EMERGING CONTAMINANTS IN WASTEWATER TREATED FOR DIRECT POTABLE REUSE: THE HUMAN HEALTH RISK PRIORITIES IN SOUTH AFRICA

CD Swartz, B Genthe, J Chamier, LF Petrik, JO Tijani, A Adeleye, CJ Coomans, A Ohlin, D Falk and JG Menge

VOLUME III: OCCURRENCE, FATE, REMOVAL AND HEALTH RISK ASSESSMENT OF CHEMICALS OF EMERGING CONCERN IN RECLAIMED WATER FOR POTABLE REUSE

WATER RESEARCH COMMISSION

TT 742/3/18

EMERGING CONTAMINANTS IN WASTEWATER TREATED FOR DIRECT POTABLE RE-USE: THE HUMAN HEALTH RISK PRIORITIES IN SOUTH AFRICA

VOLUME III:

OCCURRENCE, FATE, REMOVAL AND HEALTH RISK ASSESSMENT OF CHEMICALS OF EMERGING CONCERN IN RECLAIMED WATER FOR POTABLE REUSE

Report to the

Water Research Commission

by

CD Swartz[1], B Genthe[2], J Chamier[2], LF Petrik[3], JO Tijani[3], A Adeleye[3], CJ Coomans[1], A Ohlin[4], D Falk[4] and JG Menge[5]

[1] Chris Swartz Water Utilisation Engineers
[2] CSIR, Stellenbosch
[3] University of the Western Cape
[4] Chalmers University of Technology
[5] INREWASOL

WRC Report no. TT 742/3/17

March 2018

WATER RESEARCH COMMISSION

Obtainable from
Water Research Commission
Private Bag X03
Gezina 0031
South Africa

orders@wrc.org.za or download from www.wrc.org.za

The publication of this report emanates from a project entitled *Emerging contaminants in wastewater treated for direct potable re-use: The human health risk priorities in South Africa* (WRC Project No. K5/2369).

The outputs of this research project are presented in three separate publications:

Volume I: A concise research report **(WRC Report No TT 742/1/17)**
Volume II: A prioritization framework for monitoring contaminants of emerging concern in reclaimed water for potable use **(WRC Report No. TT 742/2/17)**
Volume III: Occurrence, fate, removal and health risk assessment of chemicals of emerging concern in wastewater treated for potable reuse **(This report)**

ISBN 978-1-4312-0956-9

Printed in the Republic of South Africa

EXECUTIVE SUMMARY

BACKGROUND

If not adequately treated, reclaimed water can act as a possible exposure pathway to a high number of emerging contaminants and their metabolites. Many of these compounds may pass through conventional wastewater treatment systems without removal and accumulate in potable water supplies. Thus, there is uncertainty over the magnitude of risk of human exposure to emerging contaminants of concern in wastewater treated for direct potable reuse. The possible presence of emerging contaminants in reclaimed municipal wastewater is of critical concern because of potential adverse impacts to human health. Specific health effects criteria in the evaluation of water recycling for human consumption include (1) primary health concerns of wastewater reuse that are the long-term health outcomes of ingesting chemical contaminants found in recycled water, (2) health risks of using recycled water as a potable water supply compared against similar risk by conventional water supplies, and (3) the need for extensive toxicity programs. This project was undertaken to identify the emerging contaminants of concern in reclaimed potable water, their sources, pathways and receptors, potential risk from exposure to these chemicals, indicative removal potential of these chemicals by water reclamation and wastewater treatment plants, and risks for potable water reuse.

AIMS

The aims of the project were as follows:

- Compile an up-to-date list of all types of emerging contaminants of concern in reclaimed potable water.
- Produce a report which identifies the sources, pathways and receptors by which these compounds enter drinking water systems, including resistance to wastewater treatment, their toxicity and the consequent potential risks from exposure to these chemicals.
- Draw up an assessment report on performance of water reclamation treatment systems and potential for failures in reliability and consequent risks for direct potable water reuse.
- Develop guidelines for implementation of appropriate treatment barriers, monitoring programmes and assessment programmes to eliminate or minimise risks.

This report (Volume III) details findings on the indicative removal potential, performance and reliance of treatment technologies typically employed at water treatment plants (both conventional water treatment and water reclamation plants) and lastly, an assessment of risks associated with human exposure to selected priority emerging contaminants in treated water.

METHOD

Although for such studies, the holistic system consisting of the wastewater collection system, wastewater treatment plant, water reclamation plant and distribution system must be considered as they form part of the multi-barrier approach towards minimizing health impacts, in this research project the collection and distribution systems were not included in the scope of study. Results from this study were obtained from three sampling campaigns, conducted during the periods; April 2015, October 2015 and January 2016. The samples were collected along various points along the treatment process and were analysed for the concentrations of selected emerging contaminants in order to evaluate removal. For assessing plant performance, historic plant data from an established water reclamation plant was analysed using various statistical analyses in order to determine the reliability of the various treatment technologies, as well as, performing a data validation analyses for performing an evaluation of the performance of the various treatment technologies. For risk assessment,

both bioassays and risk models, were used to assess the potential effects and risks associated with selected contaminants.

SUMMARY OF RESULTS

Evaluation of Indicative Removal Potential

From the results of the analyses performed on the samples collected during the three sampling campaigns, it was clear the certain CECs and PFCs are much more prevalent than others. It was also found that in most cases, all the compounds were reduced by the various treatment units. In some cases, it was found that constituent concentrations increased, but it is suspected that this is the result of plug flow characteristics caused by the time delay between treatment units that were not considered during the sampling campaigns. In all cases, however, the final water complied with all standards available for the various compounds.

Plant reliability analysis

Reliability analysis, as any data analyses, is sensitive to the quality and quantity of measurements available. Since the practical application of statistical analysis is only as good as the data on which it is based, it would be worthwhile to conduct a rigorous data collection programme, specifically for the purpose of deriving useful distribution models for reliability and performance analyses. Such a rigorous data collection programme would have the following properties:

- Consistent measurements
- Validated measurements
- Annotated measurements
- Representative measurements
- Large sample sizes

Health risk assessments

A battery of bio-assays was included in the study to illustrate their use in assessing water quality. These included the Ames mutagenicity test, the Daphnia acute toxicity test and the YES (yeast estrogen screen) test, to test for oestrogenic activity. The bio-assays showed the improvements in wastewater quality following treatment through the various treatment works, and the results showed how these bio-assays are able to be used to monitor the water quality. Findings from health risk assessment studies revealed the need to manage two risks. The first risk corresponds to the constant presence of 17α-ethinylestradiol (EE2) in the final effluent. Furthermore, the risk of children swimming in the brine channel and ingesting the contaminant EE2, has the risk priority number of 144 and is located in the unacceptable area of the risk matrix.

CONCLUSIONS AND RECOMMENDATIONS

- **Evaluation of Indicative Removal Potential** – since the project team was not able to collect 24h composite samples, it is difficult to evaluate the indicative removal potential of the treatment units since plug flow characteristics can be observed when taking grab samples. It is therefore recommended that sufficient resources be allocated in future studies that will allow for 24h composite sampling to be performed.
- **Process performance and plant reliability analysis** – overall, the current historical process data is not suited as is for deriving process monitoring models. However, there is scope, given rigorous data collection programmes, for univariate monitoring of key quality variables (slow sample rates), or multivariate monitoring of operational variables (fast sample rates). A future direction for statistical

analysis is to consider how process unit reliabilities affect other process unit reliabilities, and in turn, the reliability of the entire plant under consideration. For this, multivariate and conditional distribution fitting would be required, which would require rigorous data collection at a high data quality.

- **Human health risks** – bio-assays showed the improvements in wastewater quality following treatment through the various treatment works, and the results showed how these bio-assays are able to be used to monitor the water quality. Thus, it is recommended that a battery of bio-assays representing different trophic levels be included in a monitoring programme if direct reuse of wastewater is known to occur either intentionally or unintentionally. Different bio-assays can be selected as long as various activities are tested. For example, different oestrogen mimicking assays and anti-androgenic activity may be included.

  Findings from health risk assessment studies revealed the need to manage two risks. The first risk corresponds to the constant presence of 17α-ethinylestradiol (EE2) in the final effluent. Furthermore, the risk of children swimming in the brine channel and ingesting the contaminant EE2, has the risk priority number of 144 and is located in the unacceptable area of the risk matrix. As water reclamation processes were found not treat the water to a satisfying level with respect to EE2, countermeasures were recommended. Electrochemical removal could be a good option in a pilot project for the plant in the future, but more research needs to be completed for an appropriate design and implementation of this process. Ozonation and GAC are therefore the technologies chosen as countermeasures due to the reasons stated above. In addition, building a wall was suggested to constrain unauthorised people from reaching the brine channel. A fence has earlier been built and rebuilt several times around the area but has been stolen and is therefore not a good option to prevent the children from the community to enter. A wall was previously built around the drinking water treatment plant in the town and has been effective according to the superintendent.

ACKNOWLEDGEMENTS

The project team wishes to thank the following people for their contributions to the project.

Reference Group	Affiliation
Dr N Kalebaila	Water Research Commission (Research Manager)
Prof C de Jager	University of Pretoria
Ms L Coetzee	CSV Water
Prof OJ Okonkwo	Tshwane University of Technology
Ms I Thompson	Department of Water and Sanitation
Mr P Viljoen	Department of Water and Sanitation
Dr S Jooste	Department of Water and Sanitation
Dr D Odusanya	Department of Water and Sanitation
Mr G Grobler	Department of Water and Sanitation
Prof OS Fatoki	Cape Peninsula University of Technology
Dr WM Gitari	University of Venda
Mr G Metcalf	Umgeni Water
Mr P Thompson	Umgeni Water
Prof H Bouwman	North West University
Dr MV Sigudu	Rand Water
Prof MM Nindi	UNISA
Prof JC Ngila	University of Johannesburg

- Anna Ohlin, Debora Falk and Prof Thomas Pettersson from the Chalmers University of Technology in Gothenburg, Sweden for the risk assessment study.
- Dr B Barnard of the University of the Western Cape for assistance with field work and the sampling programs.
- Dr Werner Rössle and Christopher Wright, John Esterhuizen, Pierre Marais and Kevin Sampson for assistance with the sampling programs.
- Stellenbosch University for assistance with the analysis of samples taken during the sampling programs.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ACRONYMS AND ABBREVIATIONS

ADI	acceptable daily intake
AOP	advanced oxidation process
AOX	adsorbable organic halogens
ASP	activated sludge process
AWT	advanced water treatment
AWTP	advanced water treatment plant
BAC	biological activated carbon
BNR	biological nutrient removal
BW	body weight
CCP	critical control point
CEC	chemical of emerging concern
COD	chemical oxygen demand
CSIR	Council for Scientific and Industrial Research
DAF	dissolved air flotation
DEAT	Department of Environmental Affairs and Tourism
DOC	dissolved organic carbon
DoH	Department of Health
DPR	direct potable reuse
DWA	Department of Water Affairs
DWS	Department of Water and Sanitation
EC	electrical conductivity
ED	exposure duration
EDCs	endocrine disrupting compounds
EDSP	Endocrine Disruptor Screening Programme
EDSTAC	Endocrine Disruptor Screening and Testing Advisory Committee
EE2	17α-ethinylestradiol
EEQ	estradiol equivalents
EIA	environmental impact assessment
ELISA	Enzyme Linked Immuno-sorbent Assay
ETEM	events triggered enhanced monitoring
GAC	granular activated carbon
GC	Gas Chromatography
GC/MS	Gas Chromatography/Mass Spectrometry
GWRC	Global Water Research Coalition
GWRS	groundwater replenishing system
HPC	heterotrophic plate count

HPLC	High Pressure Liquid Chromatography
IPR	indirect potable reuse
IR	intake rate
IWA	International Water Association
IX	ion exchange
LC	Liquid Chromatography
Lft	Lifetime
LRV	log removal value
MCDA	multi-criteria decision analysis
MF	Microfiltration
MLE	Modified Ludzack-Ettinger
MS	Mass Spectrometry
NF	Nanofiltration
NLNAWQA	National Laboratory Network for Advanced Water Quality Analysis
NOEL	no-observed-effect-level
NPR	non-potable reuse
NTMP	National Toxicity Monitoring Programme (South Africa)
O_3	Ozone
PAC	powder activated carbon
PAH	Polycyclic Aromatic Hydrocarbons
PBT	persistence, bioaccumulation and toxicity
PCB	Polychlorinated Biphenyls
PFC	Perfluorinated compound
PFOS	Perfluorooctanesulfonic acid
PI	performance indicator
POP	persistent organic pollutants
PPCPs	pharmaceuticals and personal care products
QSAR	Quantitative Structural Analysis Relationship
REACH	regulation, evaluation, authorisation and restriction of chemicals
RO	reverse osmosis
SANS	South African National Standards
SCADA	supervisory control and data acquisition
TDI	tolerable daily intake
TDS	total dissolved solids
TECHNEAU	EU FP6 project
TEQ	Toxic Equivalency Factor
TOC	total organic carbon
TRI	toxic release inventory
TSS	total suspended solids

TTC	thresholds of toxicological concern
UF	Ultrafiltration
USEPA	United States Environmental Protection Agency
UV	ultraviolet irradiation
UV254	UV absorbance at 254 nm
WHO	World Health Organisation
WQG	water quality guidelines
WRC	Water Research Commission
WRP	water reclamation plant
WSP	water safety plan
WWTW	waste water treatment works

CHAPTER 1: BACKGROUND

1.1 INTRODUCTION

Several studies have been aimed at determining the removal of CECs during wastewater treatment and water reclamation. In a recent study performed in Namibia, three WWTPs and one WRP were included in order to determine the removal of certain CECs by the treatment technologies employed by these plants (Julies et al., 2013). During the study, samples were taken during March 2010, September 2010, November 2010, February 2011 and April 2011. This was done in order to ensure that the samples are representative and therefore included every season of the year. The study included steroid hormones such as estrone, Estradiol and testosterone; neurotoxicity via an acetylcholinesterase (AChE) inhibition assay; and cytotoxicity and immunotoxicity via lactate dehydrogenase (LDH), interleukin-6 (IL-6) and interleukin-10 (IL-10). The treatment plants that were included in the study made use of either activated sludge or trickling filters (or a combination of both) for treating the wastewater. The results for these plants should therefore not be compared to results obtained from samples taken at plants that employ MBR treatment processes.

Drewes et al. (2006) also performed a study on the removal capabilities of conventional water reclamation treatment trains with regard to EDCs. It was found that the main mechanism for the removal of EDCs were biodegradation. This result was also obtained in a study by Metcalf and Eddy (2006) where several EDCs, PHACs and PPCPs were monitored before undergoing various treatments in order to determine the removal efficiency of the treatment units with regard to different CECs. Summarised results from the study by Metcalf and Eddy (2006) are shown in Table 1-1.

From the results, it can be seen that the treatment processes typically employed by WWTPs (biodegradation and activated sludge) have a variable efficiency when it comes to removing CECs from wastewater. The results are therefore inconclusive, but still helpful to this study. They also tested the WWTP, which was the site for the pilot plant, and consists of a CAS treatment process with nutrient removal and secondary settling. From the study it was found that the WWTP was capable of removing the following components: Estradiol (93%), estriol (100%), 17 beta ethinyl Estradiol (90%), testosterone (95%) and progesterone (89%). The results for the more advanced processes indicated that the majority of the hormones were completely removed.

Snyder et al. (2005) conducted a study where the removal efficiency of an MBR, unused RO and fouled RO treatment process. The results from the study can be seen in Tables 1-2, 1-3 and 1-4.

In a study by Huber et al. (2003) the focus was placed on WWTP processes in order to determine the removal efficiency of certain CECs by ozonation at various ozone doses (varied from 0.5 to 5 mg/L) on water that was pre-treated using CAS, CAS with secondary settling and MBR treatment processes. The removal on the CAS only treated wastewater ranged as follows: iopromide (10-60%), roxithromycin (30-100%), sulfamethoxazole (20-100%) and 17 alpha ethinyl Estradiol (60-100%). The removal on the CAS and secondary settling treated wastewater ranged as follows: iopromide (10-65%), roxithromycin (40-100%), sulfamethoxazole (30-100%) and 17 alpha ethinyl Estradiol (30-100%). Whilst the removal for the MBR treated wastewater ranged as follows: iopromide (0-60%), roxithromycin (50-100%), sulfamethoxazole (15-100%) and 17 alpha ethinyl Estradiol (45-100%).

Table 1-1: Removal efficiency for different CECs by different treatment processes (Metcalf et al., 2013)

Group	Classification	Reverse Osmosis	BAC	Activated Carbon	Nano-filtration	Bio-degradation	Advanced Oxidation	Photo-degradation	Activated Sludge	UV	Cl_2/CLO_2	Softening	Coag/Floc
EDCs	Pesticides	E	E	E	G	v	L-E	E	v	E	v	G	P
	Industrial Chemicals	E	E	E	E	G-E	G-G	v	v	E	P	P-L	P-L
	Steroids	E	E	E	G	L-E	E	v	v	E	E	P-L	P
	Metal	E	G	G	G	P	P	v	E	P	P	F-G	F-G
	Inorganics	E	F	P-L	G	P-L	P	P-L	P-L	P	P	G	P
	Organometallics	E	G-E	G-E	G-E	L-E	L-E	L-E	L-E	F-G	P-F	P-L	P-L
PHACs	Antibiotics	E	E	F-G	E	E	L-E	G-E	v	F-G	P-G	P-L	P-L
	Anti-depressants	E	G-E	G-E	G-E	G-E	L-E	G-E	G-E	F-G	P-F	P-L	P-L
	Anti-inflammatory	E	G-E	E	G-E	E	E	v	v	E	P-F	P-L	P
	Lipid regulators	E	E	E	G-E	P	E	v	v	F-G	P-F	P-L	P
	X-ray contrast media	E	G-E	G-E	G-E	E	L-E	E	v	F-G	P-F	P-L	P-L
	Psychiatric control	E	G-E	G-E	G-E	G-E	L-E	G-E	G-E	F-G	P-F	P-L	P-L
PCPs	Synthetic musks	E	G-E	G-E	G-E	E	L-E	v	v	E	P-F	P-L	P-L
	Sunscreens	E	G-E	G-E	G-E	G-E	L-E	G-E	G-E	F-G	P-F	P-L	P-L
	Antimicrobials	E	G-E	G-E	G-E	v	L-E	F	v	F-G	P-F	P-L	P-L
	Detergents	E	E	E	E	L-E	F-G	v	v	F-G	P	P-L	P-L

E = excellent (>90%); G = good (70-90%); F = fair (40-70%); L = low (20-40%); P = poor (<20%) v = variable

Table 1-2: Removal efficiency of an MBR, unused RO and fouled RO treatment process (Snyder et al., 2005)

COMPOUND	WWTP INFLOW	MBR INFLOW	MBR EFFLUENT
Acetaminophen	172,000	<10	<10
Androstenedione	150	<10	<10
Caffeine	72,200	68	<10
Carbamazepine	189	281	<10
DEET	150	213	171
Diclofenac	<100	16	<10
Dilantin	210	192	184
Erythromycin-H2O	1050	800	34
Fluoxetine	<100	44	<10
Gemfibrozil	2210	74	<10
Hydrocodone	118	168	<10
Ibuprofen	12,000	27	43
Meprobamate	966	652	1340
Naproxen	12,500	70	<10
Oxybenzone	3810	<10	<10
Sulfamethoxazole	1110	23	<10
Triclosan	1280	17	<10
Trimethoprim	693	42	<10

Table 1-3: Removal by unused RO membranes (Snyder et al., 2005)

COMPOUND	FEED TANK	POST ANTISCALANT	BRINE RECYCLE	FINAL PERMEATE
REMOVAL EFFICIENCY BY UNUSED RO				
Androstenedione	284	306	315	<25
Caffeine	311	324	344	52
Diclofenac	26	32	31	<25
Dilantin	259	275	287	<25
Estradiol	125	66	57	<25
Estriol	128	78	58	<25
Estrone	167	57	78	<25
Ethinylestradiol	125	65	58	<25
Fluoxetine	263	284	499	<25
Gemfibrozil	230	211	218	<25
Ibuprofen	259	244	251	<25
Iopromide	165	170	158	<25
Naproxen	118	129	119	<25
Oxybenzone	218	176	192	<25
Pentoxifylline	458	483	471	45
Progesterone	285	324	312	<25
Triclosan	246	185	180	<25
Trimethoprim	265	294	268	<25

Table 1-4: Removal by fouled RO membranes (Snyder et al., 2005)

COMPOUND	FEED TANK	POST ANTISCALANT	BRINE RECYCLE	FINAL PERMEATE
Androstenedione	247	250	243	<25
Caffeine	196	193	219	<25
Dilantin	239	242	225	<25
Estradiol	27	<25	<25	<25
Estrone	83	<25	<25	<25
Ethinylestradiol	51	<25	<25	<25
Fluoxetine	564	441	451	<25
Gemfibrozil	234	234	221	<25
Ibuprofen	302	275	284	<25
Iopromide	125	115	133	72
Naproxen	91	73	77	<25
Oxybenzone	221	34	<25	<25
Pentoxifylline	169	154	160	<25
Progesterone	250	251	250	<25
Triclosan	166	105	90	<25
Trimethoprim	278	309	371	<25

In a study by Daughton and Ternes (1999) and recently in Ternes et al. (2004), several CAS WWTPs located throughout Europe were monitored, as well as the rivers downstream of the plants, in order to quantify the levels and removal of PPCPs in the effluent. An overview of the detection and removal of PPCPs in WWTP effluents are summarised (Table 1-5). Information regarding the occurrence and fate of many CECs can be found in the study, including the following compounds that were included in this study: bisphenol A, Triclosan, 17 alpha Ethynyl Estradiol, acetaminophen and carbamazepine. Unfortunately, it is not indicated what treatment processes are employed at the WWTPs were the results were obtained, but the results can still be compared with that found in this study to some degree. All these results form a good basis for the current study and therefore were used for comparison.

