser, I.S., Everett, L.G. (2004). *Groundwater resources of the world and their use; IHP-VI series on groundwater No.6*. Paris: UNESCO.

<https://unesdoc.unesco.org/ark:/48223/pf0000134433>

Zhang, Q., Wang, X., Wan, W., Hou, P., Li, R., Ouyang, Z. (2015). The spatial-temporal pattern and source apportionment of water pollution in a trans-urban river. *Polish Journal of Environmental Studies*, 24(2):841-851. [https://www.pjoes.com/pdf-89459-23401?filename=The%20Spatial Temporal.pdf](https://www.pjoes.com/pdf-89459-23401?filename=The%20Spatial%20Temporal.pdf)

Zhang, S., Zhang, Q., Darisaw, S., Ehie, E., Wang, G. (2006). Simultaneous quantification of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and pharmaceuticals and personal care products (PPCPs) in Mississippi river water, in New Orleans, Louisiana, USA. *Chemosphere*, 66(6):1057-1069.

<https://doi.org/10.1016/j.chemosphere.2006.06.067>

Zhao, L., Hu, G., Yan, Y., Yu, R., Cui, J., Wang, X., Yan, Y. (2019). Source apportionment of heavy metals in urban road dust in a continental city of eastern China: Using Pb and Sr isotopes combined with multivariate statistical analysis. *Atmospheric Environment*, 201(2019): 201-211. <https://doi.org/10.1016/j.atmosenv.2018.12.050>

Zhou, G., Chen, S., Li, A., Xu, C., Jing, G., Chen, Q., Hu, Y., Tang, S., Lv, M., Xiao, K. (2023). Pollution source apportionment of river tributary based on PMF receptor model and

water quality remote sensing in Xinjian River, China. *Water*, 15, article 7.

<https://doi.org/10.3390/w15010007>

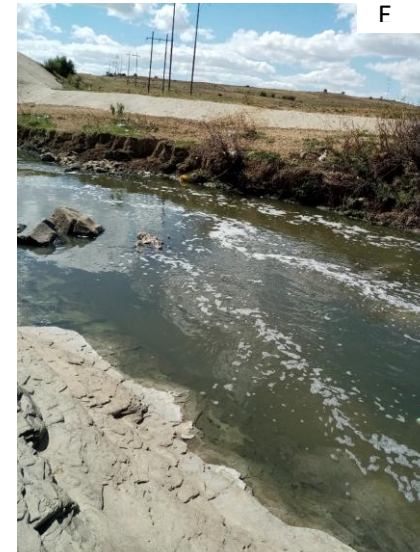
Zuccato, E., Castiglioni, S. (2009). Illicit drugs in the environment. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 367:3965-3978. <https://doi.org/10.1098/rsta.2009.0107>

Appendix A

COLLECTION AND HANDLING OF SAMPLES



Sample collection material and handling procedures during fieldwork



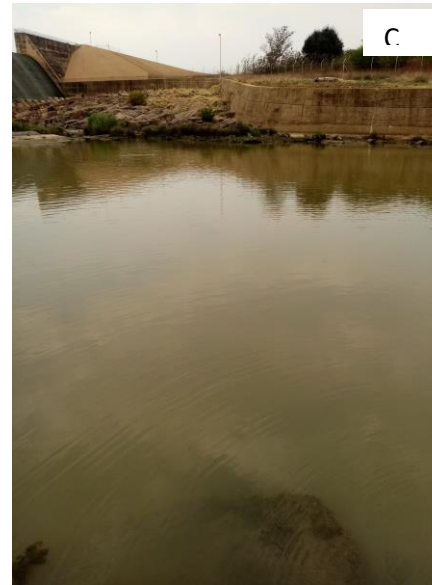
Collection of water samples at (A) Renosterspruit; (B) Bloemspruit; (C) Koringspruit; (D) Modde River; and (E) Kleinmodder River.



A



B



C



D



E

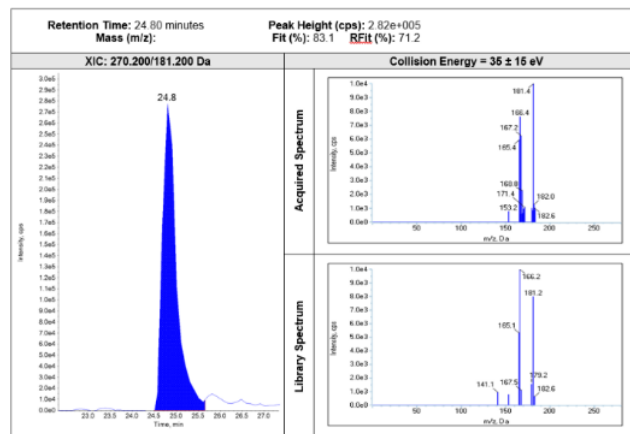
Collection of water samples at (A) Maselspoort; (B) Mockes; (C) Krugersdrift; (D) Seroalo; and (E) Rustfontein dams



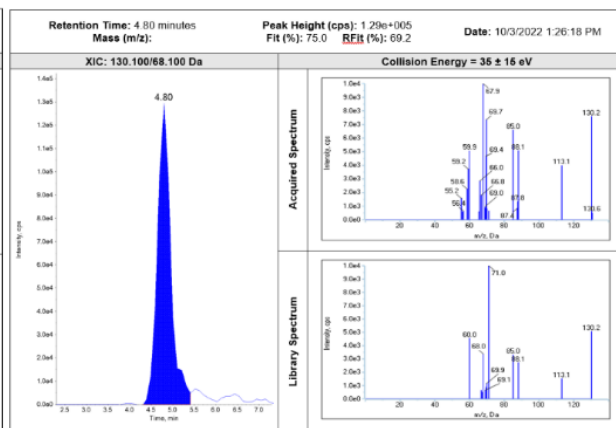
Collection of wastewater from influent (in) and effluent (ef) from (A) Bloemfontein NE; (B) Botshabelo; and (C) Bloemspuit wastewater treatment plants.

Appendix B

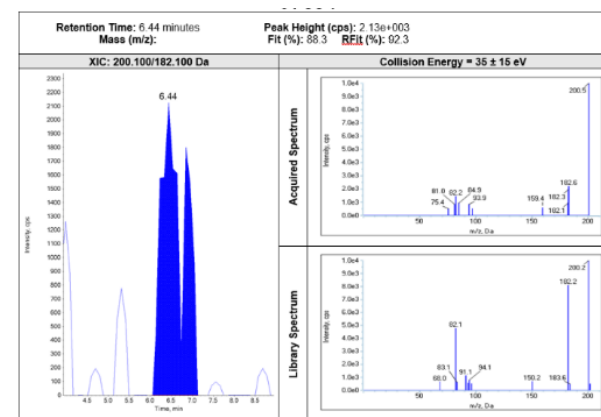
MULTIPLE REACTION MONITORING CHROMATOGRAPHY



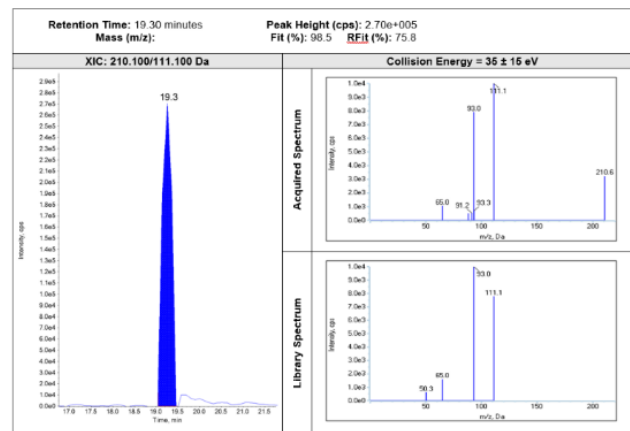
	Compound Name	Peak Area (counts)	RevFit (%)
1	Orphenadrine	6.17e+006	71.2



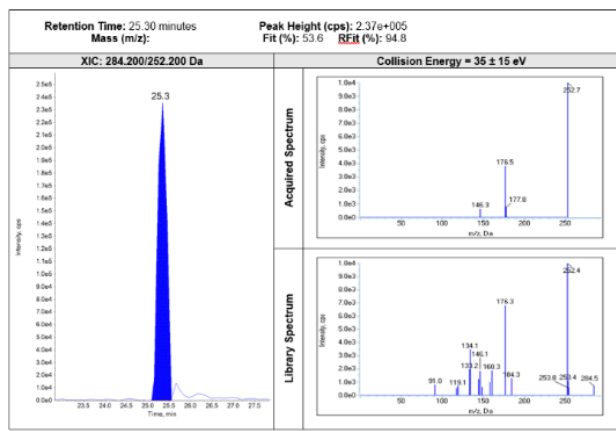
	Compound Name	Peak Area (counts)	RevFit (%)
1	Metformin	2.82e+006	69.2



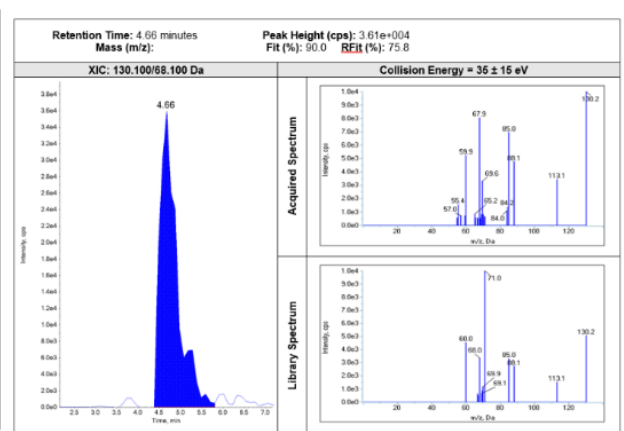
	Compound Name	Peak Area (counts)	RevFit (%)
1	Ecgoninemethyl ester	8.22e+004	92.3



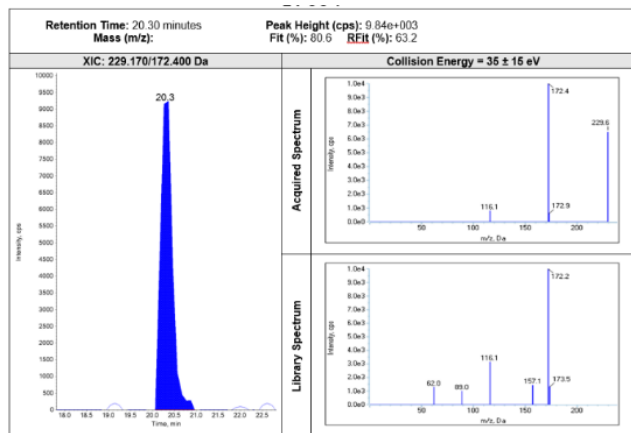
	Compound Name	Peak Area (counts)	RevFit (%)
1	Propoxur_20000	4.21e+006	75.8



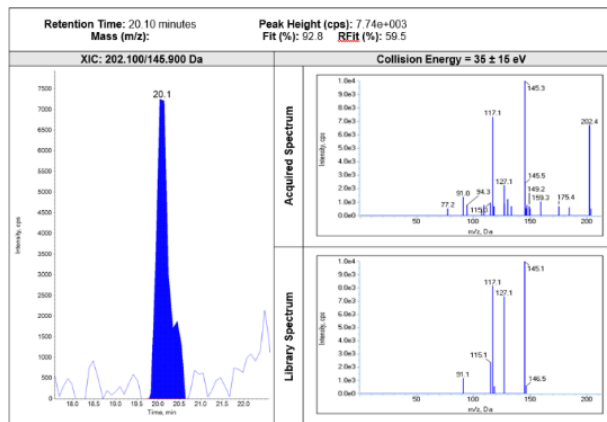
	Compound Name	Peak Area (counts)	RevFit (%)
1	Metolachlor_2000	3.47e+006	94.8



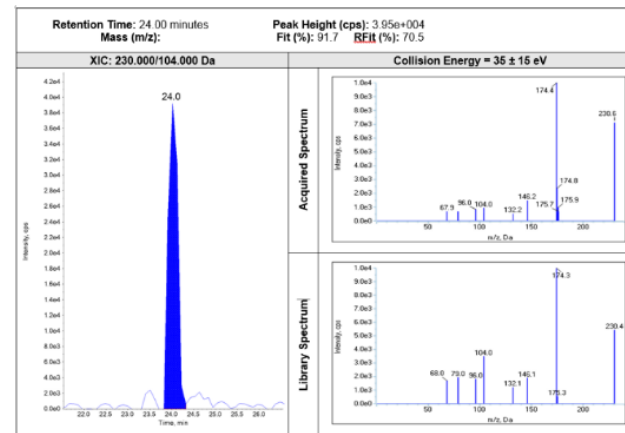
	Compound Name	Peak Area (counts)	RevFit (%)
1	Metformin	1.03e+006	75.8



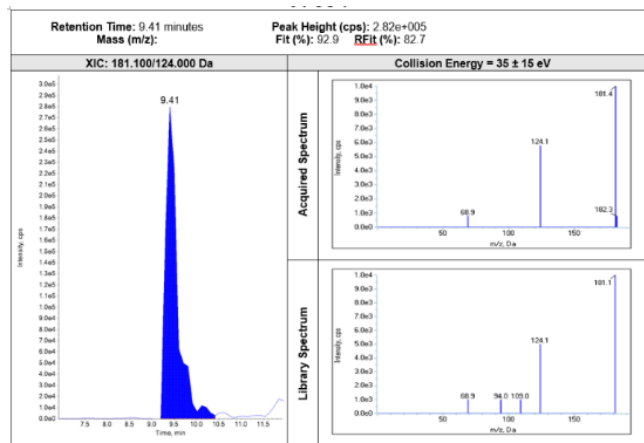
	Compound Name	Peak Area (counts)	RevFit (%)
1	Tebuthiuron_200	1.76e+005	63.2



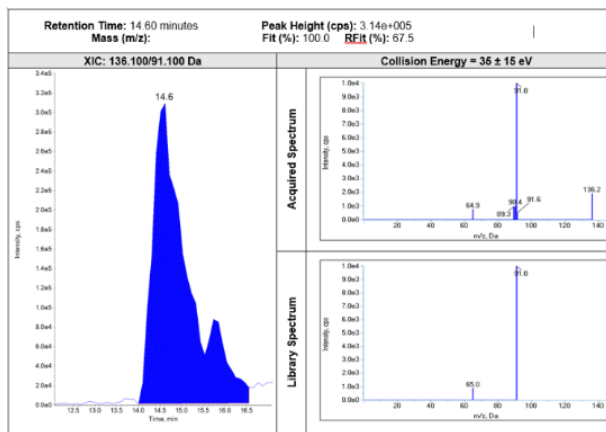
	Compound Name	Peak Area (counts)	RevFit (%)
1	Carbaid	1.56e+005	59.5



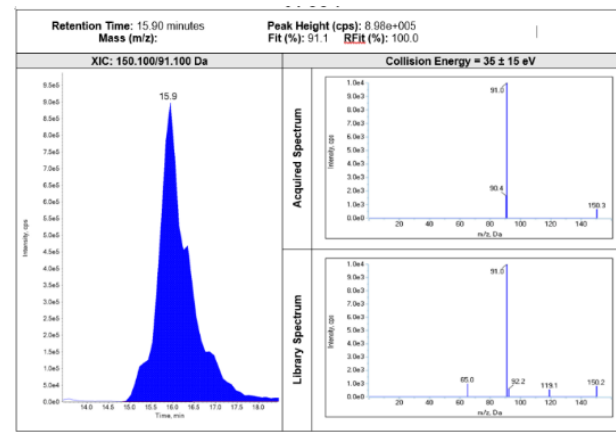
	Compound Name	Peak Area (counts)	RevFit (%)
1	Terbutylazine_2000	6.04e+005	70.5



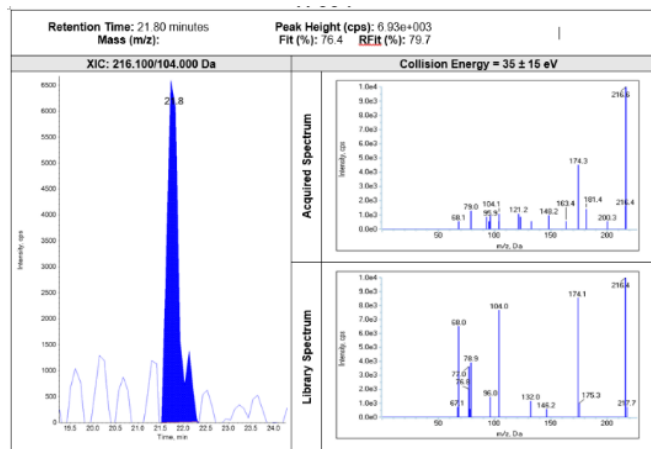
	Compound Name	Peak Area (counts)	RevFit (%)
1	Theophylline	5.30e+006	82.7



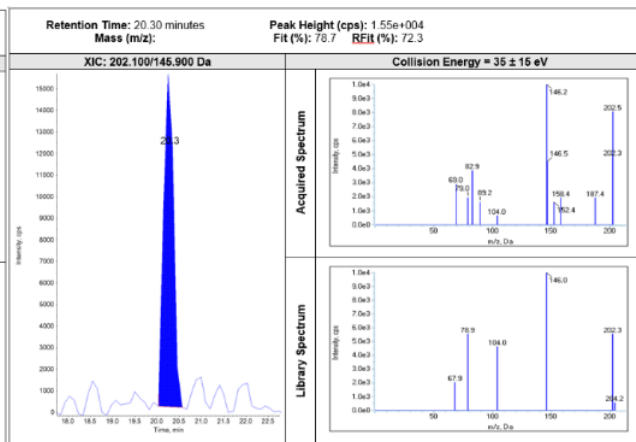
	Compound Name	Peak Area (counts)	RevFit (%)
1	Amphetamine	1.75e+007	67.5