Table 1-5: Median and (maximum) PPCP levels, in ng/L, detected at European WWTPs and rivers (Ternes et al., 2004)

PPCP	LOCATION	GER	AUT	PL	ES	FR	CH	FIN
Diclofenac	influent	3500 (28000)	3100 (6000)	1750 (2000)	n.d.	n.a.	1400 (1900)	350 (480)
	effluent	810 (2100)	1500 (2000)	n.a.	n.d.	295 (300)	950 (1140)	250 (350)
	river	150 (1200)	20 (64)	n.a.	n.a.	18 (41)	20-150	15 (40)
Ibuprofen	influent	5000 (14000)	1500 (7200)	2250 (2800)	2750 (5700)	n.a.	1980 (3480)	13 000 (19 600)
	effluent	370 (3400)	22 (2400)	n.a.	970 (2100)	92 (110)	< 50 (228)	1300 (3900)
	river	70 (530)	n.d.	n.a.	n.a.	23 (120)	n.d.-150	10 (65)
Bezafibrate	influent	4900 (7500)	2565 (8500)	780 (1000)	n.d.	n.a.	n.a.	420 (970)
	effluent	2200 (4600)	103 (611)	n.a.	n.d.	96 (190)	n.a.	205 (840)
	river	350 (3100)	20 (160)	n.a.	n.a.	102 (430)	n.a.	5 (25)
Diazepam	influent	< LOQ	n.d.	n.a.	n.d.	n.a.	n.d.	n.d.
	effluent	< LOQ (40)	n.d.	n.a.	n.d.	n.d.	n.d.	n.d.
	river	n.d.	n.d.	n.a.	n.a.	n.d.	n.d.	n.d.
Carbamazepine	influent	2200 (3000)	912 (2640)	1150 (1600)	n.a.	n.a.	690 (1900)	750 (2000)
	effluent	2100 (6300)	960 (1970)	n.a.	n.a.	1050 (1400)	480 (1600)	400 (600)
	river	250 (1100)	75 (294)	n.a.	n.a.	78 (800)	30-150	70 (370)
Roxithromycin	influent	830 (1000)	43 (350)	n.d.	n.d.	n.a.	20 (35)	n.a.
	effluent	100 (1000)	66 (290)	n.a.	n.d.	n.d.	15 (30)	n.a.
	river	<LOQ (560)	n.d.	n.a.	n.a.	9 (37)	n.a.	n.a.
Iopromide	influent	13000 (22000)	n.d. (3840)	1330 (2700)	6600	n.a.	810 (7700)	n.a.
	effluent	750 (11000)	n.d. (5060)	n.d.	9300	n.d.	790 (2000)	n.a.
	river	100 (910)	91 (211)	n.a.	n.a.	7 (17)	n.a.	n.a.
Tonalide (AHTN)	influent	400 (450)	970 (1400)	n.d.	1530 (1690)	n.a.	545 (940)	200 (230)
	effluent	90 (180)	140 (230)	n.a.	160 (200)	n.a.	410 (500)	40 (50)
Galaxolide (HHCB)	influent	1500 (1800)	2800 (5800)	610 (1200)	3180 (3400)	n.a.	1660 (2200)	750 (980)
	effluent	450 (610)	470 (920)	n.a.	500 (600)	n.a.	1150 (1720)	120 (160)

Note: Ger = Germany, Aut = Austria, PL = Poland, ES = Spain, FR = France, CH = Switzerland.

1.2 AIMS

The aims of the project were as follows:

- Compile an up-to-date list of all types of emerging contaminants of concern in reclaimed potable water.
- Produce a report which identifies the sources, pathways and receptors by which these compounds enter drinking water systems, including resistance to wastewater treatment, their toxicity and the consequent potential risks from exposure to these chemicals.
- Draw up an assessment report on performance of water reclamation treatment systems and potential for failures in reliability and consequent risks for direct potable water reuse.
- Develop guidelines for implementation of appropriate treatment barriers, monitoring programmes and assessment programmes to eliminate or minimise risks.

Volume III reports on the indicative removal potential, performance and reliance of treatment technologies typically employed at water treatment plants and lastly, an assessment of risks associated with human exposure to selected priority emerging contaminants in treated water.

1.3 SCOPE AND LIMITATIONS

The aim of this report was to report on the human health risk priorities in South Africa pertaining to contaminants of emerging concern (CECs) that may potentially be detected in wastewater used for direct potable reuse. The specific aim of this volume is to report on the methods, practical work (sampling and analyses) and results obtained in order to assess the occurrence and removal of CECs in water reclamation and wastewater treatment plants. This work consisted of three studies that were aimed at:

1) detecting and quantifying CECs and their removal in water reclamation plants (WRPs) as well as wastewater treatment plants (WWTPs)
2) conducting a treatment process performance evaluation of a WRP using historic plant data and statistical methods; and performing a plant reliability analysis on a WRP using historic plant data and statistical methods
3) conducting human health risk assessment associated with exposure to the different selected emerging contaminants.

1.4 STUDY DESIGN

1.4.1 Overview

Although for such studies, the holistic system consisting of the wastewater collection system, wastewater treatment plant, water reclamation plant and distribution system must be considered as they form part of the multi-barrier approach towards minimizing health impacts, in this research project the collection and distribution systems were not included in the scope of study.

1.4.2 Selection of treatment sites for evaluation

The following criteria were considered in the selection of the evaluation sites:

- Existing water reclamation plants in Southern Africa.
- Water supply schemes that are water stressed and where the likelihood is high to implement DPR.
- Wastewater treatment plants which are representative of treatment plants of which the secondary treated effluent will be of a quality for which direct or indirect potable reuse can be considered. These processes would be conventional activated sludge (CAS) and membrane bio-reactor (MBR) systems.
- Representative, *i.e*. select plants of various configurations that can qualify for DPR in different regions with different water and wastewater qualities.

Based on the above criteria, a total of five treatment plants were selected, consisting of two WRPs and three WWTPs. These plants are denoted by WRP A, WRP B, WWTP C, WWTP D and WWTP E. In addition, sampling was also done towards the end of the project at a large regional water treatment plant (WTP), WTP F, which treats water from a river considered to be increasingly polluted with treated wastewater, industrial effluent and agricultural run-off.

1.4.3 Description of study sites

1.4.3.1 *Water Reclamation Plant A*

This reclamation plant makes use of the modern dual-membrane treatment process. The system receives secondary treated wastewater from a conventional activated sludge WWTW with optional chemical phosphate removal before chlorination. The secondary treated wastewater enters the WRP where it is treated using a sand filter, ultrafiltration (UF) reverse osmosis (RO) membranes and finally advanced oxidation before blending with treated water from a WTP, and then distributed to the public.

1.4.3.2 *Water reclamation plant B*

This plant makes use of more conventional water reclamation process configuration that constituted the main process configuration up the middle 1990s when the application of membrane treatment systems commenced. What may once have been called a conventional reclamation design can now be referred to as alternative design since the previously mentioned dual-membrane system has become commonplace in recent years and can now be considered conventional. This alternative design receives secondary treated wastewater from a conventional WWTP making use of activated sludge followed by eight maturation ponds. The secondary treated wastewater enters the WRP and has a facility for dosing powder activated carbon (PAC) if required. The water then receives a pre-ozonation dose followed by coagulation and flocculation. As main solids removal process, the water is then treated using a dissolved air flotation (DAF) system, followed by sand filtration and the main ozonation step. After ozonation the water is passed through a single stage biological activated carbon (BAC), followed by a two-stage granular activated carbon (GAC) step. H_2O_2 (hydrogen peroxide) is available to dose before the BAC should the residual ozone be too high. Finally, the water is treated using UF membranes after which the water is stabilized and disinfected using chlorine gas.

1.4.3.3 *Wastewater treatment plant systems: WWTP C, WWTP D and WWTP E*

- WWTP C makes use of two parallel treatment trains; the one train is a conventional activated sludge process and the other train is an MBR system.
- WWTP D comprises a conventional activated sludge treatment process.
- WWTP E also makes use of three parallel treatment trains; two of the three treatment trains consist of conventional MLE activated sludge treatment processes, and the third train consists of a MBR process.

1.4.3.4 *Water treatment plant abstracting water from a polluted river*

WTP F abstracts water from a river which receives return flows from more than 20 WWTPs. The plant uses the conventional treatment processes of coagulation and flocculation, sedimentation, rapid sand filtration and chlorine disinfection.

1.4.4 Evaluating the indicative removal of selected CECs

Data for evaluating the indicative removal of selected CECs was study collected data by analysing samples collected during three sampling campaigns conducted during April 2015, October 2015 and January 2016. The sampling procedure, analytical methods and results of analyses will be discussed in detail in Chapter 2.

1.4.5 Process performance and plant reliability analysis

These studies were both conducted in co-operation with the Process Monitoring Group, of the Process Engineering Faculty of the University of Stellenbosch. These studies made use of data collected over a five-year period from a WRP that treats secondary treated wastewater to a potable standard and then supplies it (after blending with conventionally treated water) to a city. The details for these studies are discussed in Chapter 3.

1.4.6 Human health risk assessment

Based on water toxicity testing using bioassays and risk models, health effects and risks associated with exposure to selected CECs were determined. The details for these studies are discussed in Chapter 4.

CHAPTER 2: EVALUATING THE INDICATIVE REMOVAL OF SELECTED CECs

2.1 WATER RECLAMATION PLANT A

2.1.1 Treatment system description

This reclamation plant makes use of the modern dual-membrane treatment process. The system receives secondary treated wastewater from a conventional activated sludge WWTW with optional chemical phosphate removal before chlorination. The secondary treated wastewater enters the WRP where it is treated using a sand filter, ultrafiltration (UF) reverse osmosis (RO) membranes and finally advanced oxidation before blending with treated water from a WTP, and then distributed to the public.

2.1.2 Sampling Campaign 1

2.1.2.1 *Sampling*

Grab samples were collected in triplicate at different stages of the wastewater treatment process, as follows:

- Raw wastewater inflow
- After activated sludge treatment
- Before chlorination
- After chlorination
- After ultrafiltration
- After reverse osmosis
- After UV/H_2O_2 (final water)

1 litre samples were collected in methanol pre-washed, air-dried, amber bottles with a foil cover underneath the lid to ensure that the sample never came in contact with any plastics that can interfere with the analyses. Field blanks were also prepared by filling pre-washed bottles with Milli-Q water, transported to the sampling site and transported back with the samples to the laboratory. The samples were kept cool during transport to the laboratory in an ice box and was immediately transferred into a refrigerator upon arrival at the laboratory. The samples were kept at 4°C and analysed within 48 hours after sampling.

2.1.2.2 *Sample analyses*

The samples were analysed in the laboratories of the Department of Chemistry at the University of the Western Cape (UWC) for the following compounds:

- **Acetaminophen** – Pharmaceutical compounds such as acetaminophen have been identified as contaminants in sewage effluents, surface and groundwater and in drinking water. There have been increasing concerns about the possible health implications of continuous exposure to this pharmaceutical.

- **Bisphenol-A** – Bisphenol-A is a chemical compound that can be used to assess the endocrine activity of wastewater, both domestic and industrial. Bisphenol-A is commonly used in adhesives and multiple different types of paint, thermal paper and paper coatings.

- **Perfluorinated Compounds** – Perfluorinated compounds (PFCs) such as perfluorooctanoic acid (PFOA) consist of fully fluorinated hydrophobic linear carbon chains attached to one or more hydrophilic groups, and are mostly used as industrial surfactants and surface protectors for paper, food containers, leather, carpets, upholstery and fabric. They are also used as additives, coating materials and fire-fighting foams because of their ability to repel water and oil. There is concern over the health risks on exposure to PFCs. The compounds are globally distributed, environmentally persistent, bioaccumulative, magnify in the food chain and potentially toxic. They are found in the environment as stable perfluorooctanesulfonate (PFOS), perfluorohexanesulfonate (PFHxS) and perfluorocarboxylic acids (PFCAs).

2.1.2.3 *Results of analyses for the first sampling campaign*

The results of PFCs analyses are shown in Table, while those for CECs analysed are shown in Table.

Table 2-1: Perfluorinated compounds (PFCs) results: Sampling campaign 1 (all units in ng/L)

Sample point	PFHPA	PFOA	PFNA	PFOS	PFDA	PFUnDA
	(ng/ℓ)					
WWTP Inlet	35.14	3.23	18.8	nd	6.21	2.66
WWTP Activated sludge	22.1	nd	13.43	nd	5.88	2.32
WWTP Clarifier	22.23	4.952	12.11	nd	1.01	2.32
WRP Inlet	21.92	5.25	11.09	nd	1.08	2.44
WRP UF	nd	nd	18.73	nd	2.04	1.64
WRP RO	20.12	nd	7.52	nd	nd	1.42
WRP UV/H_20_2 (Final effluent)	nd	nd	1.12	nd	nd	1.23

Table 2-2: Priority CECs results: Sampling campaign 1 (all units in µg/L)

Parameter	Bisphenol A	Triclosan	17 Alpha Ethynyl Estradiol	Acetaminophen	Atrazine	Imidacloprid	Carbamazepine	Lamivudine	Simazine	Sulfamethoxazole	Terbuthylazine	Cinchonidine
Limit of detection	0.01	0.001	0.008	0.001	0.0001	0.001	0.0002	0.001	0.002	0.001	0.0001	0.001
WWTP Inlet	0.5	0.35	2.53	0.359	0.0003	nd	0.402	0.007	0.004	0.014	0.003	nd
WRP Inlet	0.179	0.05	2.38	nd	0.0006	nd	1.08	0.001	0.028	0.022	0.004	nd
WRP RO	0.029	0.008	0.154	nd	0.0003	0.003	0.94	0.001	0.018	0.01	0.001	nd
Final Water	0.015	0.002	0.13	nd	0.0001	0.002	0.72	0.0003	0.014	0.013	0.001	nd

2.1.3 Sampling Campaign 2

2.1.3.1 *Sampling*

The sampling procedure that was followed for the second sampling campaign is different to that followed during the first campaign, although only slightly. Instead of taking grab samples for all the samples, the raw wastewater and clarifier samples that were taken at the WWTP feeding WRP A were taken as three hourly composite samples. Before the wastewater enters the WRP, it is stored in a maturation river with a sufficient retention time to mitigate the value of composite sampling downstream of the dich. The samples taken at the WRP were, therefore, all normal grab samples.

2.1.3.2 *Sample analyses*

The analyses performed on the samples from the second sampling campaign are much more encompassing than the previous campaign. The following analyses were performed on the samples taken during the second sampling campaign:

- Macro-determinants: chemical and physical parameters (all samples)
  Ammonia, nitrate plus nitrite, DOC, TOC, EC, pH, COD, turbidity and UV_{254} absorbance.
- Perfluorinated compounds (PFCs) (all samples)
  Perfluoroheptanoic acid (PFHPA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorooctanesulfonate (PFOS), perfluorodecanoic acid (PFDA) and perfluoroundecanoic acid (PFUnDA)
- Priority CECs (all samples)
  Bisphenol A (BPA), triclosan, 17α ethinyl estradiol (EE2), acetaminophen, atrazine, imidacloprid, carbamazepine, lamivudine, simazine, sulfametoxazole, terbuthylazine and cinchonidine.

2.1.3.3 *Results of analyses for the second sampling campaign*

The results of the various analyses, as seen above, performed on the samples collected during the second sampling campaign can be seen in Table (Macro-determinants chemical and physical parameters, Table 2-4 (PFCs) and Table 2-5 (Priority CECs).

Table 2-3: Macro-determinants chemical and physical parameters: Sampling campaign 2

Analysis	Unit	WWTP Inlet	WWTP Clarifier	WRP Inlet	WRP SF	WRP UF	WRP RO	Final water
Ammonia	mg/L	107	2	1.5	0.62	0.59	0.05	0.05
Nitrate + Nitrite	mg/L		<0.1		12			
DOC	mg/L	108	14	14	13	12	<0.5	<0.5
TOC	mg/L	290	18	16	15	12	<0.5	<0.5
EC	mS/m	270	190	200	200	200	9	10
pH	(-)	8	7.8	7.8	7.7	7.8	6.3	6.5
COD	mg/L	5637	54	38	31	22	<5	<5
Turbidity	NTU	626	8.6	2.1	1.7	0.7	0.3	<0.2
UV absorbance (254nm)	Abs	0.813	0.267	0.237	0.239	0.23	0.015	0.007

Table 2-4: Perfluorinated compounds (PFCs): Sampling campaign 2 (all units in ng/L)

Parameter	PFHPA	PFOA	PFNA	PFOS	PFDA	PFUnDA
WWTP Inlet	16.76	17.75	26.65	nd	4.1	nd
WWTP Clarifier	11.64	13.01	14.2	nd	3.19	nd
WRP Inlet	8.97	12.62	8.47	nd	3.22	nd
WRP SF	22.22	10.11	3.22	nd	0.94	nd
WRP UF	11.72	4.33	nd	nd	ND	nd
WRP RO	9.32	0.91	nd	nd	ND	nd
Final water	5.57	1.2	nd	nd	ND	nd

Table 2-5: Priority CECs (all units in µg/L)

Parameter	Bisphenol A	Triclosan	17 Alpha Ethynyl Estradiol	Acetaminophen	Atrazine	Imidacloprid	Carbamazepine	Lamivudine	Simazine	Sulfamethoxazole	Terbuthylazine	Cinchonidine
Limit of detection	0.01	0.001	0.008	0.001	0.0001	0.001	0.0002	0.001	0.002	0.001	0.0001	0.001
WWTP Inlet	0.122	0.106	2.58	0.02	0.0004	nd	0.11	0.026	nd	0.032	0.0002	nd
WWTP Clarifier	0.082	0.096	2.86	nd	0.001	nd	0.532	0.002	0.186	0.03	0.0042	nd
WRP Inlet	0.102	0.032	2.54	nd	0.0006	nd	0.782	0.002	0.138	0.03	0.002	nd
WRP SF	0.09	0.058	3.38	nd	0.001	nd	0.744	0.002	0.138	0.034	0.003	nd
WRP UF	0.11	0.02	2.74	nd	0.0006	nd	0.712	0.002	0.128	0.022	0.0024	nd
WRP RO	nd	0.058	0.134	nd	0.0006	nd	0.038	nd	0.004	0.01	0.0006	nd
Final Water	0.086	0.0236	0.104	nd	0.0004	nd	0.024	nd	nd	0.004	0.0004	nd

2.1.4 Sampling Campaign 3

2.1.4.1 *Sampling*

The sampling procedure that was followed for the third sampling campaign is different to that followed during the first and second sampling campaign, although only slightly. Instead of taking grab samples, samples were taken at 2-hour intervals in order to make a composite sample over 12 hours. This procedure was followed for each of the sampling points within the WWTP as well as the WRP.

2.1.4.2 *Sample analyses*

The analyses performed on the samples from the third sampling campaign are identical to that of the previous campaign. Therefore, the following analyses were performed on the samples taken during the third sampling campaign:

- Macro-determinants: chemical and physical parameters (all samples)

Ammonia, nitrate plus nitrite, DOC, TOC, EC, pH, COD, turbidity and UV_{254} absorbance.

- Perfluorinated compounds (PFCs) (all samples)
  Perfluoroheptanoic acid (PFHPA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorooctanesulfonate (PFOS), perfluorodecanoic acid (PFDA) and perfluoroundecanoic acid (PFUnDA)
- Priority CECs (all samples)
  Bisphenol A (BPA), triclosan, 17α ethinyl estradiol (EE2), acetaminophen, atrazine, imidacloprid, carbamazepine, lamivudine, simazine, sulfametoxazole, terbuthylazine and cinchonidine.

2.1.4.3 *Results of analyses for the third sampling campaign*

The results of the various analyses, as seen above, performed on the samples collected during the second sampling campaign can be seen in Table (Macro-determinants chemical and physical parameters, Table (PFCs) and Table (Priority CECs).

Table 2-6: Macro-determinants chemical and physical parameters: Sampling campaign 3

Analysis	Unit	WWTP Inlet	WWTP Clarifier	WRP Inlet	WRP SF	WRP UF	WRP RO	Final water
Ammonia	mg/L	53	18					
Nitrate + Nitrite	mg/L	<0.1	0.2					
DOC	mg/L	59	16	15	13	11	<0.5	<0.5
EC	mS/m	185	146	165			8	8
pH	-	7.4	7.8	7.8	7.6	7.8	6.6	6.5
COD	mg/L	583	48					
Turbidity	NTU			4.4	2.3	0.6	0.4	
UV (254nm)	Abs			0.286	0.241	0.219	0	0

Table 2-7: Perfluorinated compounds (PFCs) results: Sampling campaign 3 (all units in ng/L)

Parameter	PFHPA	PFOA	PFNA	PFOS	PFDA	PFUnDA
WWTP Inlet	36.98	42.43	7.46	ND	27.24	ND
WWTP Clarifier	33.92	42.32	6.34	ND	2.37	ND
WRP Inlet	32.54	11.66	4.54	ND	2.85	ND
WRP SF	58.52	19.42	ND	ND	2.79	ND
WRP UF	22.32	19.95	ND	ND	5.72	ND
WRP RO	18.51	6.593	ND	ND	2.83	ND
Final water	15.28	4.132	ND	ND	2.54	ND

Table 2-8: Priority CEC results: Sampling campaign 3 (all units in µg/L)

Parameter	Bisphenol A	Triclosan	17 Alpha Ethynyl Estradiol	Acetaminophen	Atrazine	Imidacloprid	Carbamazepine	Lamivudine	Simazine	Sulfamethoxazole	Terbuthylazine	Cinchonidine
Limit of detection	0.002	0.002	0.02	0.001	0.0001	0.0006	0.002	0.0006	0.001	0.0006	0.00006	0.002
WWTP Inlet	0.432	ND	1.94	0.0046	0.0033	ND	1.02	0.009	0.102	0.0124	0.0017	ND
WWTP Clarifier	0.11	0.026	1.55		0.001	ND	0.726	ND	0.12	0.018	0.0065	ND
WRP Inlet	0.127	0.037	1.87	ND	0.0008	ND	1.04	0.0004	0.0614	0.0247	0.0031	ND
WRP SF	0.118	0.0603	1.64	ND	0.0007	ND	1.14	0.0005	0.0559	0.0341	0.0028	ND
WRP UF	0.0646	0.0357	0.991	ND	0.0009	ND	1.48	ND	0.0679	0.0468	0.0031	ND
WRP RO	0.0127	0.0577	0.0236	ND	ND	ND	0.0262	ND	ND	0.0008	ND	ND
Final Water	0.0068	0.0124	ND	ND	ND	ND	0.0365	ND	ND	ND	ND	ND

2.1.5 Comparison

Figures 2-1 to 2-17 summarise results obtained from all three sampling campaigns for purposes of comparison.

2.1.5.1 *Perfluorinated Compounds*

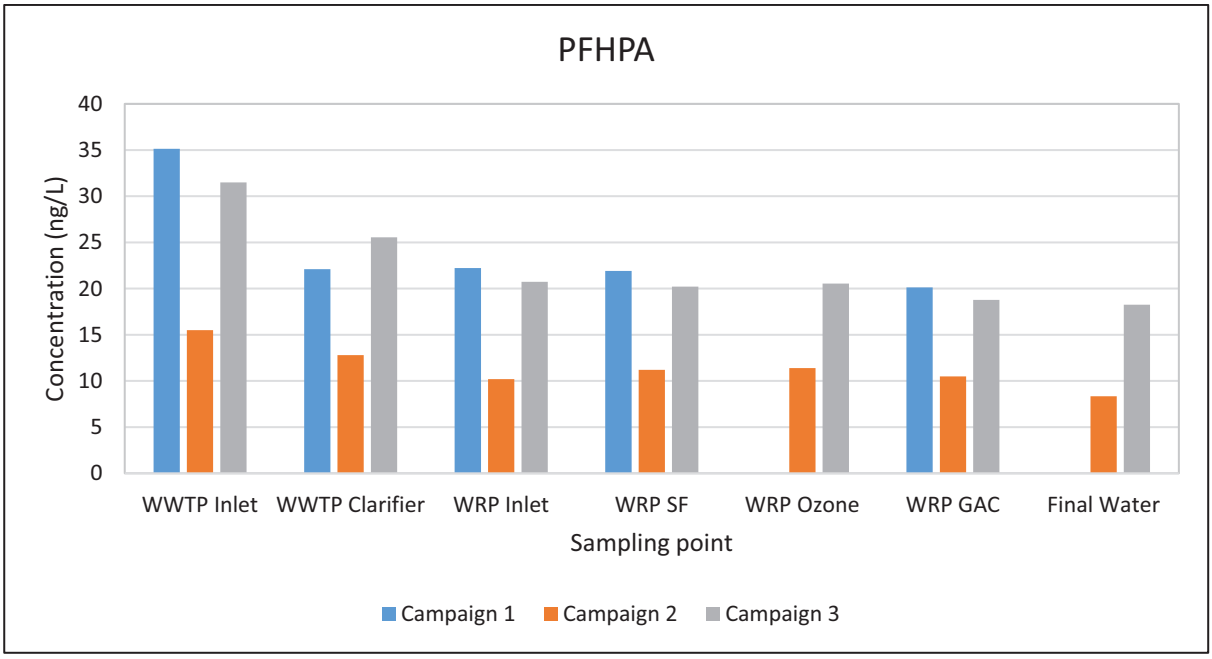

Figure 2-1: PFHPA for all the sampling campaigns for WRP A

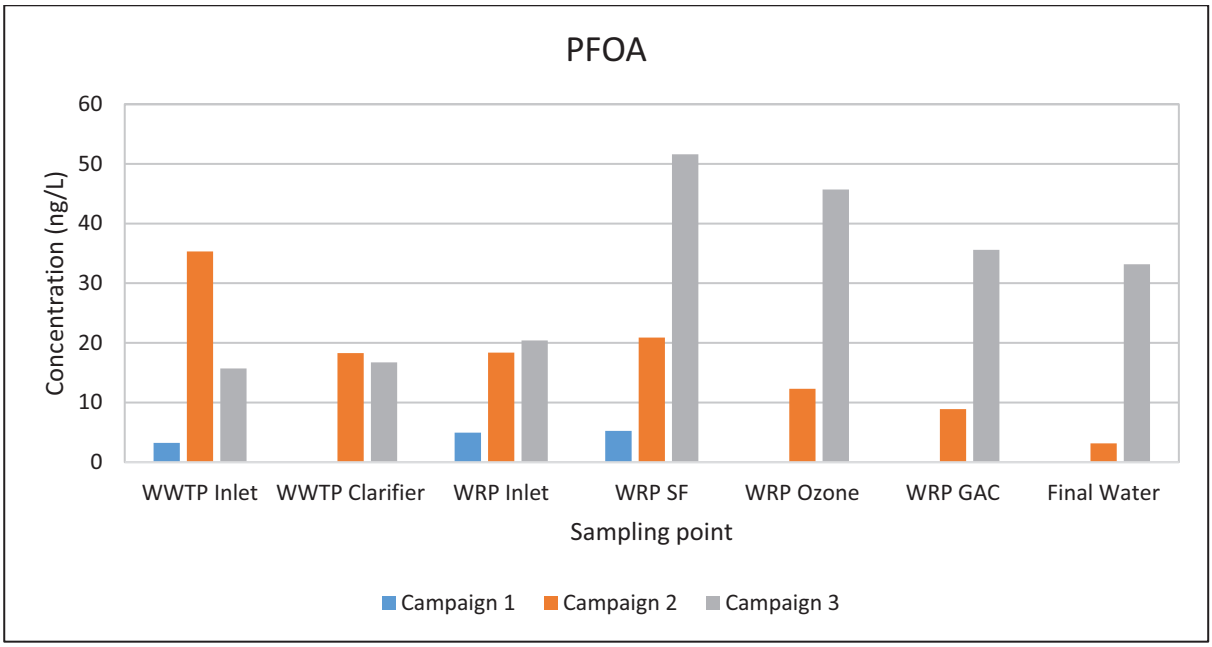

Figure 2-2: PFOA for all the sampling campaigns for WRP A

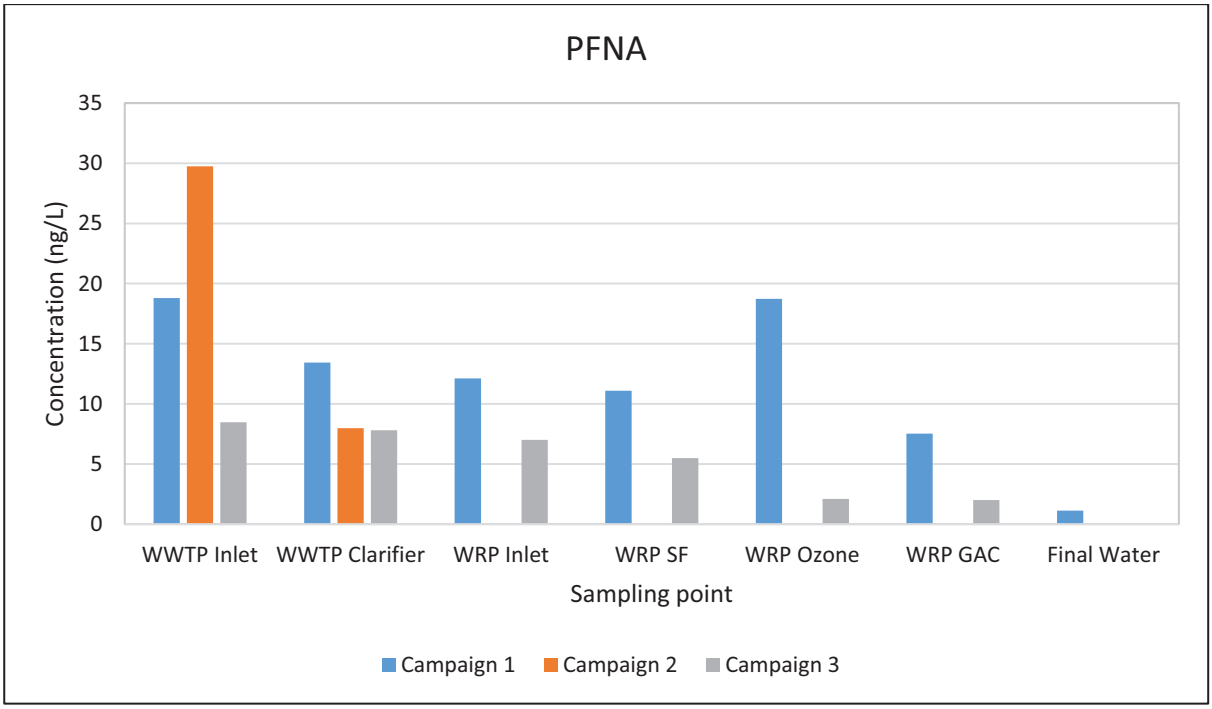

Figure 2-3: PFNA for all the sampling campaigns for WRP A

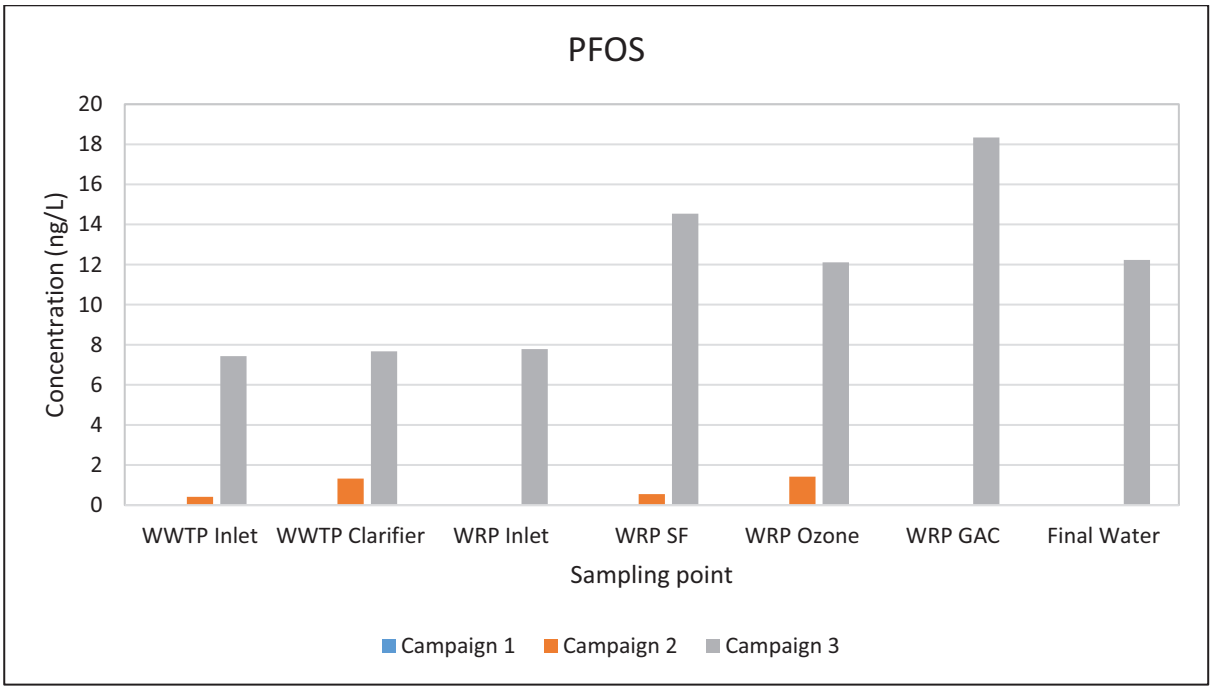

Figure 2-4: PFOS for all the sampling campaigns for WRP A

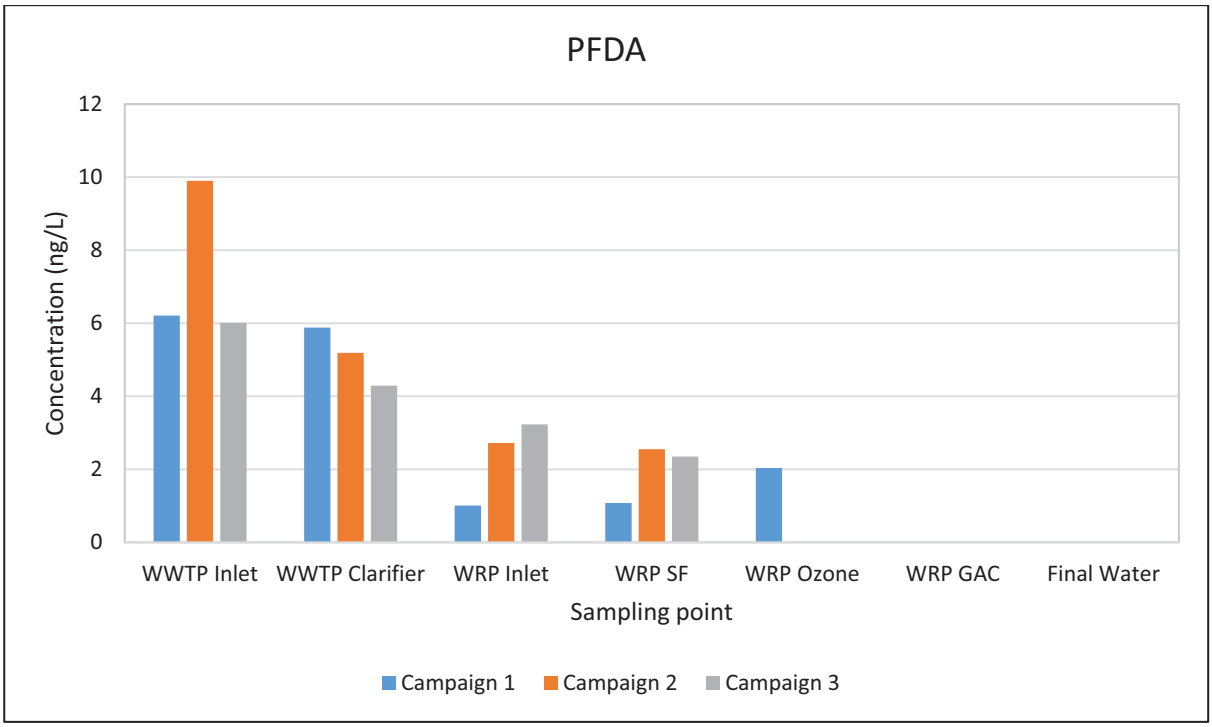

Figure 2-5: PFDA for all the sampling campaigns for WRP A

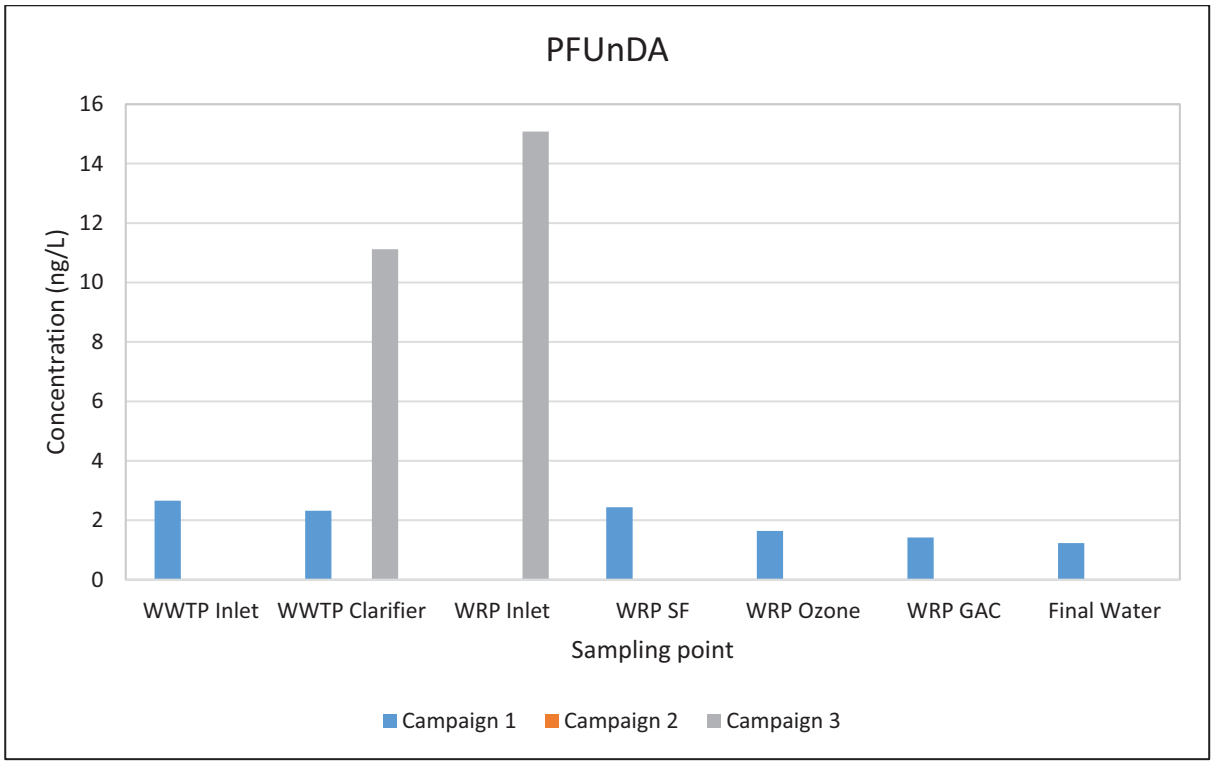

Figure 2-6: PFUnDA for all the sampling campaigns for WRP A

2.1.5.2 *Priority Chemicals of Emerging Concern*

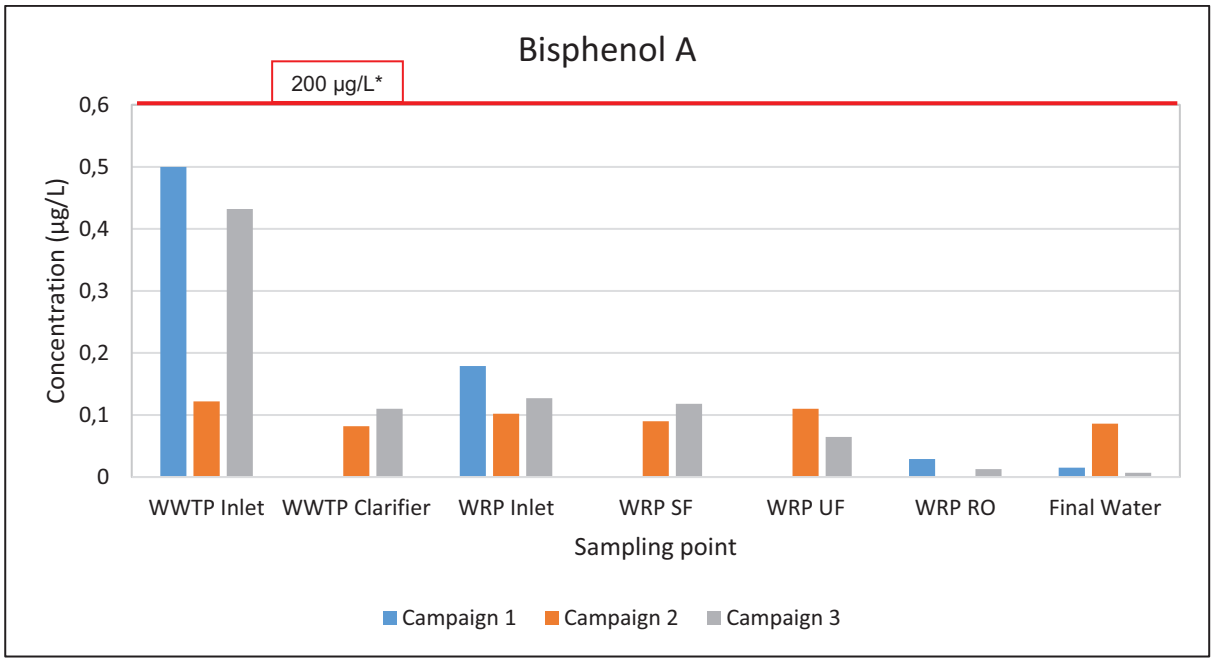

Figure 2-7: Bisphenol A for all the sampling campaigns for WRP A. * Limit proposed for potable water (NRMMC, 2008 Guideline value)