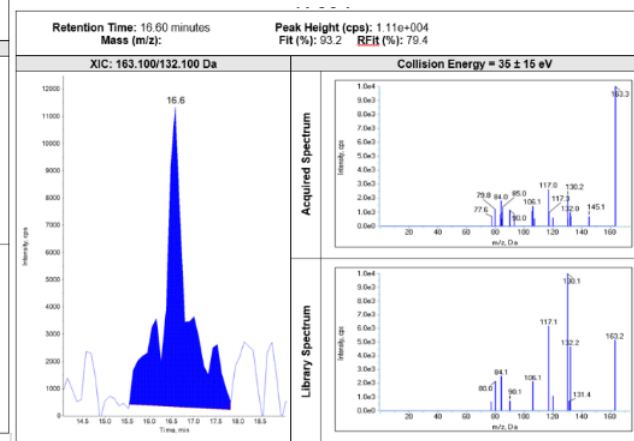
	Compound Name	Peak Area (counts)	RevFit (%)
1	Metamphetamine	4.40e+007	100.0



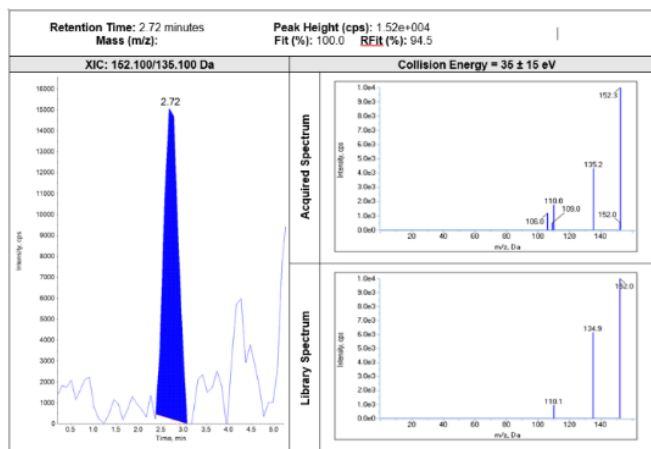
	Compound Name	Peak Area (counts)	RevFit (%)
1	Atrazin_200	1.22e+005	79.7



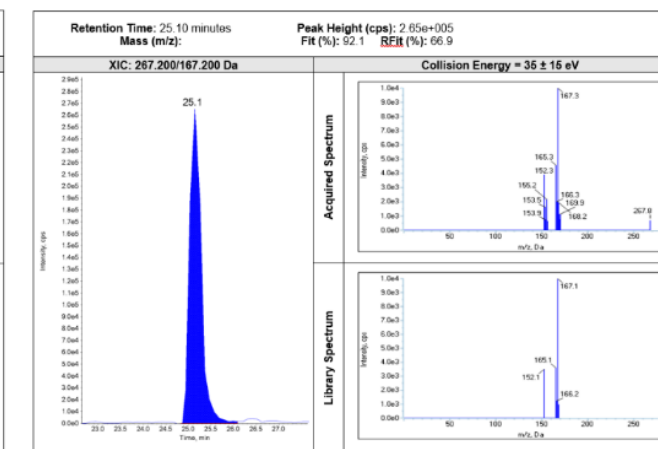
	Compound Name	Peak Area (counts)	RevFit (%)
1	Sebutylazine-desethyl_200	2.41e+005	72.3



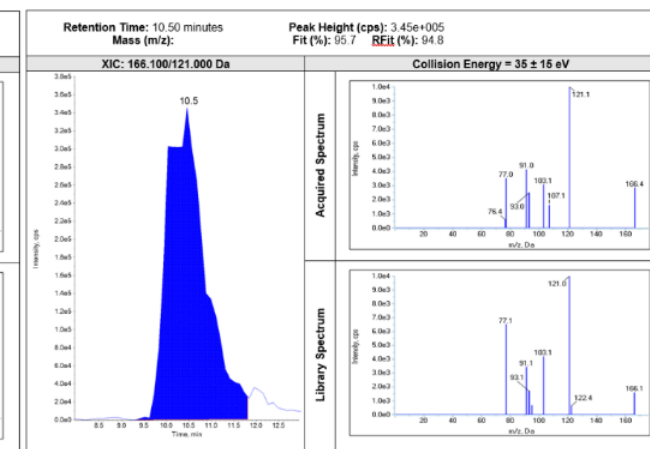
	Compound Name	Peak Area (counts)	RevFit (%)
1	Nicotine	4.18e+005	79.4



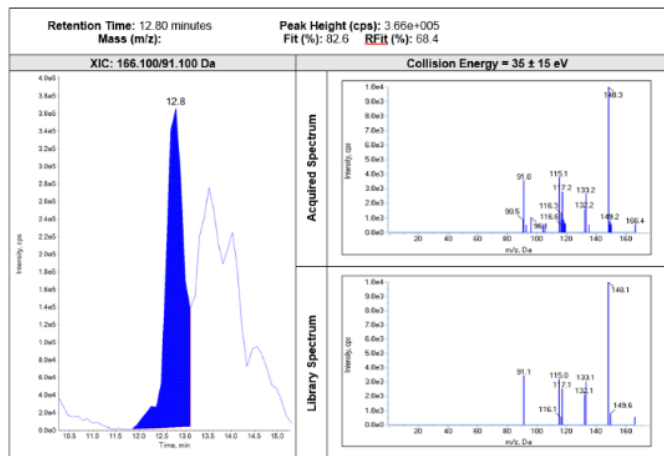
	Compound Name	Peak Area (counts)	RevFit (%)
1	Paracetamol	3.34e+005	94.5



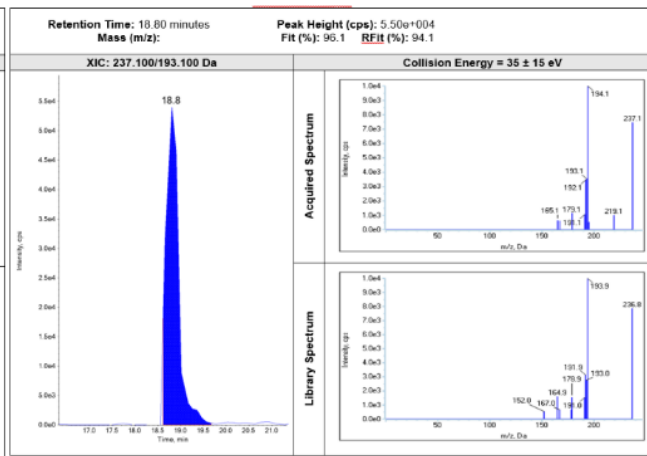
	Compound Name	Peak Area (counts)	RevFit (%)
1	Cyclicine	4.82e+006	66.9



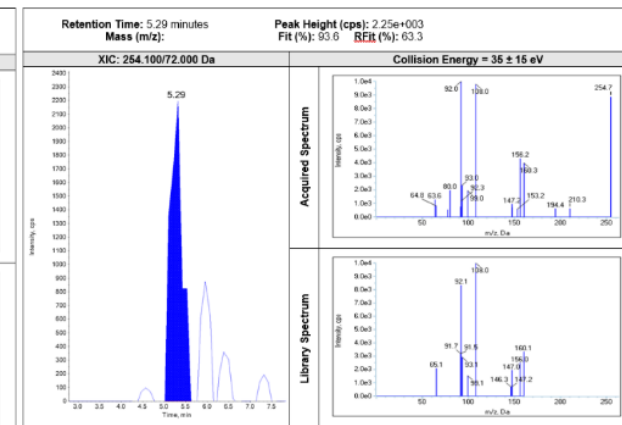
	Compound Name	Peak Area (counts)	RevFit (%)
1	Hordenine	2.09e+007	94.8



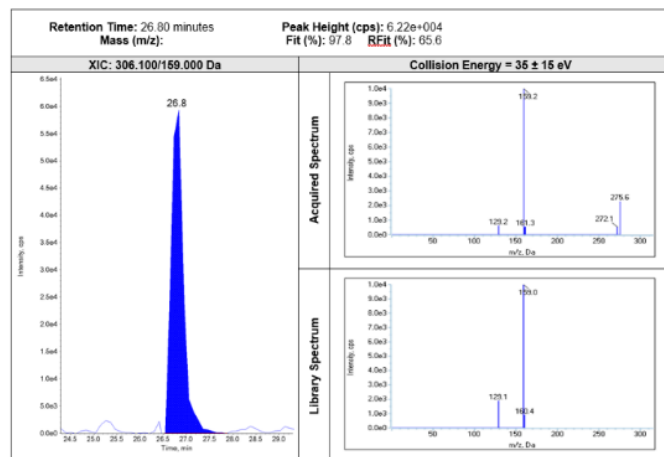
	Compound Name	Peak Area (counts)	RevFit (%)
1	Ephedrine	9.75e+006	68.4



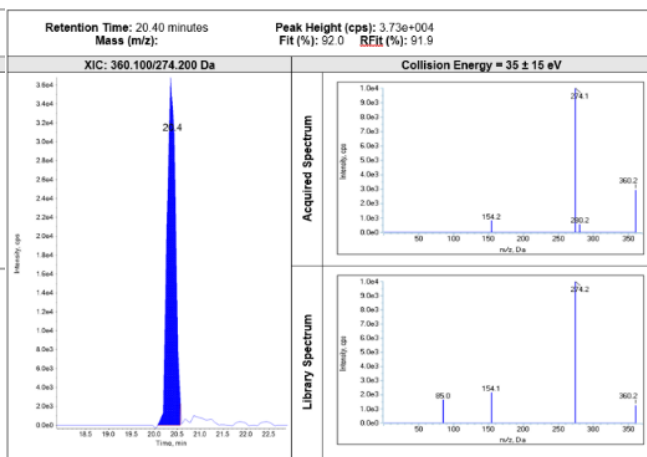
	Compound Name	Peak Area (counts)	RevFit (%)
1	Carbamazepine	9.75e+005	94.1