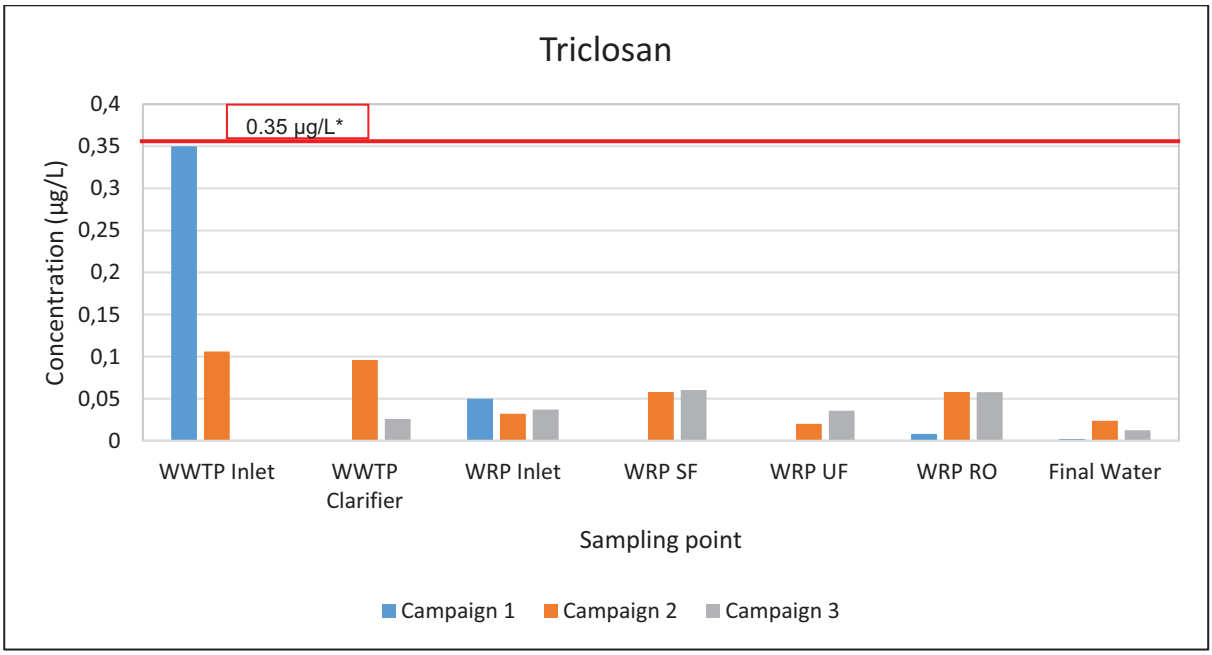

Figure 2-8: Triclosan for all the sampling campaigns for WRP A. * Limit proposed for potable water (NRMMC, 2008 Guideline value)

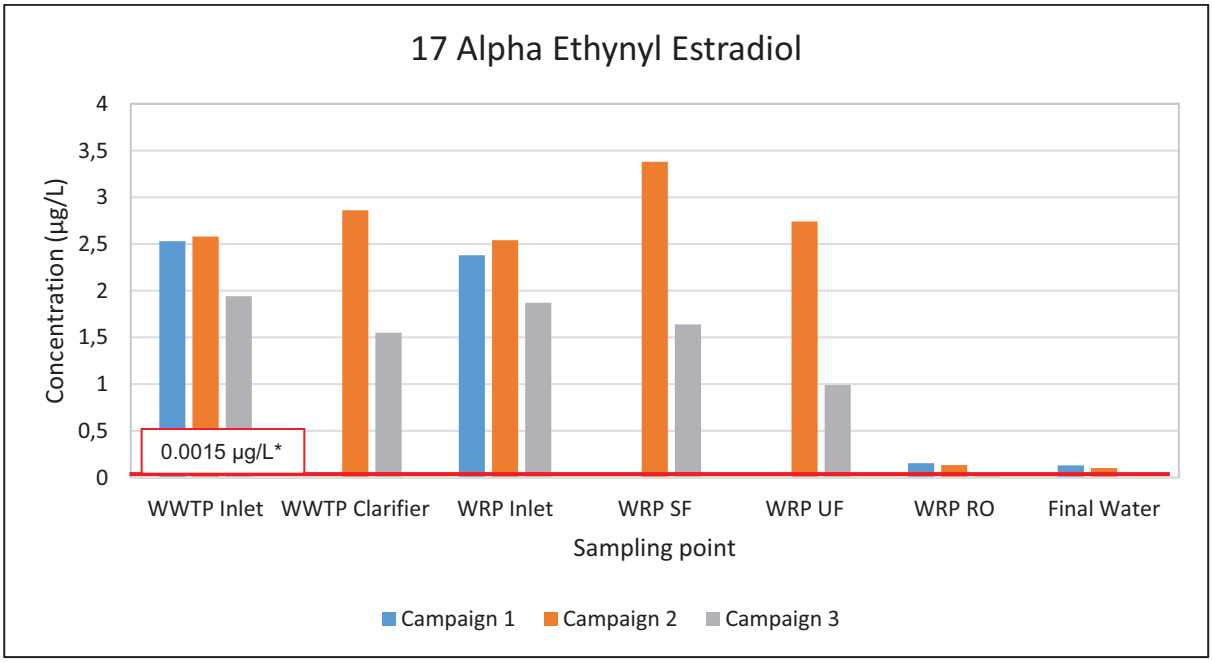

Figure 2-9: 17 Alpha Ethynyl Estradiol for all the sampling campaigns for WRP A. * Limit proposed for potable water (NRMMC, 2008 Guideline value)

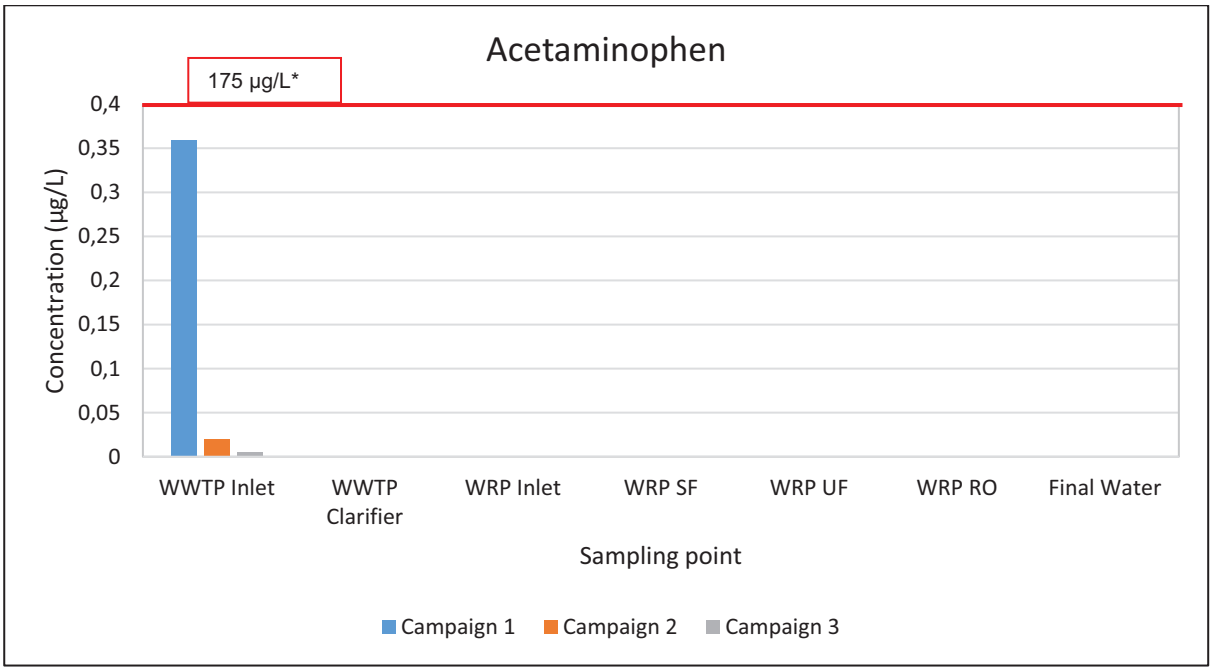

Figure 2-10: Acetaminophen for all the sampling campaigns for WRP A. * Limit proposed for potable water (NRMMC, 2008 Guideline value)

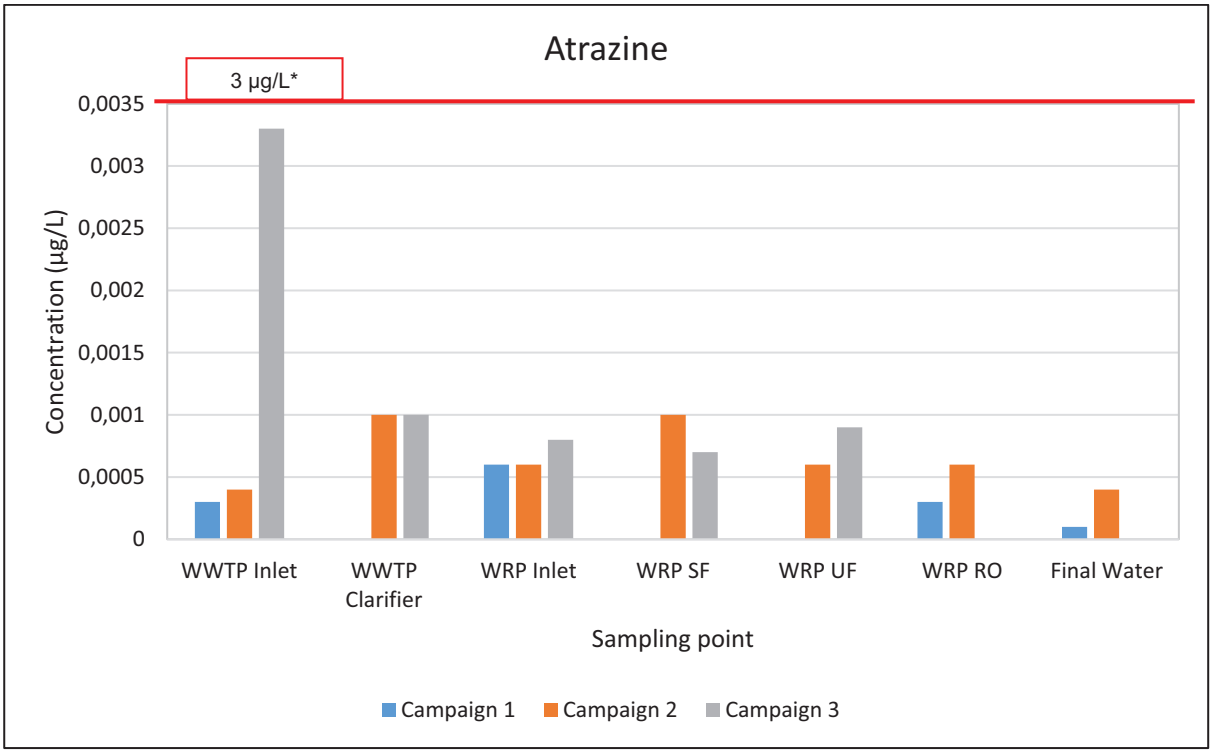

Figure 2-11: Atrazine for all the sampling campaigns for WRP A. * Limit proposed for potable water (EPA, 2012 California drinking water limits)

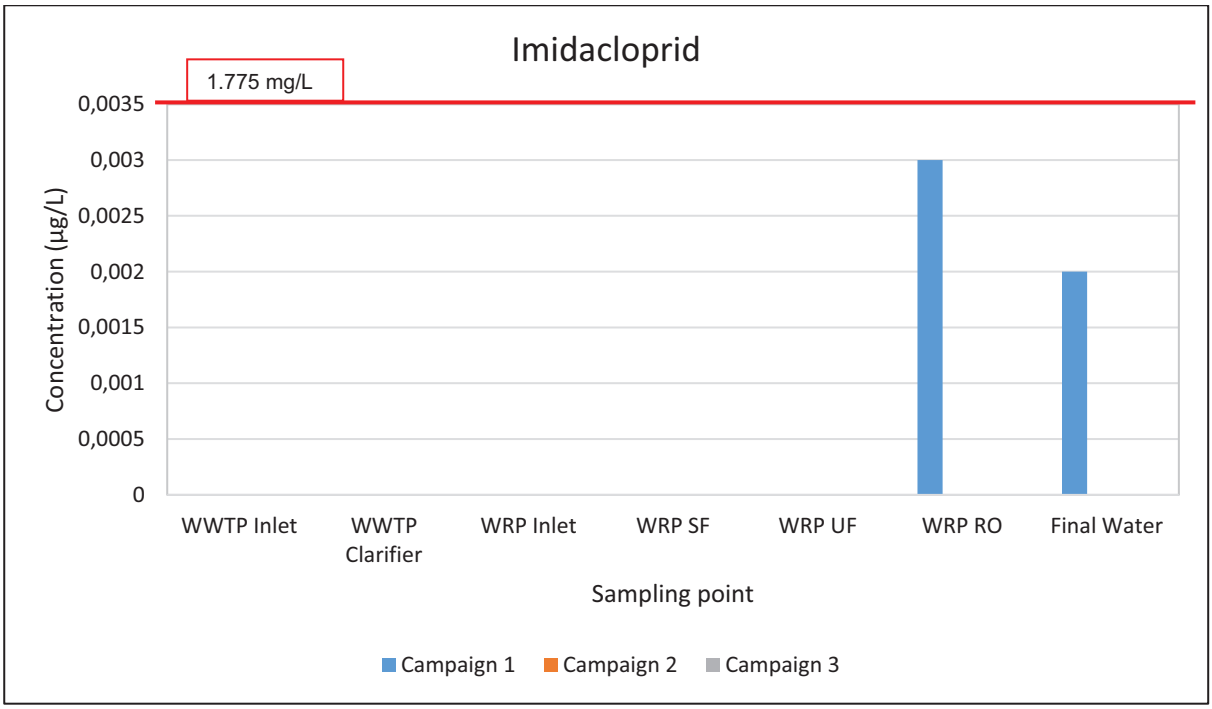

Figure 2-12: Imidacloprid for all the sampling campaigns for WRP A. * Limit proposed for potable water (EPA, 2005 California drinking water limits)

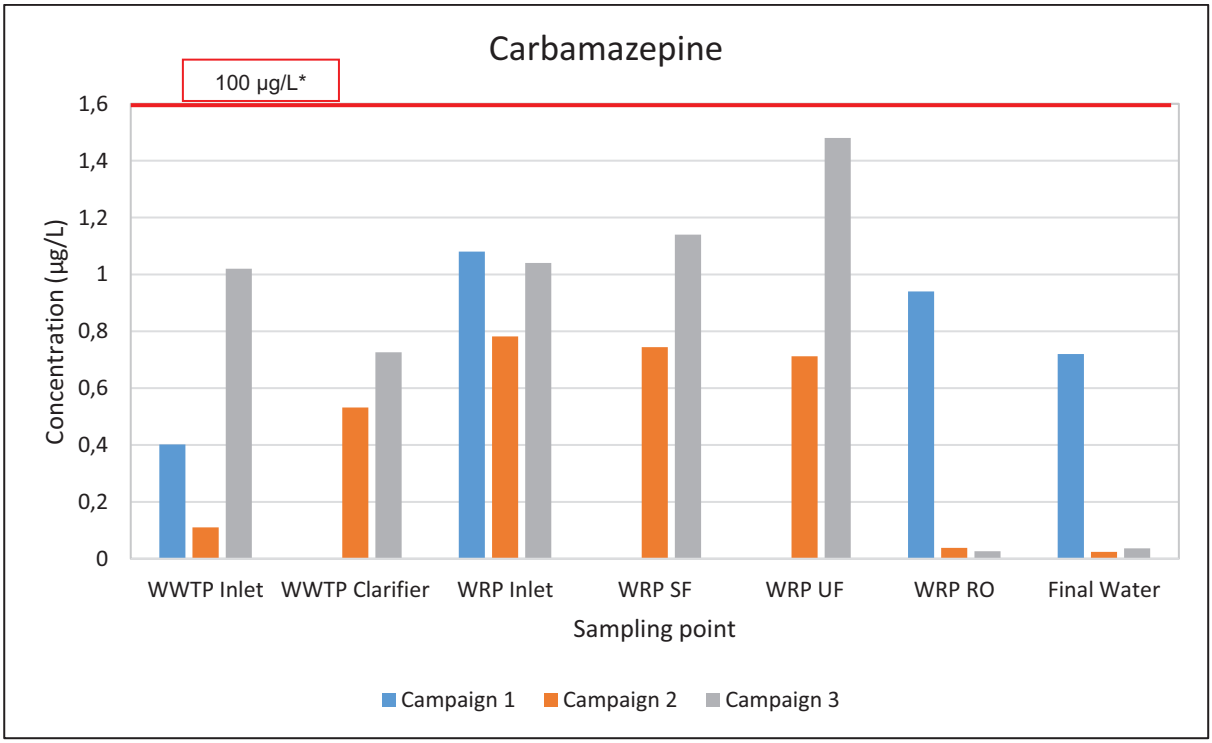

Figure 2-13: Carbamazepine for all the sampling campaigns for WRP A. * Limit proposed for potable water (NRMMC, 2008 Guideline value)

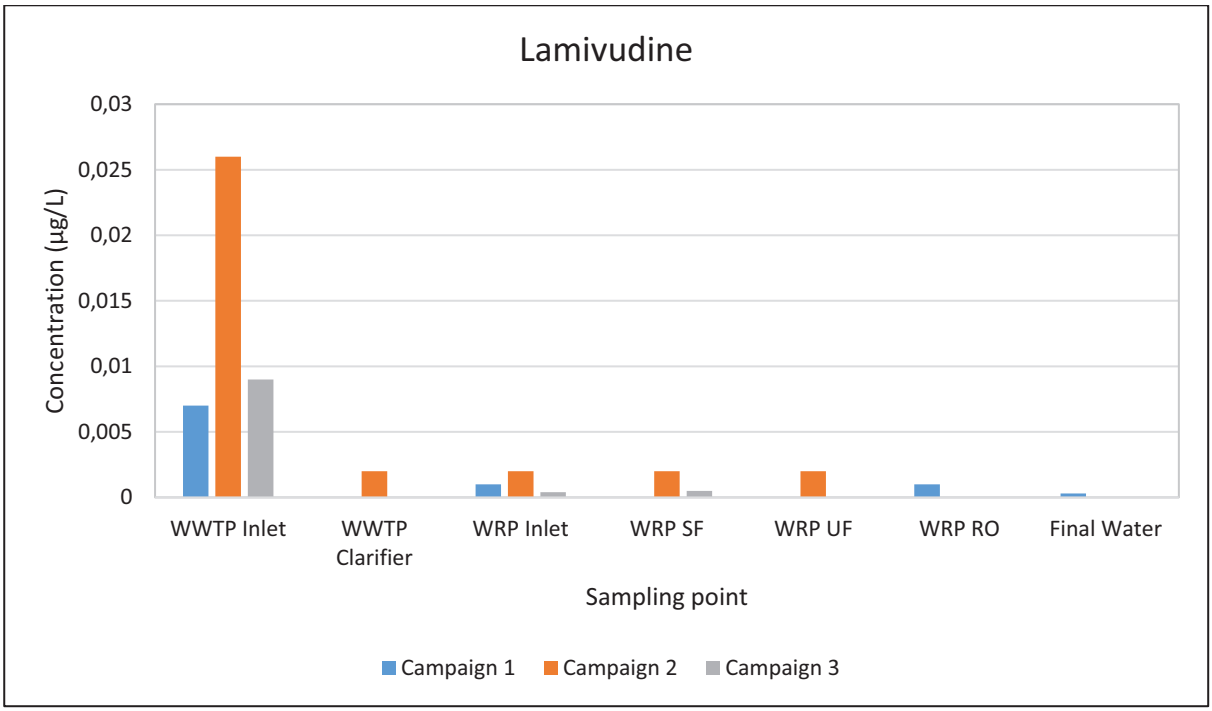

Figure 2-14: Lamivudine for all the sampling campaigns for WRP A

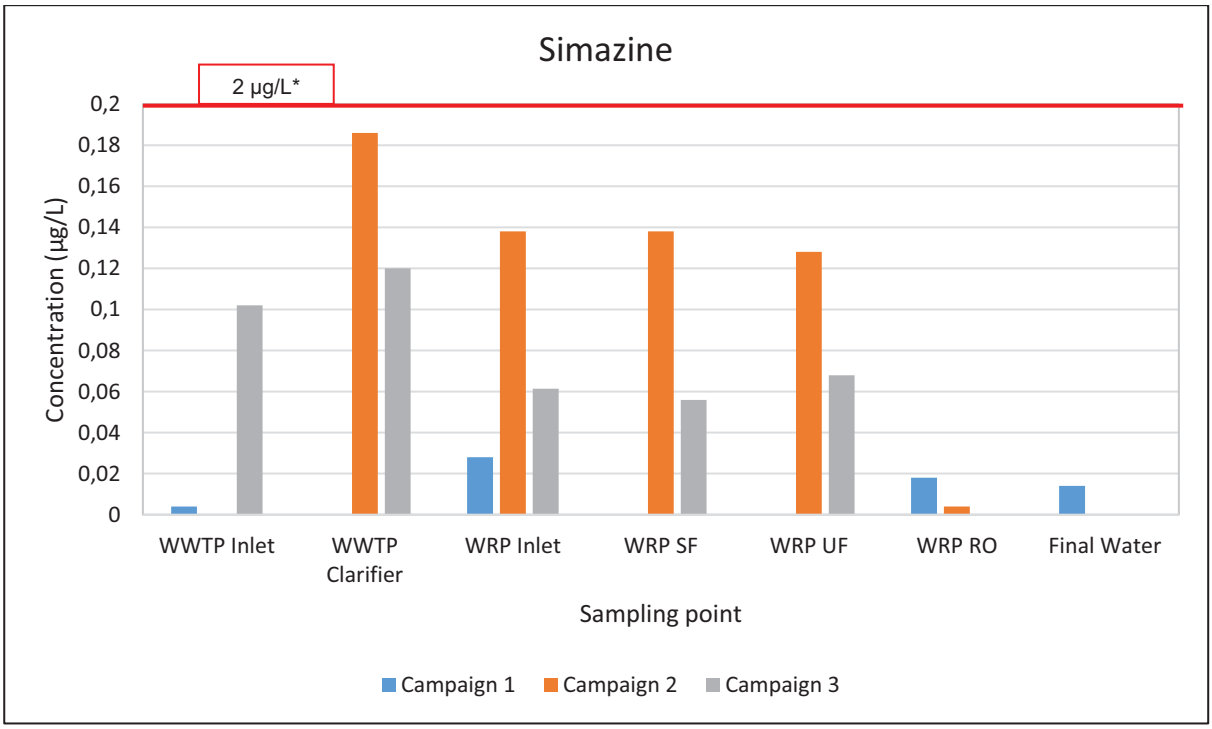

Figure 2-15: Simazine for all the sampling campaigns for WRP A. * Limit proposed for potable water (WHO, 2011c Guideline value)

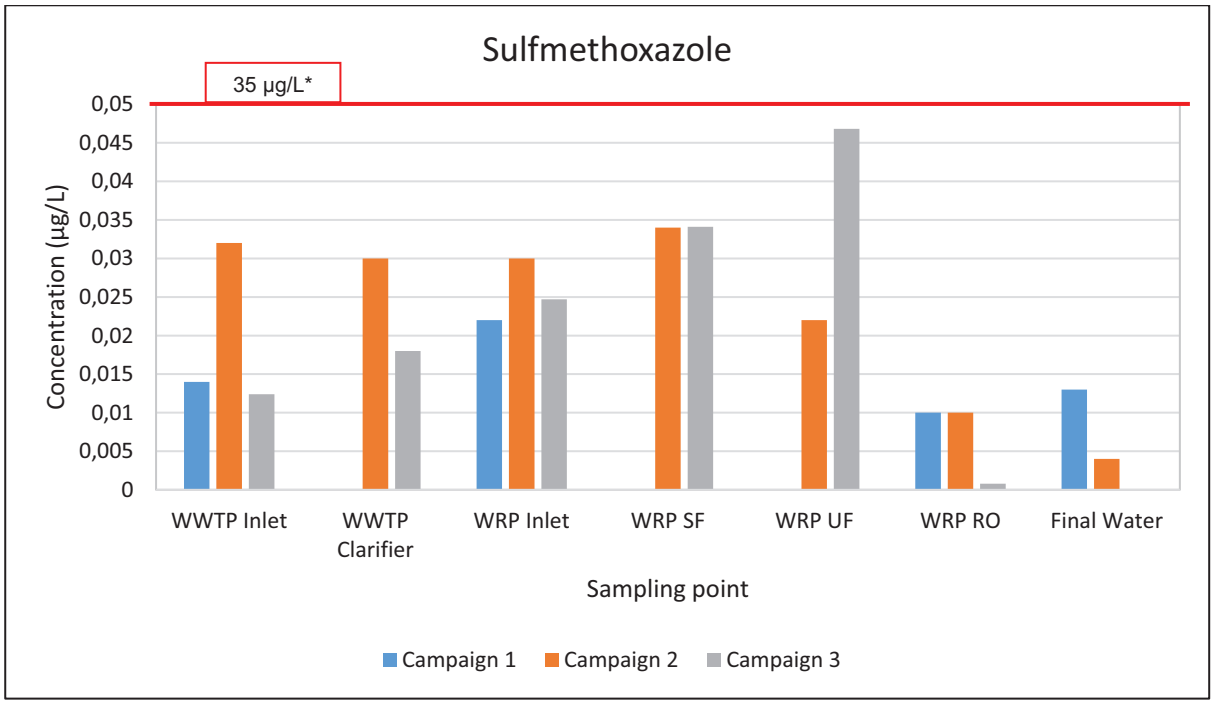

Figure 2-16: Sulfamethoxazole for all the sampling campaigns for WRP A. * Limit proposed for potable water (NRMMC, 2008 Guideline value)

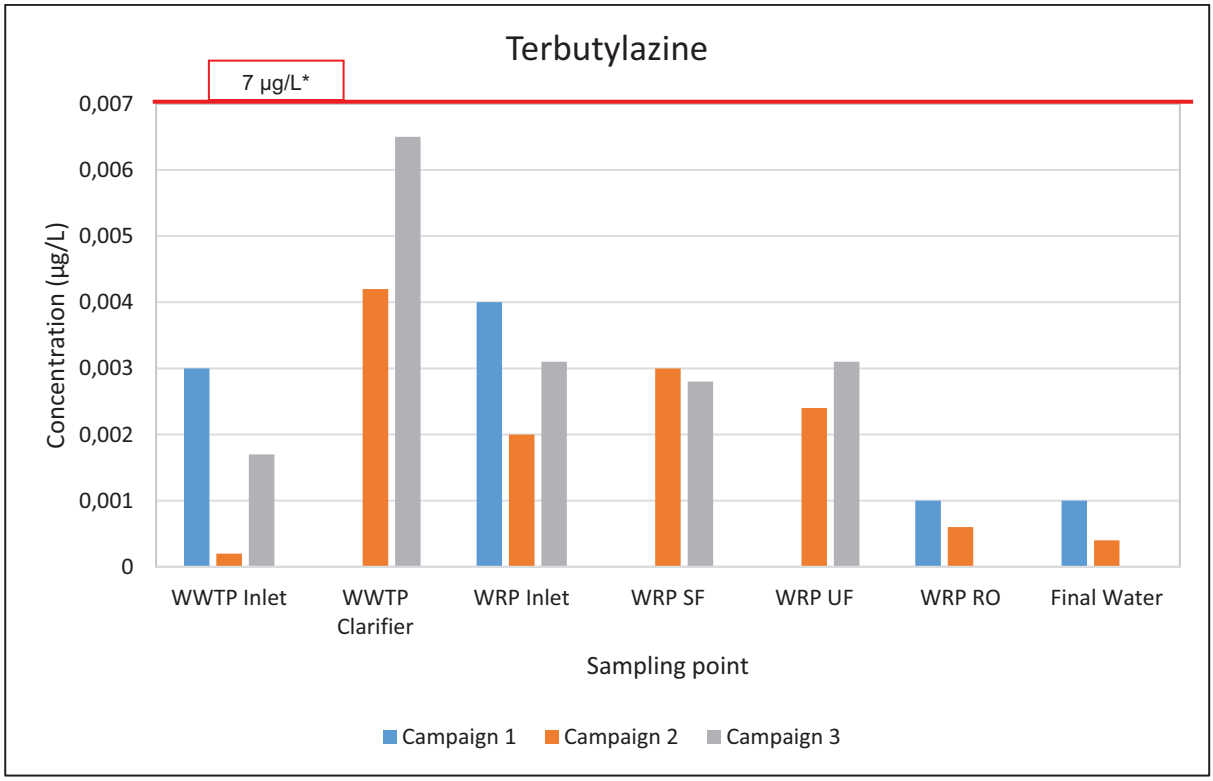

Figure 2-17: Terbuthylazine for all the sampling campaigns for WRP A. * Limit proposed for potable water (WHO, 2011c Guideline value)

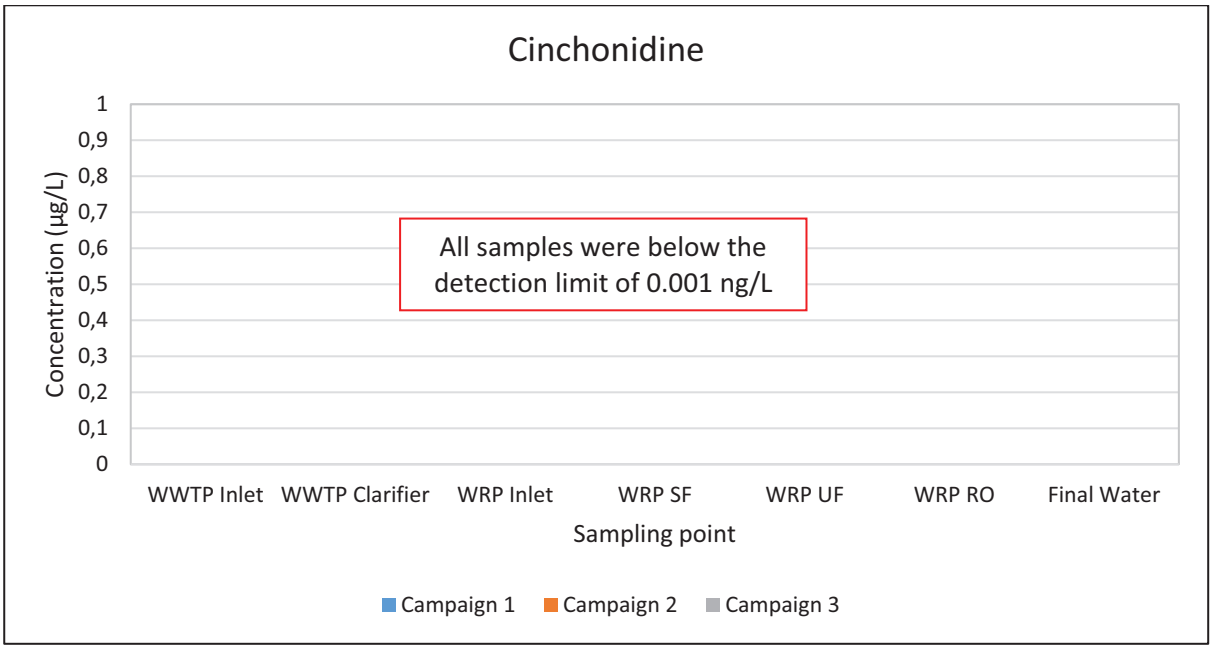

Figure 2-18: Cinchonidine for all the sampling campaigns for WRP A

2.2 WATER RECLAMATION PLANT B

2.2.1 Treatment System Description

This plant makes use of more conventional water reclamation process configuration that constituted the main process configuration up the middle 1990s when the application of membrane treatment systems commenced. What may once have been called a conventional reclamation design can now be referred to as alternative design since the previously mentioned dual-membrane system has become commonplace in recent years and can now be considered conventional. This alternative design receives secondary treated wastewater from a conventional WWTP making use of activated sludge followed by eight maturation ponds. The secondary treated wastewater enters the WRP and has a facility for dosing powder activated carbon (PAC) if required. The water then receives a pre-ozonation dose followed by coagulation and flocculation. As main solids removal process, the water is then treated using a dissolved air flotation (DAF) system, followed by sand filtration and the main ozonation step. After ozonation the water is passed through a single stage biological activated carbon (BAC), followed by a two-stage granular activated carbon (GAC) step. H_2O_2 (hydrogen peroxide) is available to dose before the BAC should the residual ozone be too high. Finally, the water is treated using UF membranes after which the water is stabilized and disinfected using chlorine gas.

2.2.2 Sampling Campaign 2

2.2.2.1 *Sampling*

The sampling performed at WRP B made use of the existing sampling infrastructure in place at the plant. The plant has been operating for almost 50 years and contains several sampling locations for each of the treatment units, most of which are connected to an automatic sampler that makes composite samples over 24-hour periods. These samples were collected during the second sampling campaign. After a sample has been taken it was immediately placed in a cooler box with ice packs in order to ensure that the samples remain at a temperature near 4°C. The majority of the samples were taken in class bottles with a foil cover underneath the lid to ensure that the sample never came in contact with any plastics that can interfere with the analyses.

2.2.2.2 *Sample analyses*

The analyses performed on the samples from the second sampling campaign are much more encompassing than the previous campaign. The following analyses were performed on the samples taken during the second sampling campaign:

- Macro-determinants: chemical and physical parameters (all samples)
  Ammonia, nitrate plus nitrite, DOC, TOC, EC, pH, COD, turbidity and UV_{254} absorbance.
- Perfluorinated compounds (PFCs) (all samples)
  Perfluoroheptanoic acid (PFHPA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorooctanesulfonate (PFOS), perfluorodecanoic acid (PFDA) and perfluoroundecanoic acid (PFUnDA)
- Priority CECs (all samples)
  Bisphenol A (BPA), triclosan, 17α ethinyl estradiol (EE2), acetaminophen, atrazine, imidacloprid, carbamazepine, lamivudine, simazine, sulfametoxazole, terbuthylazine and cinchonidine.

2.2.2.3 *Results of analyses for the second sampling campaign*

The results of the various analyses, as seen above, performed on the samples collected during the second sampling campaign can be seen in Table 2-9 (Macro-determinants chemical and physical parameters), Table 2-10 (PFCs) and Table 2-11 (Priority CECs).

Table 2-9: Macro-determinands chemical and physical parameters: Sampling campaign 2

Parameter	Unit	WWTP Inlet	WWTP Clarifier	WWTP Maturation Ponds	WRP SF	WRP Ozone	WRP GAC	WRP Final Water
pH	-	7.95	7.91	7.91	8.1	7.75	7.49	7.89
Conductivity	mS/m	195	160	158.75	186.25	180	178.75	186
NO3 as N	mg/L	0.5	7.7	11.55				12.75
NO2 as N	mg/L	0.08	0.21	0.05				0.05
Ammonia	mg/L	61	1.04	0.28				0.13
Ortho phosphate (P)	mg/L	4.8	1.6	3.15				0.23
TKN	mg/L	92	2.5	2.55				0.5
COD	mg/L	1020	42					
COD*	mg/L			34	20	18	9	11
DOC	mg/L			7.98	3.66	3.89	1.7	1.65
UV 254*	abs/cm			0.267	0.124	0.106	0.058	0.026
Turbidity	NTU			4.5	0.18	0.08	0.12	0.09

* Indicates samples that were filtered with a 0.45-micron filter before analysing

Table 2-10: Perfluorinated compounds results: Sampling campaign 2 (all units in ng/L)

Parameter	PFHPA	PFOA	PFNA	PFOS	PFDA	PFUnDA
WWTP Inlet	15.5	35.32	29.74	0.41	9.9	ND
WWTP Clarifier	12.8	18.27	7.98	1.32	5.19	ND
WRP Inlet	10.2	18.36	ND	ND	2.72	ND
After SF	11.2	20.89	ND	0.55	2.55	ND
After O_3	11.4	12.3	ND	1.42	ND	ND
After UF	10.5	8.9	ND	ND	ND	ND
Final water	8.35	3.14	ND	ND	ND	ND

Table 2-11: Priority CECs: Sampling campaign 2 (all units in µg/L)

Parameter	Bisphenol A	Triclosan	17 Alpha Ethynyl Estradiol	Acetaminophen	Atrazine	Imidacloprid	Carbamazepine	Lamivudine	Simazine	Sulfamethoxazole	Terbuthylazine	Cinchonidine
Limit of detection	0.01	0.001	0.008	0.001	0.0001	0.001	0.0002	0.001	0.002	0.001	0.0001	0.001
WWTP Inlet	nd	nd	3.9	0.008	0.0006	0.002	0.016	0.034	nd	0.01	0.0002	nd
WWTP Clarifier	nd	0.03	2.12	nd	0.0006	0.008	nd	nd	0.022	0.02	0.0004	nd
WRP Inlet	nd	0.032	2.28	nd	0.0006	0.004	0.074	nd	0.06	0.026	0.0004	nd
WRP SF	nd	0.01	1.962	nd	0.0004	0.004	0.03	nd	0.042	0.008	0.0004	nd
WRP O_3	nd	nd	0.078	nd	0.0004	nd	nd	nd	0.012	nd	0.0006	nd
WRP GAC	nd	nd	0.024	nd	0.0006	nd	nd	nd	nd	nd	0.0004	nd
Final Water	nd	nd	0.006	nd	0.0004	nd	nd	nd	nd	nd	0.0004	nd

2.2.3 Sampling Campaign 3

2.2.3.1 *Sampling*

The sampling performed at WRP B made use of the existing sampling infrastructure in place at the plant. The plant has been operating for almost 50 years and contains several sampling locations for each of the treatment units, most of which are connected to an automatic sampler that makes composite samples over 24-hour periods. These samples were collected during the second sampling campaign. After a sample has been taken it was immediately placed in a cooler box with ice packs in order to ensure that the samples remain at a temperature near 4°C. The majority of the samples were taken in class bottles with a foil cover underneath the lid to ensure that the sample never came in contact with any plastics that can interfere with the analyses.

2.2.3.2 *Sample analyses*

The analyses that were performed on the samples of the third sampling campaign were identical to the analyses performed on the samples from the second sampling campaign. Therefore, the following analyses were performed on the samples taken during the third sampling campaign:

- Macro-determinants: chemical and physical parameters (all samples)
  Ammonia, nitrate plus nitrite, DOC, TOC, EC, pH, COD, turbidity and UV_{254} absorbance.
- Perfluorinated compounds (PFCs) (all samples)
  Perfluoroheptanoic acid (PFHPA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorooctanesulfonate (PFOS), perfluorodecanoic acid (PFDA) and perfluoroundecanoic acid (PFUnDA)
- Priority CECs (all samples)
  Bisphenol A (BPA), triclosan, 17α ethinyl estradiol (EE2), acetaminophen, atrazine, imidacloprid, carbamazepine, lamivudine, simazine, sulfametoxazole, terbuthylazine and cinchonidine.

2.2.3.3

2.2.3.4 *Results of analyses for the third sampling campaign*

The results of the various analyses, as seen above, performed on the samples collected during the third sampling campaign can be seen in Table 2-12 (Macro-determinants chemical and physical parameters), Table 2-13 (PFCs) and Table 32-14 (Priority CECs).