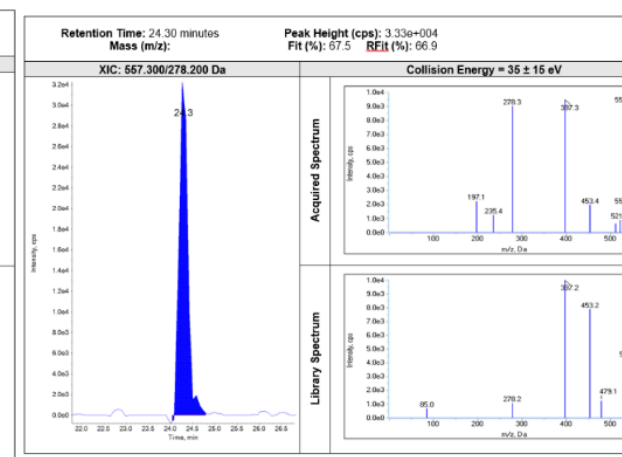
	Compound Name	Peak Area (counts)	RevFit (%)
1	Sulfamethoxazole	4.27e+004	63.3
2	Sulfamethoxazole	4.27e+004	63.6



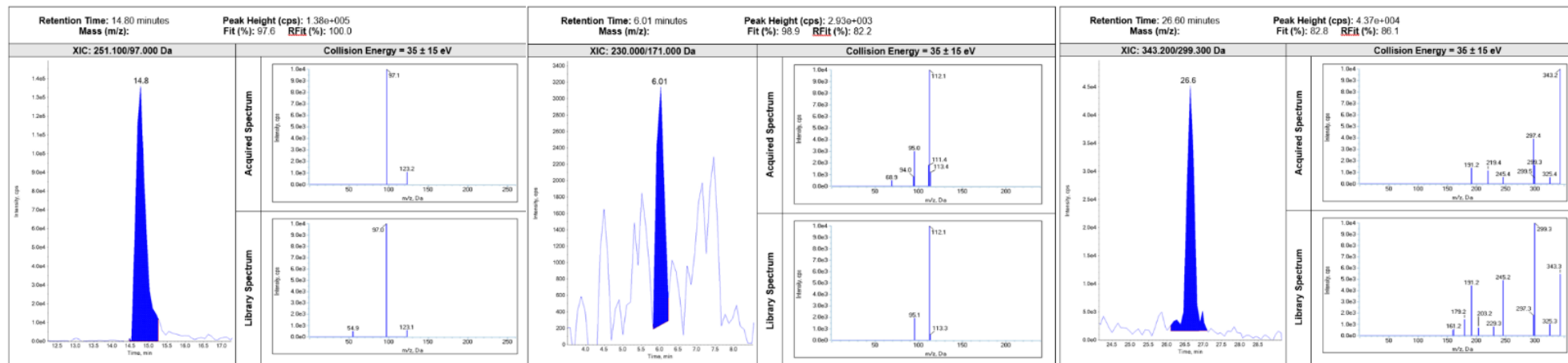
	Compound Name	Peak Area (counts)	RevFit (%)
1	Sertraline	1.10e+006	65.6



	Compound Name	Peak Area (counts)	RevFit (%)
1	Bozafibrate	4.71e+005	91.9



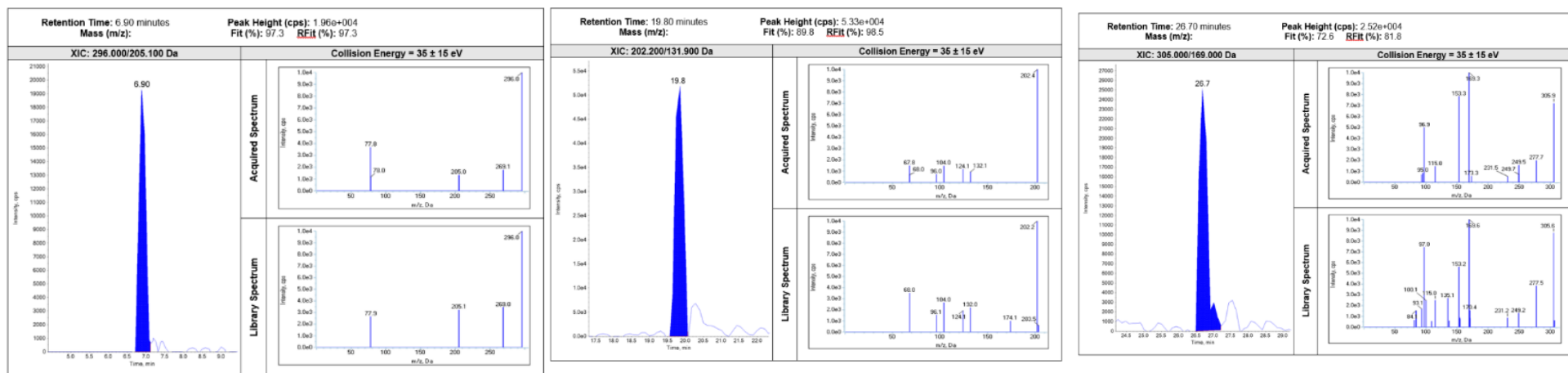
	Compound Name	Peak Area (counts)	RevFit (%)
1	Atorvastatin	4.46e+005	66.9



	Compound Name	Peak Area (counts)	RevFit (%)
1	Cimotidine	2.57e+006	100.0

	Compound Name	Peak Area (counts)	RevFit (%)
1	Lamivudine	4.25e+004	82.2

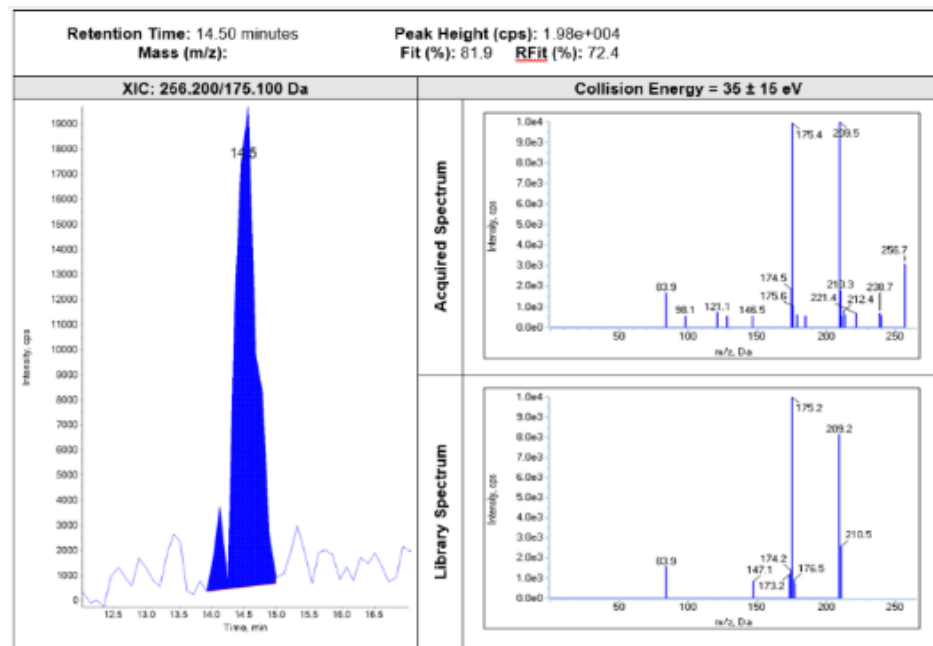
	Compound Name	Peak Area (counts)	RevFit (%)
1	THC-COOH	6.40e+005	86.1