Table 2-12: Macro-determinants chemical and physical parameters: Sampling campaign 3

Parameter	Unit	WWTP Inlet	WWTP Clarifier	WWTP Maturation Ponds	WRP SF	WRP Ozone	WRP GAC	WRP Final Water
pH	-	7.09	7.66	8.07	8.05	7.81	7.51	7.84
Conductivity	mS/m	193	165	153	173	170	165	173
NO3 as N	mg/L	0.5	7.5	6.4				6.6
NO2 as N	mg/L	0.05	0.37	0.15				0.05
Ammonia	mg/L	49	0.98	0.58				0.15
Ortho phosphate (P)	mg/L	5.6	0.37	0.47				0.23
TKN	mg/L	94	4.3	2.8				0.62
COD	mg/L	930	38					
COD*	mg/L			31	19	16		8.75
DOC	mg/L			7.63	3.55	3.67	1.50	1.50
UV 254*	abs/cm			0.249	0.118	0.062	0.023	0.022
Turbidity	NTU			3.10	0.127	0.065	0.356	0.122

* Indicates samples that were filtered with a 0.45 micron filter before analysing

Table 2-13: Perfluorinated compounds (PFCs) results: Sampling campaign 3 (all units in ng/L)

Parameter	PFHPA	PFOA	PFNA	PFOS	PFDA	PFUnDA
WWTP Inlet	31.49	15.71	8.47	7.43	6.01	ND
WWTP Clarifier	25.56	16.74	7.81	7.67	4.29	11.12
WRP Inlet	20.74	20.41	7	7.78	3.23	15.08
WRP SF	20.22	51.61	5.49	14.54	2.35	ND
WRP O_3	20.55	45.69	2.09	12.11	ND	ND
WRP GAC	18.77	35.59	2	18.34	ND	ND
Final Water	18.26	33.17	ND	12.23	ND	ND

Table 2-14: Priority CEC results: Sampling campaign 3 (all units in µg/L)

Parameter	Bisphenol A	Triclosan	17 Alpha Ethynyl Estradiol	Acetaminophen	Atrazine	Carbamazepine	Imidacloprid	Lamivudine	Simazine	Sulfamethoxazole	Terbuthylazine	Cinchonidine
Limit of detection	0.002	0.002	0.02	0.001	0.0001	0.002	0.0006	0.0006	0.001	0.0006	0.00006	0.002
WWTP Inlet	0.493	0.0113	1.47	0.0115	0.0005	0.0527	ND	0.029	0.0144	0.0191	0.0002	ND
WWTP Clarifier	0.0334	0.023	0.73	ND	0.0007	0.224	0.007	ND	0.0412	0.0234	0.001	ND
WRP Inlet	0.0184	0.0142	0.709	ND	0.0007	0.131	0.0088	ND	0.0445	0.0258	0.0012	ND
WRP SF	0.0253	0.0044	0.909		0.0006	0.0849	0.0077	ND	0.0346	0.0186	0.0012	ND
WRP O_3	0.01	ND	ND	ND	0.0003	0.0022	ND	ND	ND	ND	0.0005	ND
WRP GAC	0.0125	ND	ND	ND	0.0002	0.0019	ND	ND	ND	ND	0.0002	ND
Final Water	0.0088	ND	ND	ND	0.0002	0.0024	ND	ND	ND	ND	0.0005	ND

2.2.4 Comparison

Figures 2-19 to results of the second and third sampling campaigns for purposes of comparison.

2.2.4.1 *Perfluorinated Compounds*

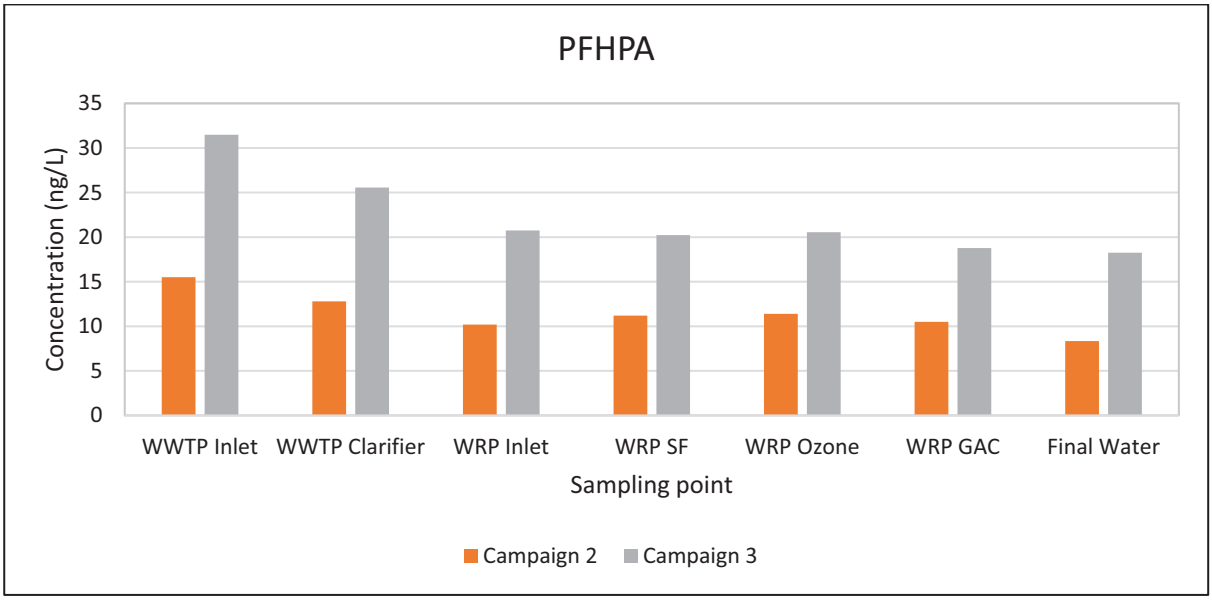

Figure 2-19: PFHPA for all the sampling campaigns for WRP B

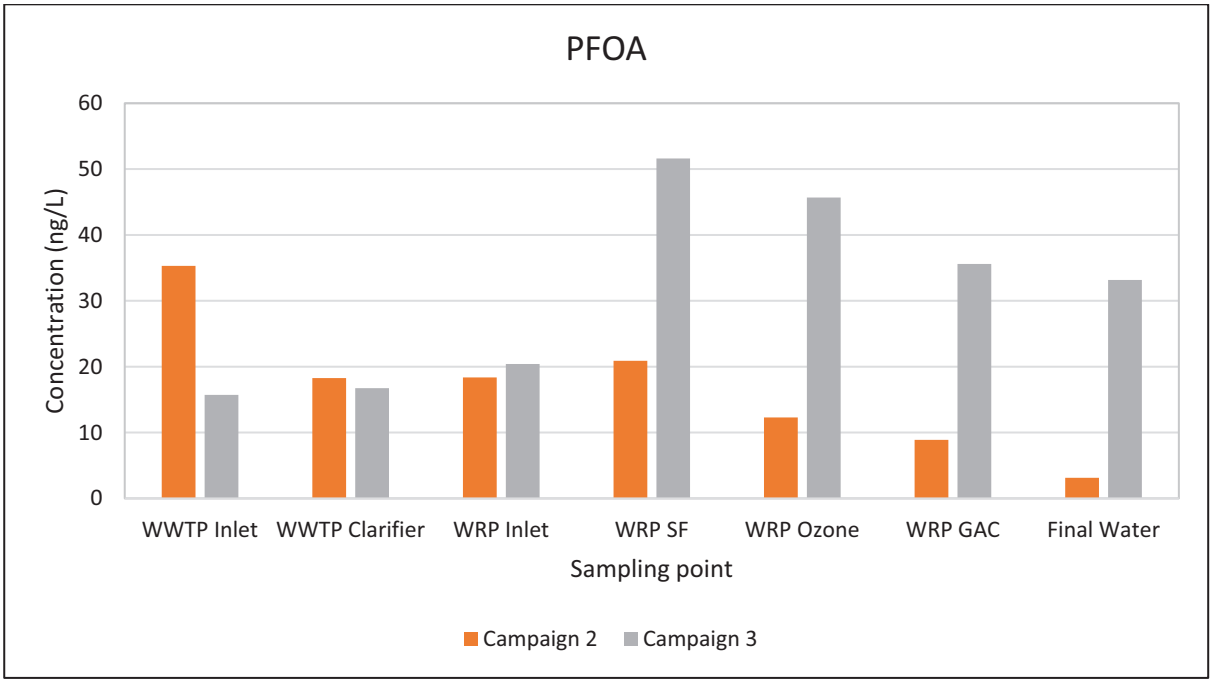

Figure 2-20: PFOA for all the sampling campaigns for WRP B

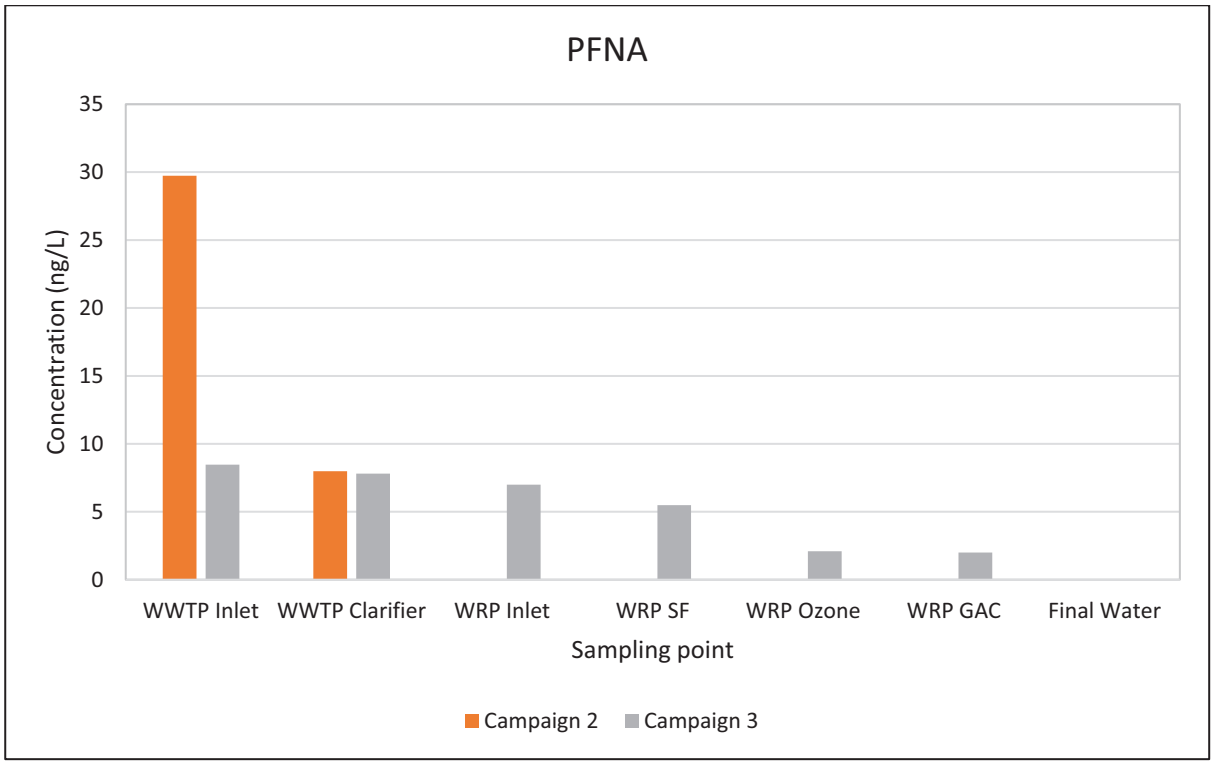

Figure 2-21: PFNA for all the sampling campaigns for WRP B

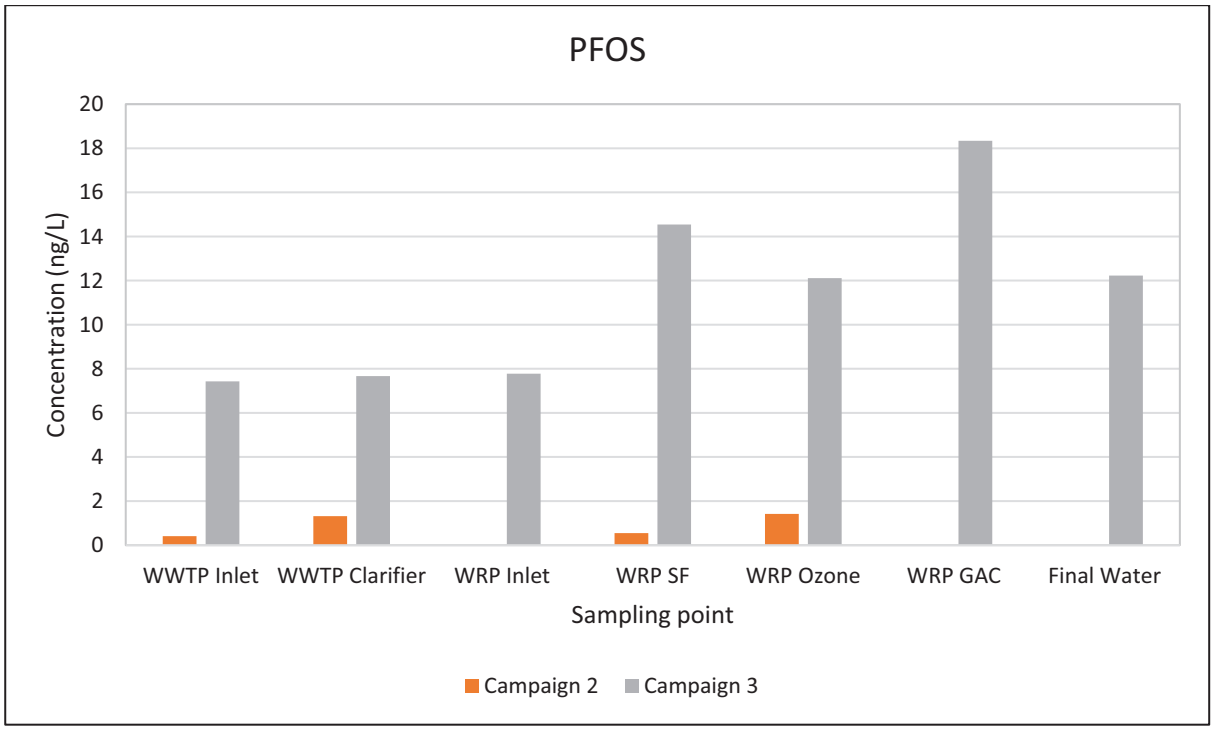

Figure 2-22: PFOS for all the sampling campaigns for WRP B

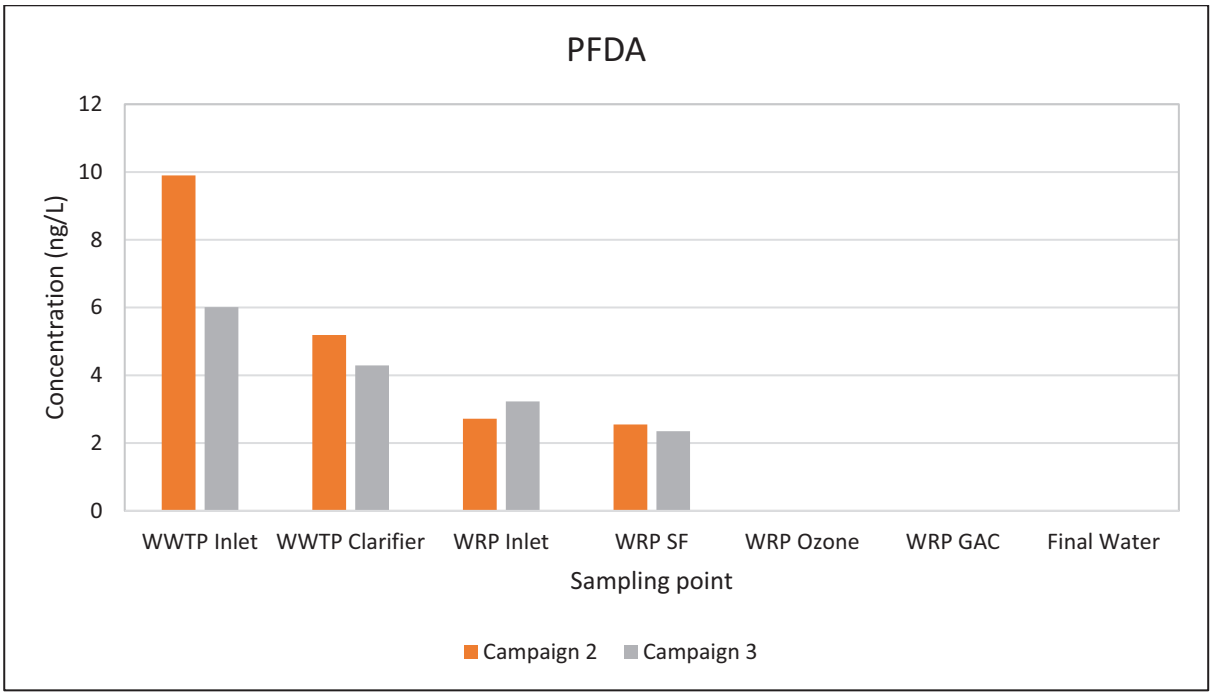

Figure 2-23: PFDA for all the sampling campaigns for WRP B

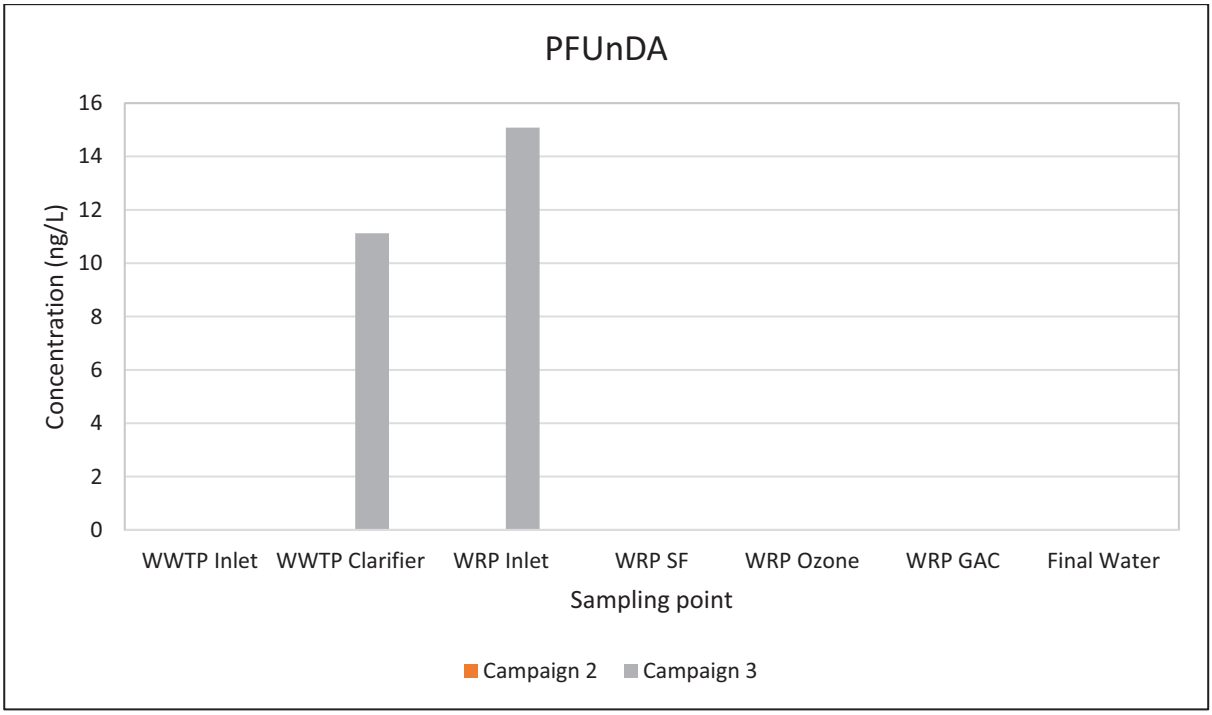

Figure 2-24: PFUnDA for all the sampling campaigns for WRP B

2.2.4.2 *Priority Chemicals of Emerging Concern*

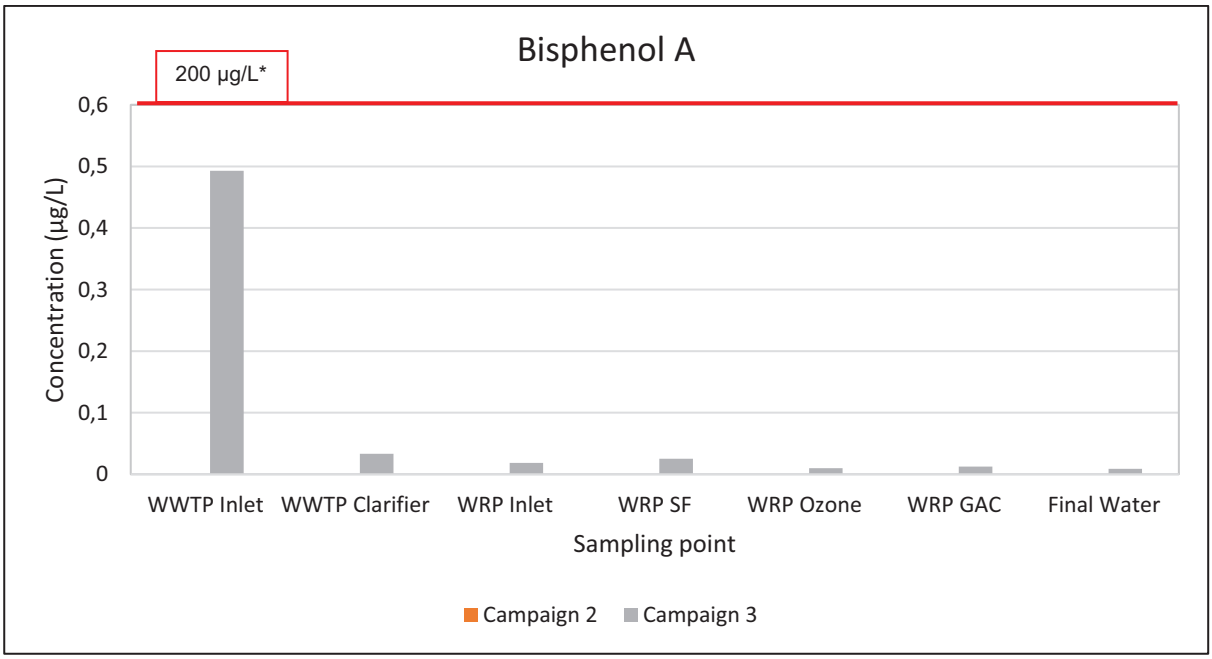

Figure 2-25: Bisphenol A for all the sampling campaigns for WRP B. * Limit proposed for potable water (NRMMC, 2008 Guideline value)

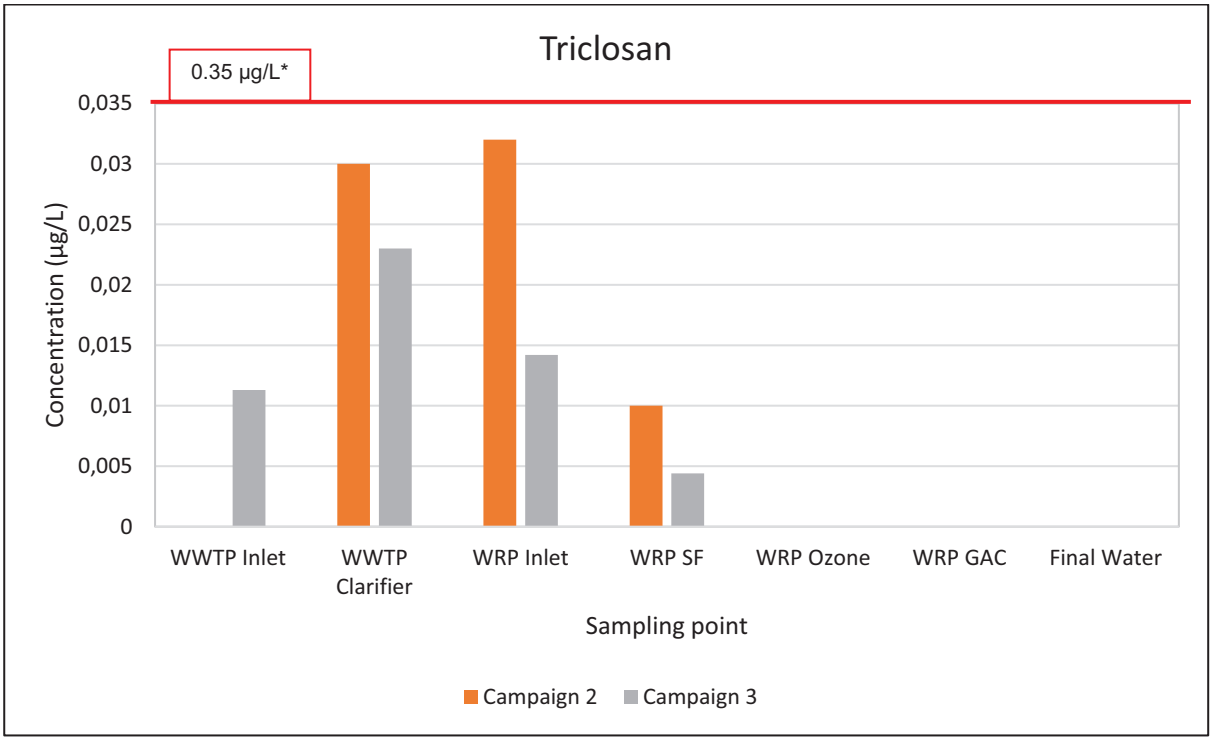

Figure 2-26: Triclosan for all the sampling campaigns for WRP B. * Limit proposed for potable water (NRMMC, 2008 Guideline value)

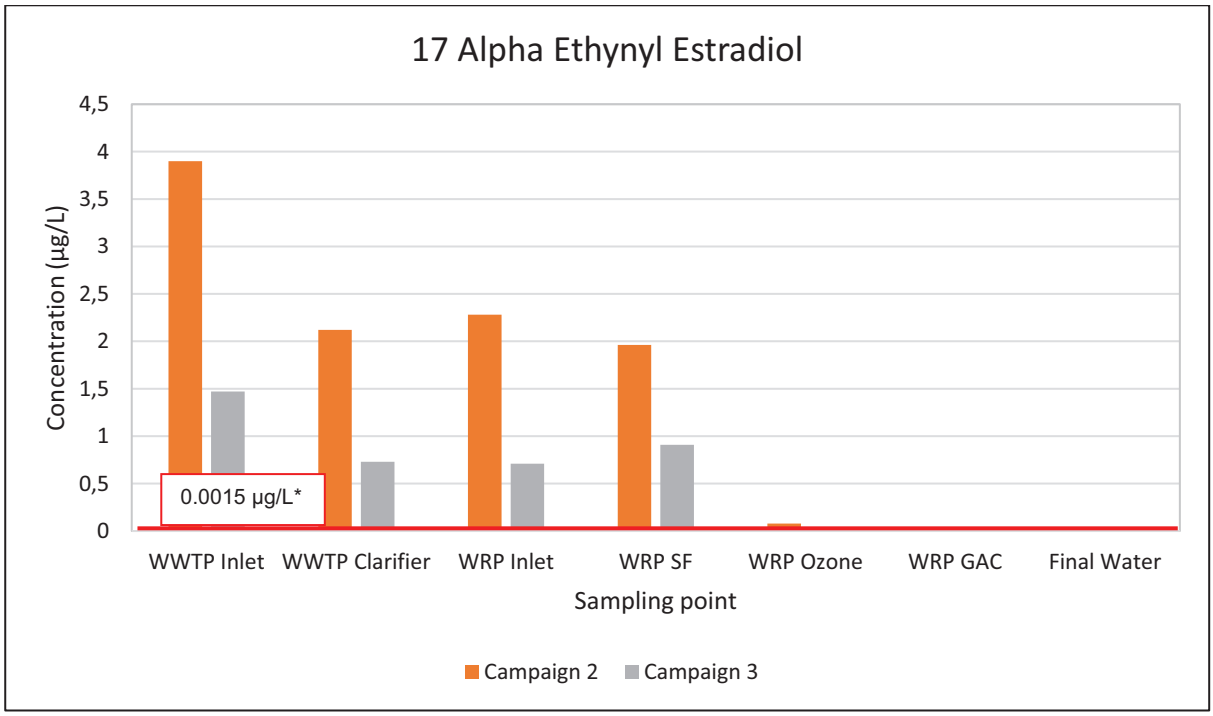

Figure 2-27: 17 Alpha Ethynyl Estradiol for all the sampling campaigns for WRP B. * Limit proposed for potable water (NRMMC, 2008 Guideline value)

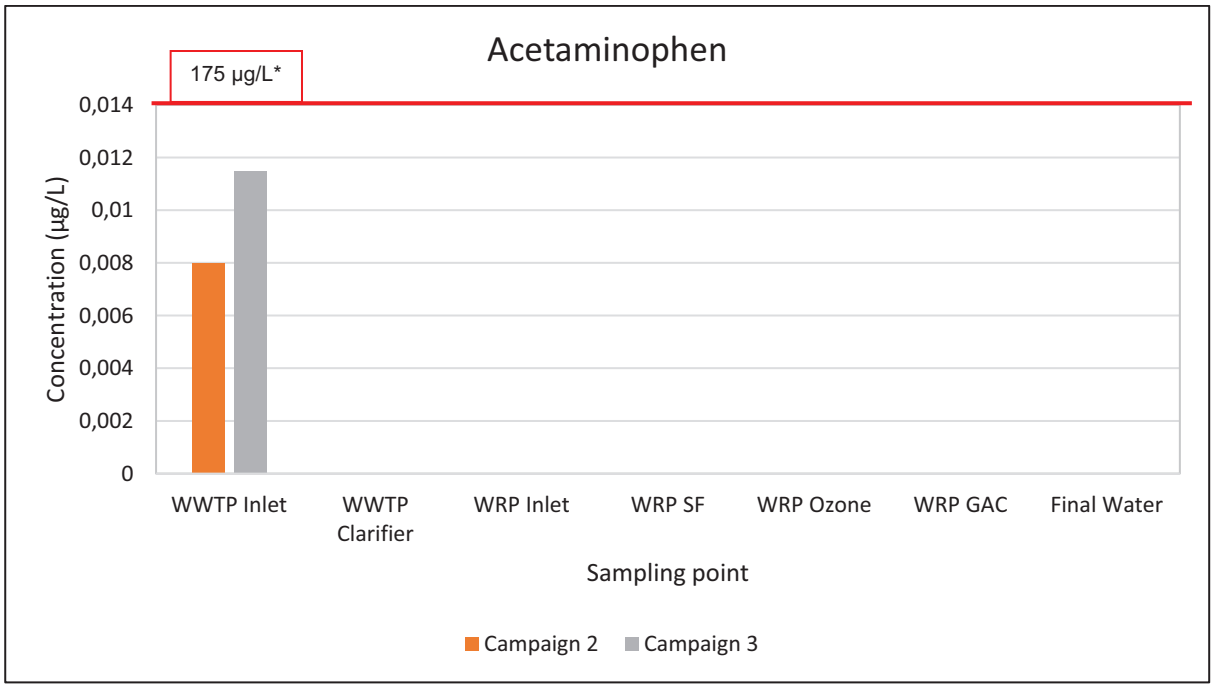

Figure 2-28: Acetaminophen for all the sampling campaigns for WRP B. * Limit proposed for potable water (NRMMC, 2008 Guideline value)

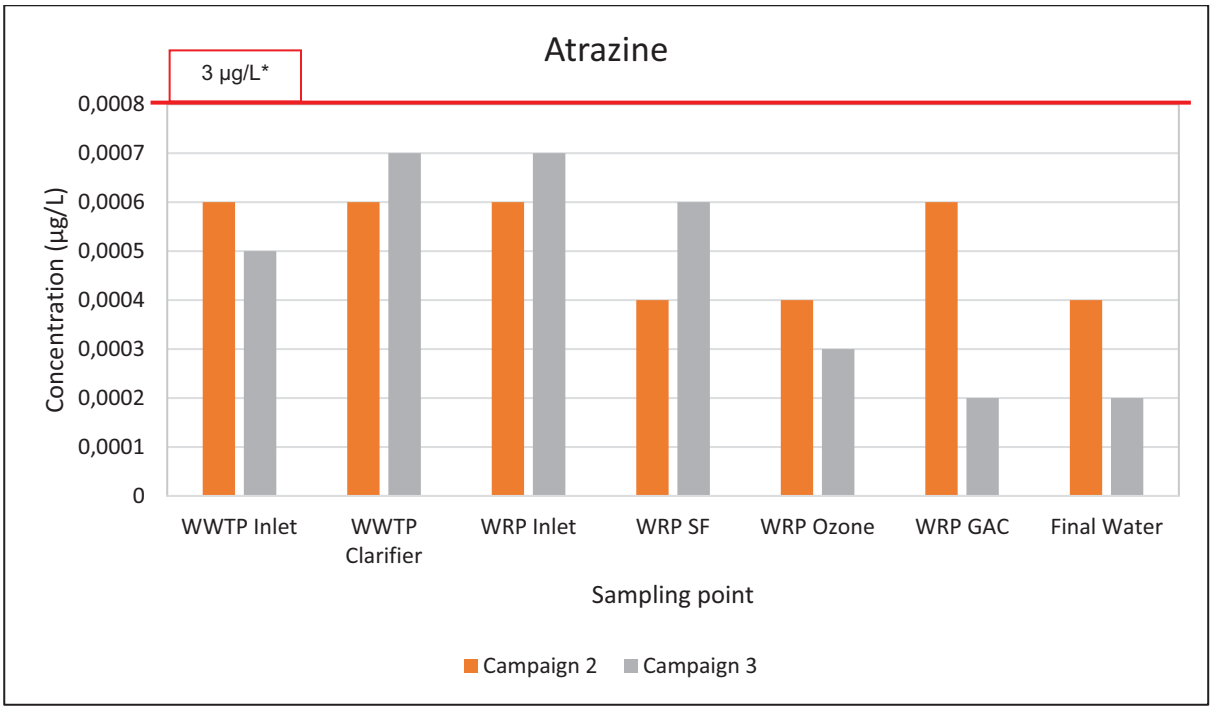

Figure 2-29: Atrazine for all the sampling campaigns for WRP B. * Limit proposed for potable water (EPA, 2012 California drinking water limits)

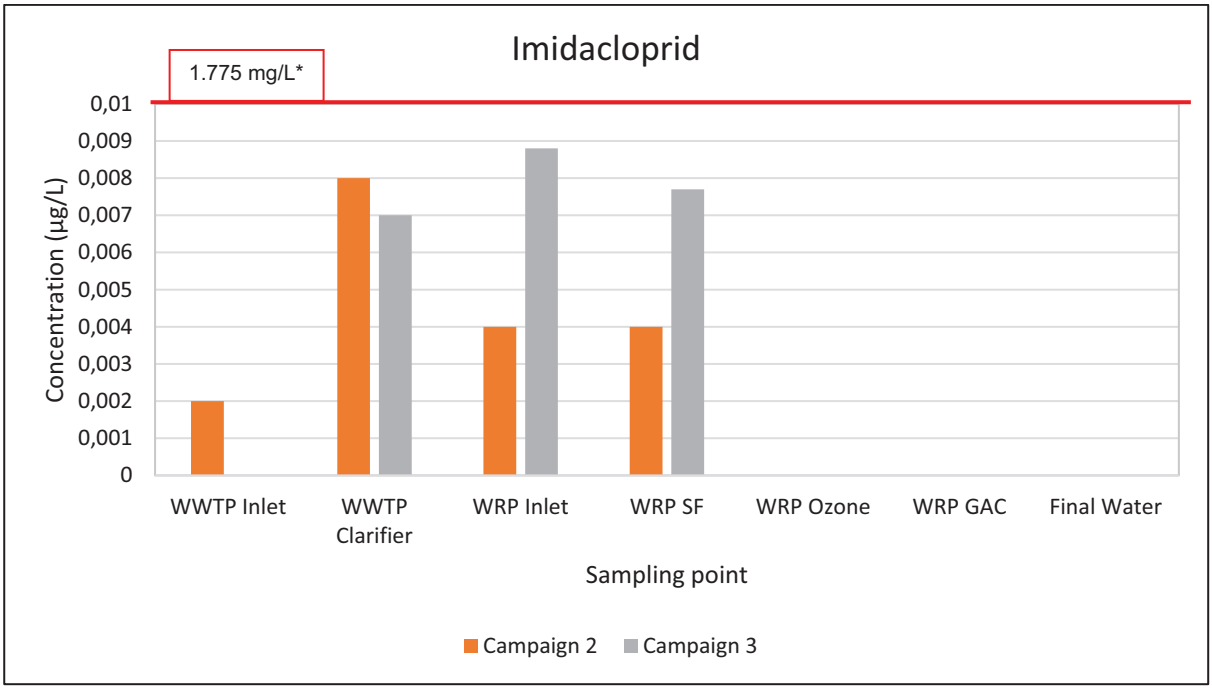

Figure 2-30: Imidacloprid for all the sampling campaigns for WRP B. * Limit proposed for potable water (EPA, 2005 California drinking water limits)

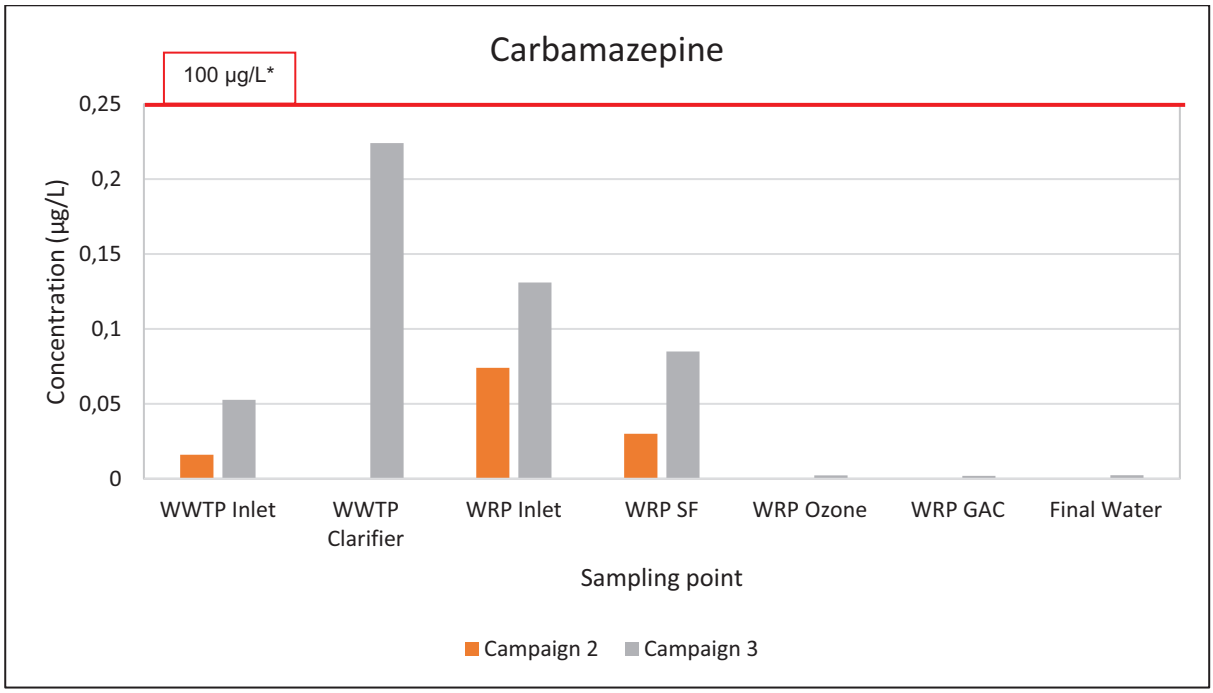

Figure 2-31: Carbamazepine for all the sampling campaigns for WRP B. * Limit proposed for potable water (NRMMC, 2008 Guideline value)