	Compound Name	Peak Area (counts)	RevFit (%)
1	Hydrochlorothiazide	2.44e+005	97.3

	Compound Name	Peak Area (counts)	RevFit (%)
1	Simazine	8.51e+005	98.5

	Compound Name	Peak Area (counts)	RevFit (%)
1	Diazinon_2000	4.27e+005	81.8



	Compound Name	Peak Area (counts)	RFit (%)
1	Imidacloprid_2000	4.59e+005	72.4

Appendix C

TARGET ANALYTES MULTIPLE REACTION MONITORING TRANSITION VALUES

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

Appendix D

TOXICITY DATA

Compound	Taxon	Acute toxicity			Chronic toxicity		
		Specie	EC ₅₀ /LC ₅₀	References	Specie	NOEC	References
Ibuprofen	Algae	<i>Desmodesmus subspicatus</i>	315 mg/l	Cleuvers, 2004	<i>Pseudokirchneriella subcapitata</i>	0.01 mg/l	Brun et al. 2006
	Invertebrate	<i>Daphnia magna</i>	0.032 mg/l	Brun et al. 2006	<i>Daphnia magna</i>	1.23 mg/l	Ericson et al. 2010
	Fish	<i>Oryzias latipes</i>	100 mg/l	Kim et al. 2009a	<i>Danio rerio</i>	0.001 mg/l	David and Pancharatna, 2009
Acetaminophen	Algae	<i>S. Subcapitata</i>	134 mg/l	Kosma et al. 2014	<i>Chlorella vulgaris</i>	46 mg/l	ECOTOX, 2018
	Invertebrate	<i>Daphnia magna</i>	9.2 mg/l	Kosma et al. 2014	<i>Daphnia magna</i>	5.72 mg/l	ECOTOX, 2018
	Fish	<i>B. Rerio</i>	378 mg/l	Kosma et al. 2014	<i>Oryzias latipes</i>	9.5 mg/l	ECOTOX, 2018
Carbamazepine	Algae	<i>C. maneghiniana</i>	31.6 mg/l	Ferrari et al. 2004	<i>P. subcapitata</i>	10 mg/l	Kosma et al. 2014
	Invertebrate	<i>Daphnia magna</i>	6.36 mg/l	Santos et al. 2007	<i>C. dubia</i>	0.025 mg/l	Kosma et al. 2014
	Fish	<i>Pimephales promelas</i>	35.4 mg/l	Kuzmanovic et al. 2015	<i>D. rerio</i>	25 mg/l	Kosma et al. 2014
Triclosan	Algae	<i>P. Subcapitata</i>	0.56 mg/l	ECOTOX, 2018	<i>P. subcapitata</i>	0.2 mg/l	Brausch and Rand, 2011
	Invertebrate	<i>Daphnia magna</i>	0.39 mg/l	ECOTOX, 2018	<i>Daphnia magna</i>	200 mg/l	Brausch and Rand, 2011
	Fish	<i>Lepomis microchirus</i>	0.26 mg/l	ECOTOX, 2018	<i>O. mykiss</i>	71.3 mg/l	Brausch and Rand, 2011

Compound	Taxon	Acute toxicity			Chronic toxicity		
		Specie	EC ₅₀ /LC ₅₀	References	Specie	NOEC	References
17-alpha-ethynyl-estradiol	Algae	<i>Fathead minnows</i>	0.0008 mg/l	Adjei et al. 2022	–	–	–
	Invertebrate	<i>Daphnia magna</i>	0.0012 mg/l	Adjei et al. 2022	–	–	–
	Fish	<i>T. pyriformis</i>	0.002 mg/L	Adjei et al. 2022	<i>Oryzias latipes</i>	0.03 mg/l	Liu et al. 2020a
Estradiol	Algae	<i>Fathead minnows</i>	0.0016 mg/l	Adjei et al. 2022	–	–	–
	Invertebrate	<i>Daphnia magna</i>	0.003 mg/l	Adjei et al. 2022	–	–	–
	Fish	<i>T. pyriformis</i>	0.003 mg/l	Adjei et al. 2022	<i>Oncorhynchus mykiss</i>	0.42 mg/l	Liu et al. 2020a
Progesterone	Algae	<i>Fathead minnows</i>	0.001 mg/l	Adjei et al. 2022	–	–	–
	Invertebrate	<i>Fathead minnows</i>	0.007 mg/l	Adjei et al. 2022	–	–	–
	Fish	<i>T. pyriformis</i>	–	–	–	–	–
Testosterone	Algae	<i>Fathead minnows</i>	0.0014 mg/l	Adjei et al. 2022	–	–	–
	Invertebrate	<i>Fathead minnows</i>	0.006 mg/l	Adjei et al. 2022	–	–	–
	Fish	<i>T. pyriformis</i>	–	–	<i>Oncorhynchus kisutch</i>	30 mg/l (LOEC)	Liu et al. 2020a
Atrazine	Algae	<i>P. Subcapitata</i>	0.059 mg/l	ECOTOX, 2018; Kock-schulmeeyer et al. 2012	<i>P. Subcapitata</i>	0.1 mg/l	ECOTOX, 2018; Kock-schulmeeyer et al. 2012

Compound	Taxon	Acute toxicity			Chronic toxicity		
		Specie	EC ₅₀ /LC ₅₀	References	Specie	NOEC	References
Metolachlor	Invertebrate	<i>Daphnia magna</i>	6.9 mg/l	ECOTOX, 2018; Kock-schulmeeyer et al. 2012	<i>Daphnia magna</i>	0.1 mg/l	ECOTOX, 2018; Kock-schulmeeyer et al. 2012
	Fish	<i>Oncorhynchus mykiss</i>	4.5 mg/l	ECOTOX, 2018; Kock-schulmeeyer et al. 2012	<i>Oncorhynchus mykiss</i>	2 mg/l	ECOTOX, 2018; Kock-schulmeeyer et al. 2012
	Algae	<i>P. Subcapitata</i>	57.1 mg/l	ECOTOX, 2018; Kock-schulmeeyer et al. 2012	<i>P. Subcapitata</i>	3.0 mg/l	ECOTOX, 2018; Kock-schulmeeyer et al. 2012
	Invertebrate	<i>Daphnia magna</i>	23.5 mg/l	ECOTOX, 2018; Kock-schulmeeyer et al. 2012	<i>Daphnia magna</i>	3.0 mg/l	ECOTOX, 2018; Kock-schulmeeyer et al. 2012
	Fish	<i>Oncorhynchus mykiss</i>	3.9 mg/l	ECOTOX, 2018; Kock-schulmeeyer et al. 2012	<i>Oncorhynchus mykiss</i>	1.0 mg/l	ECOTOX, 2018; Kock-schulmeeyer et al. 2012
Simazine	Algae	<i>P. Subcapitata</i>	0.04 mg/l	ECOTOX, 2018; Kock-schulmeeyer et al. 2012	<i>P. Subcapitata</i>	0.6 mg/l	ECOTOX, 2018; Kock-schulmeeyer et al. 2012
	Invertebrate	<i>Daphnia magna</i>	1.1 mg/l	ECOTOX, 2018; Kock-schulmeeyer et al. 2012	<i>Daphnia magna</i>	0.6 mg/l	ECOTOX, 2018; Kock-schulmeeyer et al. 2012
	Fish	<i>Oncorhynchus mykiss</i>	9.0 mg/l	ECOTOX, 2018; Kock-schulmeeyer et al. 2012	<i>Oncorhynchus mykiss</i>	0.7 mg/l	ECOTOX, 2018; Kock-schulmeeyer et al. 2012
Terbuthylazine	Algae	<i>P. Subcapitata</i>	0.02 mg/l	NRA, 2001	<i>P. Subcapitata</i>	–	–

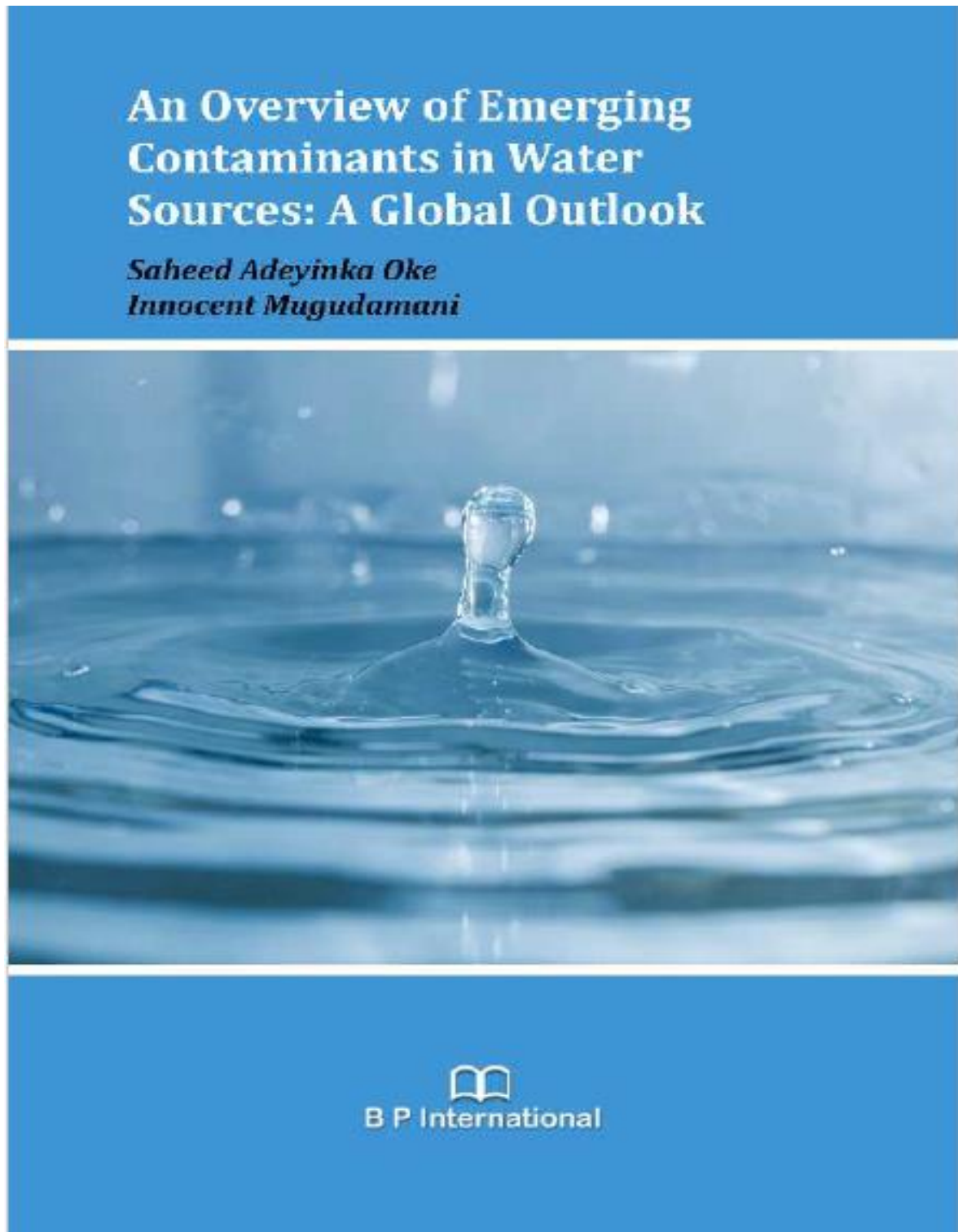
Compound	Taxon	Acute toxicity			Chronic toxicity		
		Specie	EC ₅₀ /LC ₅₀	References	Specie	NOEC	References
	Invertebrate	<i>Daphnia magma</i>	39.4 mg/l	NRA, 2001	<i>Daphnia magma</i>	0.21 mg/l	NRA, 2001
	Fish	<i>Oncorhynchus mykiss</i>	3.6 mg/l	NRA, 2001	<i>Mysid shrimp</i>	0.13 mg/l	NRA, 2001

Notation: LOEC=Lowest observed effect concentration

Appendix E

LIST OF PUBLICATIONS

Books



An Overview of Emerging Contaminants in Water Sources: A Global Outlook

Saheed Adeyinka Oke ^{a*} and Innocent Mugudamani ^b

DOI: 10.9734/bp/mono/978-81-19761-78-4

ABSTRACT

Advance in methods of detection for some organic chemicals in water sources has steered the screening and quantification of high quantity of contaminants collectively with their end products, which formerly were not identified in water sources and are currently recognized as emerging contaminants. The accumulation and discovery of levels of these emerging contaminants in water sources has reduced water quality and made it risky for aquatic and human life. Exposure to these organic contaminants may trigger serious health effects. The aim of this book is to give a comprehensive review of global occurrence of emerging contaminants in various water sources such as surface water, groundwater, treated drinking water and wastewater influent and effluent. The book introduces audience to concepts of water sources, emerging contaminants, point sources and non-point sources of emerging contaminants. It offers a glimpse of international and South African case studies on the occurrence of emerging contaminants precisely herbicides, pharmaceutical, steroid hormones and personal care products in water sources as well as in wastewater treatment works. The analytical and removal methods of emerging contaminants in water sources are also covered. Moreover, information on possible environmental health impacts ensuing from exposure to emerging contaminants and their possible mitigation measures (such as classification and labelling methods; point source separation methods; regulating the release of emerging contaminants) are discussed. The occurrence of emerging contaminants around the world (Africa, America, Asia, Europe, and Oceania) is likely to upsurge in water sources and wastewater treatment works as a results of rise in population which is a public health concern. Therefore, more studies that report on the widespread of emerging contaminants in water sources, and their associated environmental health risks are needed to help regulators in establishing priority measures for management of water resources.

^a Civil Engineering Department, Central University of Technology, Bloemfontein, Free State, South Africa.

^b Department of Life Sciences, Central University of Technology, Bloemfontein, Free State, South Africa.

*Corresponding author: E-mail: okesaheed@gmail.com

Book Chapters

Chapter 3

Monitoring of Emerging Contaminants in Selected Wastewater Treatment Works Around Bloemfontein, South Africa: Initiative for Environmental Protection



Innocent Mugudamani , Saheed A. Oke , Thandi P. Gumede ,
and Samson Senbore 

Abstract The study monitored the occurrence of emerging contaminants such as acetaminophen, carbamazepine, ibuprofen, triclosan, atrazine, metolachlor, simazine, terbutylazine, 17-alpha-ethinyl-estradiol, progesterone, testosterone and estradiol in selected wastewater treatment works (influent and effluent) around Bloemfontein during autumn season. Samples collected from influent ($n = 3$) and effluent ($n = 3$) were analysed by high performance liquid chromatography. To assess the performance of wastewater treatment works in removing the targeted compounds the removal efficiency (%) method was used. The average concentration of acetaminophen, carbamazepine, ibuprofen, triclosan, atrazine, metolachlor, simazine, terbutylazine, 17-alpha-ethinyl-estradiol, progesterone, testosterone and estradiol in influent samples were 28.15 $\mu\text{g/ml}$, 0.35 $\mu\text{g/ml}$, 7.95 $\mu\text{g/ml}$, 0.62 $\mu\text{g/ml}$, 0.04 $\mu\text{g/ml}$, 0.03 $\mu\text{g/ml}$, 0.15 $\mu\text{g/ml}$, 0.04 $\mu\text{g/ml}$, 37.53 $\mu\text{g/ml}$, <LOQ, 0.04 $\mu\text{g/ml}$, and 0.03 $\mu\text{g/ml}$ while in effluent were as <LOQ, 0.63 $\mu\text{g/ml}$, 2.07 $\mu\text{g/ml}$, <LOQ, 0.05 $\mu\text{g/ml}$, 0.06 $\mu\text{g/ml}$, 0.24 $\mu\text{g/ml}$, 0.02 $\mu\text{g/ml}$, 41.4 $\mu\text{g/ml}$, <LOQ, and <LOQ respectively. In influent samples, 17-alpha-ethinyl-estradiol, acetaminophen, and simazine were the leading contaminants while in effluent it was 17-alpha-ethinyl-estradiol, ibuprofen, and simazine who recorded the highest mean concentrations. There was negative removal rates of compounds such as carbamazepine, atrazine, metolachlor, simazine and 17-alpha-ethinyl-estradiol. Considering the insufficient removal rates

I. Mugudamani (✉) · T. P. Gumede
Department of Life Sciences, Central University of Technology, Bloemfontein, Free State, South Africa
e-mail: imugudamani@gmail.com

T. P. Gumede
e-mail: TGumende@cut.ac.za

S. A. Oke · S. Senbore
Department of Civil Engineering, Centre for Sustainable Smart Cities, Central University of Technology, Bloemfontein, Free State, South Africa
e-mail: soke@cut.ac.za

© The Author(s), under exclusive license to Springer Nature Switzerland AG 2024
H. Xu (ed.), *The 6th International Symposium on Water Resource and Environmental Management*, Environmental Science and Engineering,
https://doi.org/10.1007/978-3-031-55989-1_3

25

Article

Herbicides in Water Sources: Communicating Potential Risks to the Population of Mangaung Metropolitan Municipality, South Africa

Innocent Mugudamani ^{1,*}, Saheed A. Oke ², Thandi Patricia Gumede ¹ and Samson Senbore ²

¹ Department of Life Sciences, Central University of Technology, Free State, Bloemfontein 9301, South Africa; tgumede@cut.ac.za

² Department of Civil Engineering, Centre for Sustainable Smart Cities, Central University of Technology, Free State, Bloemfontein 9301, South Africa; sokes@cut.ac.za or oke-saheed@gmail.com (S.A.O.); senboresamson@gmail.com (S.S.)

* Correspondence: imugudamani@gmail.com or innomugudamani@outlook.com

Abstract: Pesticides are an important tool for maintaining and improving the global population's standard of living. However, their presence in water resources is concerning due to their potential consequences. Twelve water samples from rivers, dams/reservoirs, and treated drinking water were collected from Mangaung Metropolitan Municipality in South Africa. The collected samples were analysed using high-performance liquid chromatography linked to a QTRAP hybrid triple quadrupole ion trap mass spectrometer. The ecological and human health risks were assessed by risk quotient and human health risk assessment methods, respectively. Herbicides, such as atrazine, metolachlor, simazine and terbuthylazine, were analysed in water sources. The average concentrations of simazine in rivers (1.82 mg/L), dams/reservoirs (0.12 mg/L), and treated drinking water (0.03 mg/L) were remarkable among all four herbicides detected. Simazine, atrazine, and terbuthylazine posed high ecological risks for both acute and chronic toxicity in all water sources. Moreover, simazine is the only contaminant in the river water that poses a medium carcinogenic risk to adult. It can be concluded that the level of herbicide detected in water sources may affect aquatic life and human beings negatively. This study may aid in the development of pesticide pollution management and risk reduction strategies within the municipality.

Keywords: pesticide and herbicide; potential risks; water sources; ecological and health risks; Mangaung; residue



Citation: Mugudamani, I.; Oke, S.A.; Gumede, T.P.; Senbore, S. Herbicides in Water Sources: Communicating Potential Risks to the Population of Mangaung Metropolitan Municipality, South Africa. *Toxics* **2023**, *11*, 538. <https://doi.org/10.3390/toxics11060538>

Academic Editor: Ilaria Guagliardi

Received: 6 May 2023

Revised: 6 June 2023

Accepted: 13 June 2023

Published: 16 June 2023

1. Introduction

Water resources play an important role in our daily lives as a source of water [1]. They are, however, increasingly exposed to an extensive kind of organic chemical of an anthropogenic source, such as pesticides [2]. Pesticides are chemicals or mixtures of chemicals that are primarily utilised for the protection of agricultural yields from weeds, insects, and pests, and humans from diseases [3,4]. Pesticides' beneficial effects make them an important tool for maintaining and improving the global populations' living standards.

Environmental Risk Assessment of Exposure to Selected Emerging Contaminants in Dams and Wastewater Effluent Around the City of Bloemfontein, South Africa

Saheed Adeyinka Oke ¹, Innocent Mugudamani ², Thandi Patricia Gumede ³, Samson Senbore ⁴

^{1,4} Department of Civil Engineering, Centre for Sustainable Smart Cities, Central University of Technology, Free State, South Africa.

^{2,3} Department of Life Sciences, Central University of Technology, Free State, South Africa.

Abstract

The number of emerging contaminants in the aquatic environment is growing continuously every year. Their occurrence in water sources could be a troubling problem to aquatic ecosystem and human health. The aim of this study was to assess the environmental risks of selected emerging contaminants in dams/reservoirs and wastewater effluent samples around the city of Bloemfontein, South Africa. The high-performance liquid chromatography connected to a QTRAP hybrid triple quadrupole ion trap mass spectrometer was used to analyse emerging contaminants such as acetaminophen, carbamazepine, ibuprofen, triclosan, 17- α -ethynyl-estradiol, estradiol, progesterone and testosterone in dams/reservoirs and wastewater effluents. The single and mixture substance ecological risks were evaluated using the risk quotient (RQ) and risk mixture (RQmix) methods respectively. For acute toxicity in dams, results showed that emerging contaminants such as carbamazepine, and 17- α -ethynyl-estradiol posed high ecological risks on all aquatic organisms. In effluent, carbamazepine, ibuprofen, triclosan, 17- α -ethynyl-estradiol, estradiol, and progesterone posed high risks to all selected species. For chronic toxicity, ibuprofen posed high ecological risks on algae, daphnids, and fish in dams and effluents. The RQmix values in all water sources exceeded the acceptable limit for both acute and chronic toxicity on algae, daphnids, and fish. Their acute mixture risks on aquatic species were as algae>daphnids>fish in targeted water sources while chronic mixture risks were as fish>algae>daphnids in the targeted water sources. Therefore, the level of emerging contaminants in dams/reservoirs and wastewater effluent in this study is likely to negatively pose serious adverse implications on aquatic life and human beings. The outcomes of this study constitute the initial contribution for a better understanding of emerging contaminants risks on aquatic ecosystems and human health and may help in pollution control, protection of aquatic ecosystem and water consumers.

Keywords: emerging contaminants, environmental risk assessment, individual risk assessment, mixture risk assessment, water sources.

1. Introduction

As a result of population growth and widespread use of medications for human and veterinary purposes, there are more emerging contaminants in the water environment every year [1]. Emerging contaminants can enter water sources in a number of ways, including surface runoff from agriculture and animal husbandry, hospital and industrial effluents, and wastewater effluents. Among these, the wastewater effluents are a key pathway for emerging contaminants to enter the water environment [2]. These emerging contaminants (steroid hormones, pesticides, antibiotics, pharmaceuticals and personal care products) find their way to the water bodies

either alone or in mixtures posing a world-wide risk to the aquatic organisms and deleteriously to human health [1]. The occurrence of emerging contaminants in water sources such as surface water, groundwater and wastewater effluents has been notably explored in many parts of the world [2, 3, 4] including South Africa [5, 6, 7]. However, the individual and mixture risks evaluation of these chemical compounds in water sources is hardly ever reported particularly in South Africa. In the light of the above, there is an urgent need to continuously monitor these compounds in water sources and assess their potential environmental risks to aquatic ecosystems. This will guarantee a good water quality in the country

1077

Current Analytical Chemistry

VOLUME 20, , NUMBER , 2024

Impact Factor: Current: 1.8

5 - Year: 1.7

ISSN: 1875-6727 (Online) - ISSN: 1573-4110 (Print)



Risk Assessment Of Emerging Contaminants In Urban And Natural Water Sources Around Bloemfontein, South Africa: Implication For Environmental Sustainability.

Authors:

Innocent Mugudamani, Saheed Adeyinka Oke, Thandl Patricia Gumede and Samson Senbore

Affiliation:

Department of Life Sciences, Central University of Technology, Free State, South Africa

Abstract:

Introduction: Emerging contaminants are present in the water and need to be monitored and managed as they are of major environmental and health concern universally. Exposure to emerging contaminants in water sources can pose a significant risk to both aquatic species and human health. This study assessed the risks of emerging contaminants in urban and natural water sources.

Methods: A high-performance liquid chromatography connected to a hybrid triple quadrupole ion trap mass spectrometer was used to analyse the targeted emerging contaminants. The ecological and human health risk assessment methods were used to assess the possible risks of contaminants.

Results: Emerging contaminants such as 17-ethinyl-estradiol, simazine, ibuprofen, atrazine, carbamazepine, terbutylazine, and metolachlor showed the possibility of high ecological risks to aquatic species. Risk mixture values in all water sources showed that the aquatic species are at high risk in all seasons. The non-carcinogenic risk of all selected herbicides in all water sources showed risk quotient values below 1 for the entire population, signifying that the population is safe. Atrazine is the only contaminant that showed high carcinogenic risk to the adult group in river water during the summer season.

Conclusion: It can be concluded that aquatic species and public health are at risk. The outcomes of the study may aid in the development of environmental quality standards for regulatory and environmental sustainability purposes.



To access the Full-text article at 10% discount,
please visit: <https://www.eurekaselect.com/230644/article>

Quote the Discount Code: **BSPHAF2023**

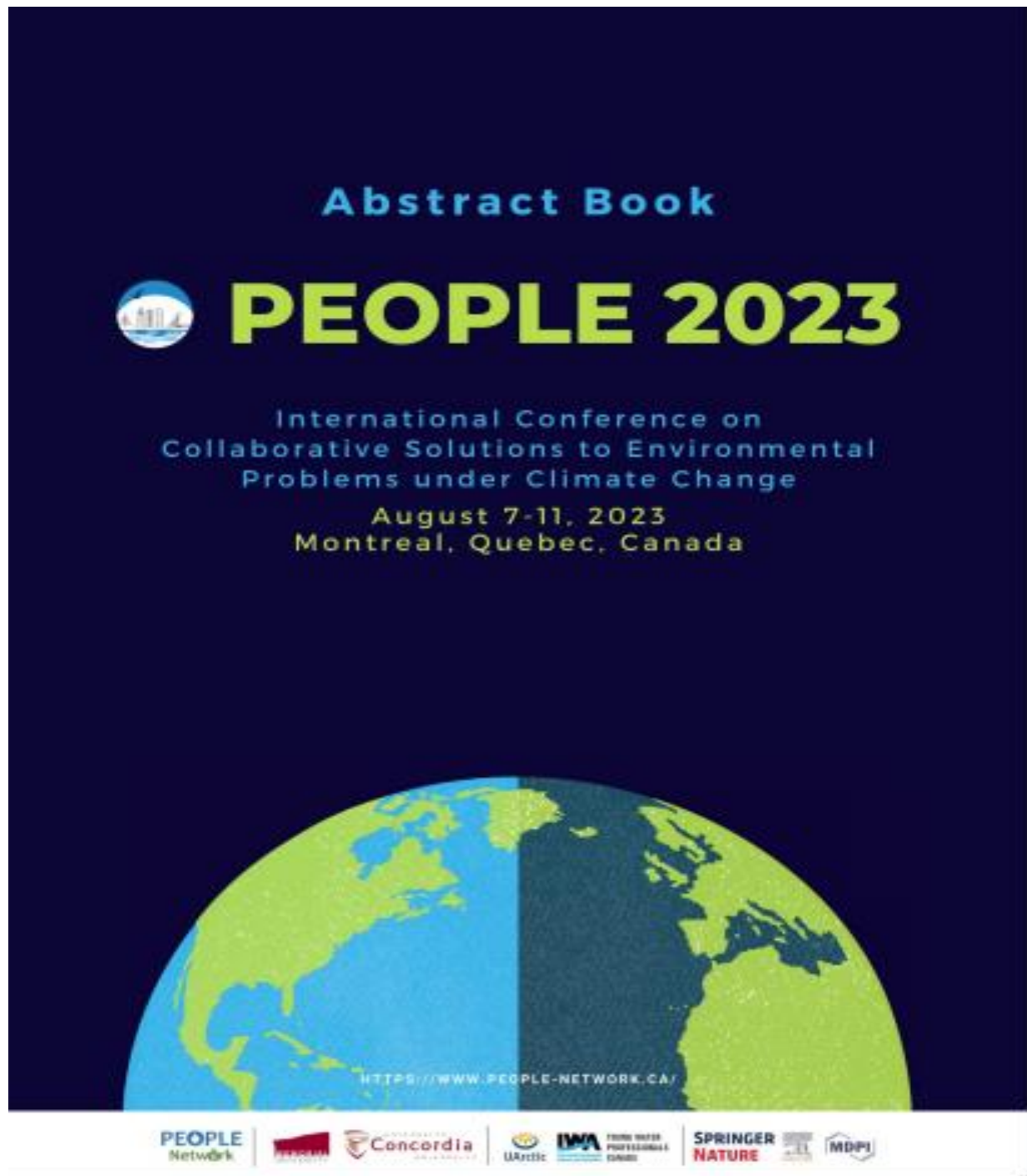
For Subscription

Contact: subscriptions@benthamscience.net

For Advertising & Free Online Trial

Contact: marketing@benthamscience.net
www.benthamscience.com

Conference Presentation (Oral)



The Investigation and Monitoring of Emerging Contaminants from Point Sources on the Modder River Catchment System in Free State, South Africa (Session 25 #4)

Sahced Oke¹, Thandi Gamede¹, Innocent Mugudumani¹, Samson Senboee¹

¹Central University of Technology, Bloemfontein, South Africa

The presence of pharmaceuticals, herbicides, endocrine-disrupting compounds, and personal care products has recently attracted the interest of researchers due to their concern with regard to a wide variety of emerging contaminants in the environment as a result of inadequate wastewater treatment processes. Apart from the provision of water in particular clean water to the South African public, most treatment facilities are faced with increased pressure to provide improved sanitation services, which contributes to environmental and human health impacts. The aim of the study is to detect the concentration levels of emerging contaminants (pharmaceuticals, herbicides, Personal care products, and Endocrine-Disrupting compounds) that might be of health risk at wastewater treatment works, water treatment plants, and surface water and drinking water. It also aims to determine the major sources and pathways of emerging contaminants within the Modder River catchment system. Samples were extracted with Solid Phase Extraction processes which vary on the type of the chemical compound. High-performance liquid chromatography was used as a method of quantification. The research provides information on the concentration and sources of emerging contaminants in water sources. The research is looking at investigating the appropriate remediation measures based on the identified sources. This will aid in the development of pollution management and toxic compound risk reduction strategies within the region.

Keywords

emerging contaminants, Modder River catchment, pharmaceuticals, pesticides, personal care products, endocrine-disrupting compounds



**International Conference on
Global Warming, Climate Change and
Pollution Control
(GWCCPC-23)**

**Montreal, Canada
14th - 15th December 2023|**

Association for Scientific and Academic Research

www.asar.net.in

International Conference on

Global Warming, Climate Change and Pollution Control

Environmental risk assessment of exposure to selected emerging contaminants in dams and wastewater effluent around the city of Bloemfontein, South Africa

^[1] Innocent Mugudamani, ^[2] Saheed, Adeyinka Oke *, ^[3] Thandi Patricia Gumedede,
^[4] Samson Senbore

^{[1][3]} Department of Life Sciences, Central University of Technology, Free State, South Africa.

^{[2][4]} Department of Civil Engineering, Centre for Sustainable Smart Cities, Central University of Technology, Free State, South Africa.

Abstract

The number of emerging contaminants in the aquatic environment is growing continuously every year. Their occurrence in water sources could be a troubling problem to aquatic ecosystem and human health. The aim of this study was to assess the environmental risks of selected emerging contaminants in dams/reservoirs and wastewater effluent samples around the city of Bloemfontein, South Africa. The high-performance liquid chromatography connected to a QTRAP hybrid triple quadrupole ion trap mass spectrometer was used to analyse emerging contaminants such as acetaminophen, carbamazepine, ibuprofen, triclosan, 17-alpha-ethynyl-estradiol, estradiol, progesterone and testosterone in dams/reservoirs and wastewater effluents. The single and mixture substance ecological risks were evaluated using the risk quotient (RQ) and risk mixture (RQmix) methods respectively. For acute toxicity in dams, results showed that emerging contaminants such as carbamazepine, and 17-alpha-ethynyl-estradiol posed high ecological risks on all aquatic organisms. In effluent, carbamazepine, ibuprofen, triclosan, 17-alpha-ethynyl-estradiol, estradiol, and progesterone posed high risks to all selected species. For chronic toxicity, ibuprofen posed high ecological risks on algae, daphnids, and fish in dams and effluents. The RQmix values in all water sources exceeded the acceptable limit for both acute and chronic toxicity on algae, daphnids, and fish. Their acute mixture risks on aquatic species were as algae>daphnids>fish in targeted water sources while chronic mixture risks were as fish>algae>daphnids in the targeted water sources. Therefore, the level of emerging contaminants in dams/reservoirs and wastewater effluent in this study is likely to negatively pose serious adverse implications on aquatic life and human beings. The outcomes of this study constitute the initial contribution for a better understanding of emerging contaminants risks on aquatic ecosystems and human health and may help in pollution control, protection of aquatic ecosystem and water consumers.

Index Terms

Emerging contaminants, environmental risk assessment, individual risk assessment, mixture risk assessment, water sources

Appendix F

LABORATORY ANALYSES

Rivers

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

Notation: <LOQ is represented by a dash (–).

Dams

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

Notation: <LOQ is represented by a dash (-).

Treated Drinking Water

Sample ID	Acetaminophen	Simazine	Atrazine	Terbutylazine	Carbamazepine	Metolachlor	Testosterone	Progesterone	Ibuprofen	Estradiol	Triclosan	17 alpha ethyn	Comment
Spring													
TWWRUS01	–	–	0.019	0.020	0.010	0.009	–	–	–	–	–	0.145	Rustfontein
TWWMSP02	0.102	0.027	0.015	0.019	0.253	0.010	–	–	0.014	–	–	2.780	Maselspoort
Summer													
TWWRUS01	–	–	0.0175	0.0155	–	0.00652	–	–	–	–	–	0.144	Rustfontein
TWWMSP02	–	0.039	0.119	0.161	–	0.0939	–	–	–	–	–	0.259	Maselspoort
Autumn													
TWWRUS01	–	–	0.0083	0.0039	–	0.0038	–	–	–	–	–	0.4220	Rustfontein
TWWMSP02	–	–	0.0297	0.0172	–	0.0390	–	–	–	–	–	1.0400	Maselspoort
Winter													
TWWRUS01	0.28	–	0.0092	0.00597	–	0.00232	–	–	–	–	–	0.155	Rustfontein
TWWMSP02	–	–	0.0283	0.0102	–	0.023	–	–	–	–	–	0.727	Maselspoort

Notation: <LOQ is represented by a dash (–).

Wastewater Influent

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

Notation: <LOQ is represented by a dash (–).

Wastewater Effluent

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

Notation: <LOQ is represented by a dash (–).

Appendix G

APPROVED AND LINGUISTICALLY REVISED TITLE

04 August 2022

DECLARATION

I hereby declare that I am a qualified and professional language practitioner with the following qualification from the Central University of Technology, Free State:

- MTech Language Practice (2013)

In this capacity, I have linguistically revised (in English) the following title:

FORMER TITLE: Environmental health risk assessment of potential emerging contaminants identified from water sources around Bloemfontein in Free State Province of South Africa

NEW TITLE: Environmental health risk assessment of potential emerging contaminants identified from water sources around Bloemfontein in the Free State province of South Africa

DEGREE: PhD in Environmental Health

STUDENT: I Mugudamani (student number: 221002562)

INSTITUTION: Central University of Technology, Free State
Faculty of Health and Environmental Sciences

Signed:



.....
TANIA OOSTHUIZEN
SENIOR LANGUAGE PRACTITIONER
CENTRAL UNIVERSITY OF TECHNOLOGY, FREE STATE

Contact details:

Tel.: (051) 507 3607

E-mail: tvvuuren@cut.ac.za

Appendix H

TECHNICAL EDITING CONFIRMATION LETTER



PO Box 38917
Langenhovenpark, Bloemfontein 9330
technicalediting.dora@gmail.com

082 635 0214

CONFIRMATION OF TECHNICAL FORMATTING AND LANGUAGE EDITING

I hereby confirm that I have done the technical formatting and language editing for the following doctoral thesis:

Student: Innocent Mugudamani
Student number: 221002562
Title: Environmental Health Risk Assessment of Potential Emerging Contaminants Identified from Water Sources around Bloemfontein in the Free State Province of South Africa
Degree: Doctor of Philosophy: Environmental Health
Faculty: Department of Life Sciences, Faculty of Health and Environmental Sciences
University: Central University of Technology, Free State

Technical formatting included the layout done on an MS Word template that I created specifically for this thesis. Technical editing focused on the correct use of citations, style and formatting. I also checked that all references mentioned in the reference list are cited in the text. I also made sure that dates and author names used in the text matched those in the list of references, and notified the student on missing references that still needed to be added.

Language editing focused on punctuation, spelling, vocabulary, sentence structure and grammar. I tried to retain the student's own writing style, while making sure that the student's intended meaning was not altered during the editing process. All amendments were marked with the Microsoft Word Track Changes feature. I also left comments for issues that the student needed to check or revise. The student, therefore, had the option to accept or reject the suggestions and recommended changes to the document.

I have more than 40 years of experience in typing, formatting of documents and language editing for postgraduate students from universities all over South Africa and also abroad. I gained my experience during the years I was typing student dissertations and theses and while working at different departments at the University of the Free State from 1978 to 1981 and again from 1998 to 2014. I also assisted in compiling a document on technical layout and referencing methods and have presented a couple of guest lectures on referencing methods and technical layout issues to postgraduate students at the University of the Free State. In the past couple of years, I have also done language editing for a number of journal articles as well as seven books for publication.

Disclaimer: The ultimate responsibility for accepting or rejecting the amendments and recommendations made by means of track changes rests with the student. The editor cannot be held responsible for any later changes to the document in terms of format and style and subsequent amendments or additions to the text.

Yours sincerely



Dorathea (Dora) du Plessis
Technical & Language Editor

3 July 2024