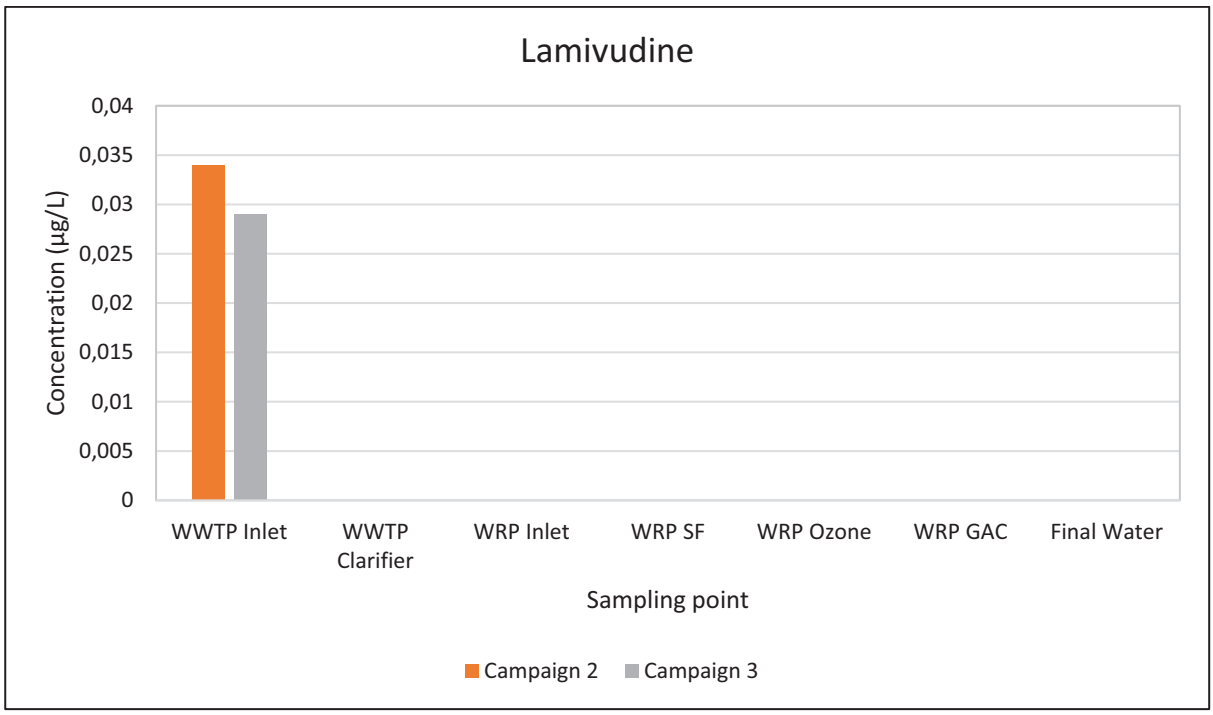

Figure 2-32: Lamivudine for all the sampling campaigns for WRP B

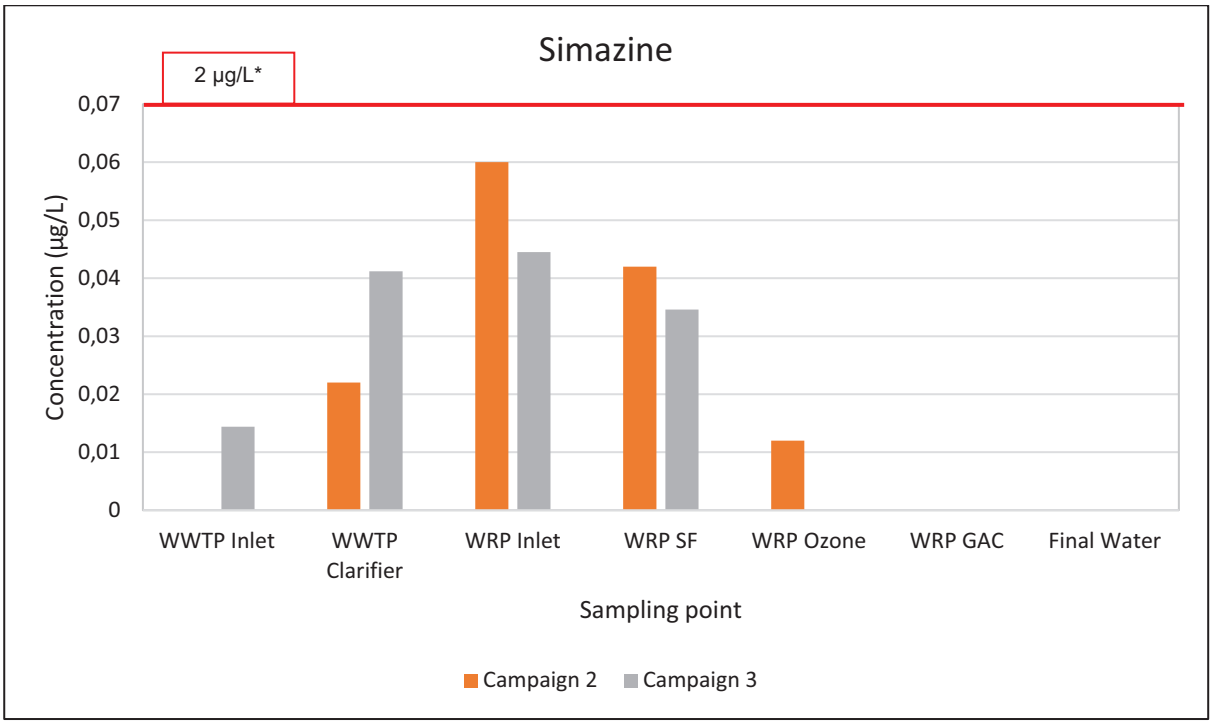

Figure 2-33: Simazine for all the sampling campaigns for WRP B. * Limit proposed for potable water (WHO, 2011c Guideline value)

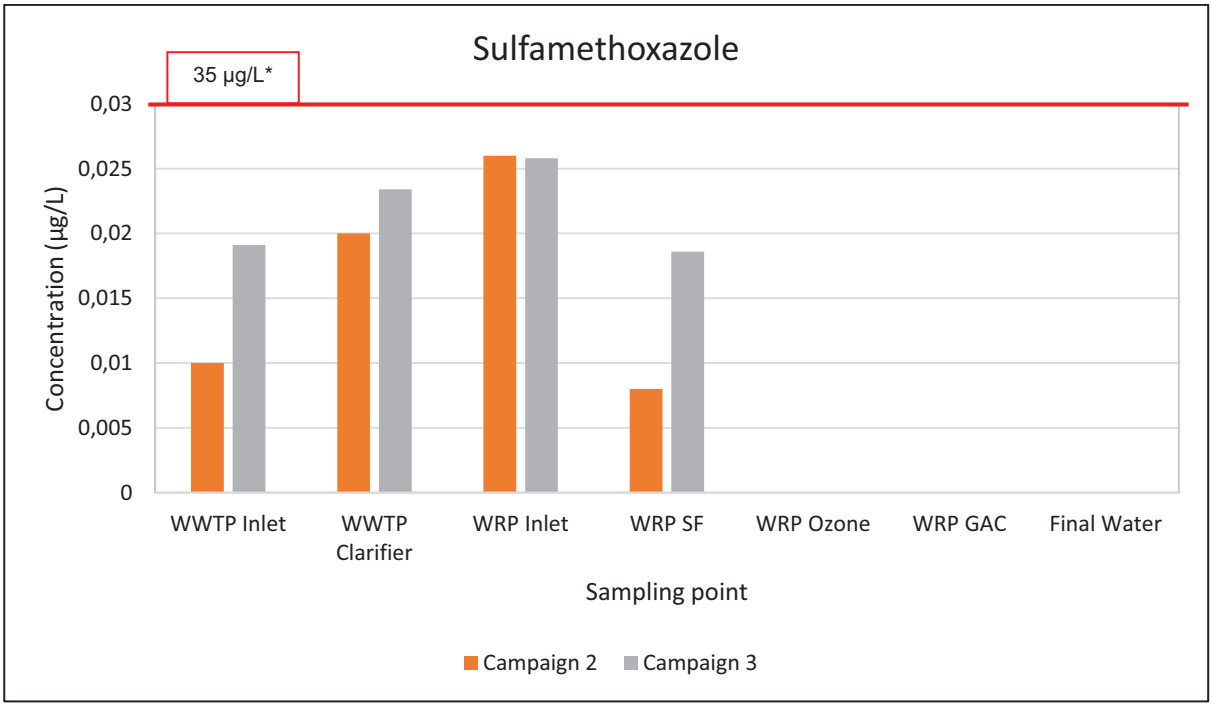

Figure 2-34: Sulphamethoxazole for all the sampling campaigns for WRP B. * Limit proposed for potable water (NRMMC, 2008 Guideline value)

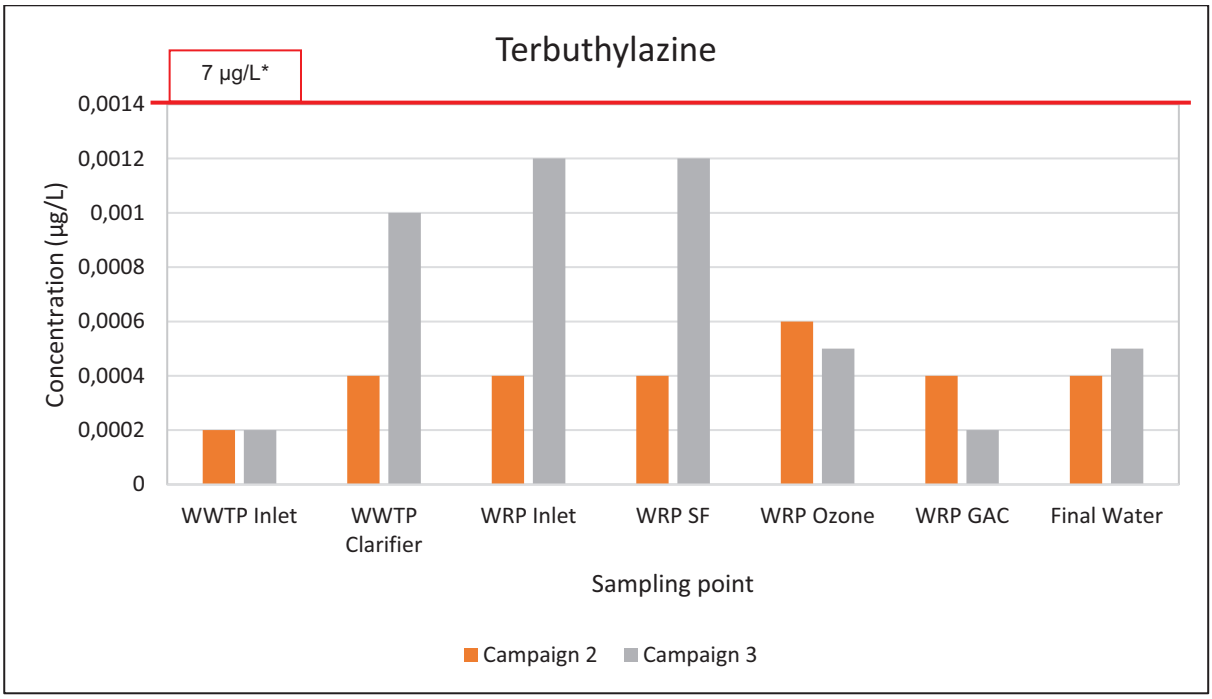

Figure 2-35: Terbuthylazine for all the sampling campaigns for WRP B. * Limit proposed for potable water (WHO, 2011c Guideline value)

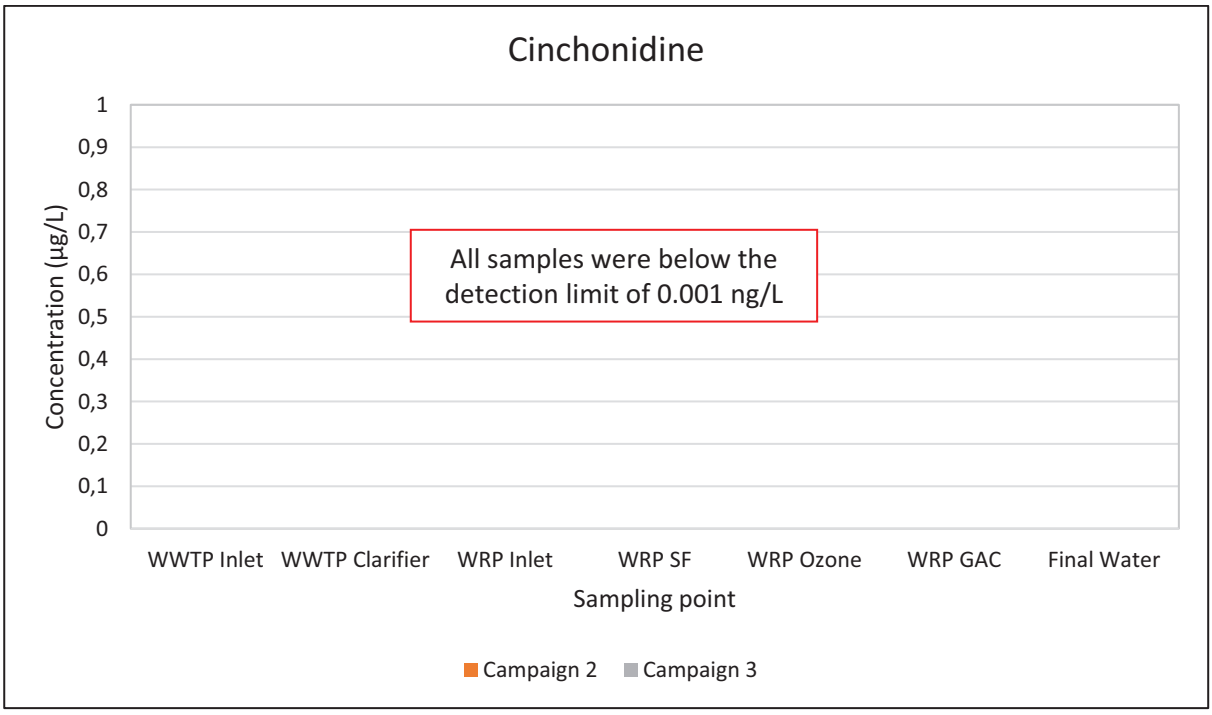

Figure 2-36: Cinchonidine for all the sampling campaigns for WRP B

2.3 WASTEWATER TREATMENT PLANT SYSTEMS

2.3.1 Description of the Wastewater Treatment Plants (WWTP)

WWTP C makes use of two parallel treatment trains; the one train is a conventional activated sludge process and the other train is an MBR system.

WWTP D comprises a conventional activated sludge treatment process.

WWTP E also makes use of three parallel treatment trains; two of the three treatment trains consists of conventional MLE activated sludge treatment processes, and the third train consists of a MBR process.

2.3.2 Sampling Campaign 1

2.3.2.1 *Sampling*

Grab samples were collected in triplicate at different stages of the wastewater treatment process (as indicated above). 1 litre samples were collected in methanol pre-washed air dried amber glass bottles with a foil cover underneath the lid to ensure that the sample never came in contact with any plastics that can interfere with the analyses.

Field blanks were also prepared by filling pre-washed glass bottles with MilliQ water, transported to the sampling site and transported back with the samples to the laboratory. The samples were kept cool *en route* to the laboratory in an ice box and was immediately transferred into a refrigerator upon arrival at the laboratory. The samples were kept at 4°C and analysed within 48 hours after sampling. In order to sample the WWTPs in question, it was decided to make as much use as possible, of the existing sampling infrastructure that exists on each of the plants. The WWTPs in question indicated that several 24h composite samples would be available, however, when the samples were collected it was discovered that a majority of the composite samplers were out of commission. The majority of the samples that were taken at the WWTPs were therefore grab samples, with only one or two composite samples being available.

2.3.2.2 *Sample analyses*

The following chemicals of emerging concern were analysed for in the samples from the three wastewater treatment plants:

- Perfluorinated Compounds

  Perfluorinated compounds (PFCs) such as perfluorooctanoic acid (PFOA) consist of fully fluorinated hydrophobic linear carbon chains attached to one or more hydrophilic groups, and are mostly used as industrial surfactants and surface protectors for paper, food containers, leather, carpets, upholstery and fabric. They are also use as additives, coating materials and fire-fighting foams because of their ability to repel water and oil. There is concern over the health risks on exposure to PFCs. The compounds are globally distributed, environmentally persistent, bioaccumulative, magnify in the food chain and potentially toxic. They are found in the environment as stable perfluorooctane sulfonate (PFOS), perfluorohexane sulfonate (PFHxS) and perfluorocarboxylic acids (PFCAs).

2.3.2.3 *Method of analyses*

Analytical methods for analysis of PFCs were developed and validated in this study using Solid Phase Extraction and UPLC/MS. The analyses performed on the samples from the sampling campaign were

aimed at identifying and quantifying several chemical compounds that form part of a group called perfluorinated compounds (PFCs). The compounds specifically analysed for are:

- Perfluoroheptanoic acid (PFHpA)
- Perfluorooctanoic acid (PFOA)
- Perfluorononanoic acid (PFNA)
- Perfluorooctanesulfonate (PFOS)
- Perfluorodecanoic acid (PFDA)
- Perfluoroundecanoic acid (PFUnDA)
- Total PFCs

2.3.2.4 *Results of analyses for the first sampling campaign*

The results of the PFC analyses, as seen above, performed on the samples collected during the first sampling campaign can be seen in Table 2-15 (PFCs).

Table 2-15: Results of analysis of PFCs, bisphenol A and acetaminophen in Wastewater Treatment Plants A, B and C

Treatment Plant	Sample point	PFHPA	PFOA	PFNA	PFOS	PFDA	PFUnDA
		(ng/ℓ)					
WWTP C	Influent	22.78	2.59	32.3	9.50	3.25	3. 23
	After aerobic treatment	9.21	2.32	19.84	9.30	1.87	2.67
	Maturation pond effluent	8.21	7.34	15.52	10.20	nd	1.03
	Effluent (after chlorination)	7.62	7.22	10. 2	10.24	nd	nd
WWTP D	Influent	6.10	3.17	nd	nd	nd	4.22
	Effluent	nd	4.01	nd	1.02	nd	1.13
WWTP E	Influent	48.53	7.32	10.2	nd	nd	nd
	MBR	nd	5.62	10.5	nd	nd	nd

2.3.3 Sampling Campaign 2

2.3.3.1 *Sampling*

The sampling procedure for the second sampling campaign was the same as the sampling procedure for the first sampling campaign. Again only a few of the composite samples were available. The sampling was also carried out at the same time of day as the first sampling campaign.

2.3.3.2 *Sample analyses*

The analyses performed on the samples from the second sampling campaign are much more encompassing than the previous campaign. The following analyses were performed on the samples taken during the second sampling campaign:

- Macro-determinants: chemical and physical parameters (all samples)
  Ammonia, nitrate plus nitrite, DOC, TOC, EC, pH, COD, turbidity and UV_{254} absorbance.
- Perfluorinated compounds (PFCs) (all samples)

Perfluoroheptanoic acid (PFHPA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorooctanesulfonate (PFOS), perfluorodecanoic acid (PFDA) and perfluoroundecanoic acid (PFUnDA)

- Priority CECs (all samples)
  Bisphenol A (BPA), triclosan, 17α ethinyl estradiol (EE2), acetaminophen, atrazine, imidacloprid, carbamazepine, lamivudine, simazine, sulfametoxazole, terbuthylazine and cinchonidine.

2.3.3.3 *Results of analyses for the second sampling campaign*

The results of the various analyses, as seen above, performed on the samples collected during the second sampling campaign can be seen in Table 2-16 and Table 2-17 (Macro-determinants chemical and physical parameters), Table 2-18 (PFCs), Table 2-19 and Table 2-20 (Priority CECs).

Table 2 16: Macro-determinants chemical and physical parameters for WWTP D and WWTP E

Analysis	Unit	WWTP D Raw	WWTP D Clarifier	WWTP D Final effluent	WWTP E Raw WW	WWTP E MBR Out
Ammonia	mg/L	65	1.3	0.14	57	11
Nitrate + Nitrite	mg/L	<0.1	3.1	4.1	<0.1	0.4
DOC	mg/L	77	9	7.3	90	8.8
EC	mS/m	94	49	48	100	68
pH		7.3	7.2	7.4	7.1	7.6
COD	mg/L	104	26	23	804	18
UV (254nm)	Abs			0.151		

Table 2-17: Macro-determinants chemical and physical parameters for WWTP C

Analysis	Unit	WWTP C AS Raw	WWTP C MBR Raw	WWTP C AS Out	WWTP C MBR Out	WWTP C Combined Final
Ammonia	mg/L	69	43	2.7	<0.05	4.3
Nitrate + Nitrite	mg/L	<0.1	<0.1	8.7	8.5	7.7
DOC	mg/L	106	51	10	9.5	9.9
EC	mS/m	116	100	86	62	90
pH		7.3	7.5	7.5	7.3	7.7
COD	mg/L	882	361	23	18	25
UV (254nm)	Abs					0.254

Table 2-18: Perfluorinated compounds (PFCs): Sampling campaign 2 (all units in ng/L)

Parameter	PFHPA	PFOA	PFNA	PFOS	PFDA	PFUnDA
WWTP C MBR Raw	96.7	24.19	51.46	nd	5.5	12.2
WWTP C MBR Final	38.8	37.89	31.64	nd	1	nd
WWTP C AS Raw	31.6	14.02	21.76	nd	4.9	2.1
WWTP C AS Final	17.5	11.5	8	nd	nd	1.3
WWTP C Combined final	22.9	88.5	8.7	nd	0.3	1.15
WWTP D RAW WW	14.25	40.73	18.73	nd	9.4	nd
WWTP D Clarifier	13.48	43.12	15.7	nd	7.5	nd
WWTP D Final Effluent	8.22	46.27	13.73	nd	0.2	nd
WWTP E RAW WW	19.04	28.83	22.35	nd	4.3	nd
WWTP E MBR	7.47	16.71	4.27	nd	0.35	nd

Table 2-19: Priority CECs for WWTP C: Sampling campaign 2 (all units in µg/L)

Parameter	Bisphenol A	Triclosan	17 Alpha Ethynyl Estradiol	Acetaminophen	Atrazine	Imidacloprid	Carbamazepine	Lamivudine	Simazine	Sulfamethoxazole	Terbuthylazine	Cinchonidine
Limit of detection	0.01	0.001	0.008	0.001	0.0001	0.001	0.0002	0.001	0.002	0.001	0.0001	0.001
WWTP C MBR Raw	0.802	ND	4.24	0.008	0.018	0.032	0.032	0.004	0.896	0.004	0.0244	nd
WWTP C AS Raw	6.56	0.004	2.08	0.08	0.166	0.06	0.06	0.004	11.66	0.004	0.736	nd
WWTP C MBR Final	0.342	0.092	1.828	nd	0.022	0.122	0.122	nd	0.832	0.004	0.148	nd
WWTP C AS Final	nd	0.052	1.528	nd	0.226	0.156	0.156	nd	7.56	0.01	0.532	nd
WWTP C Combined Final	0.14	0.04	1.352	nd	0.196	0.306	0.126	nd	6.1	0.01	0.55	nd

Table 2-20: Priority CECs for WWTP D and WWTP E WWTPs: Sampling campaign 2 (all units in µg/L)

Parameter	Bisphenol A	Triclosan	17 Alpha Ethynyl Estradiol	Acetaminophen	Atrazine	Imidacloprid	Carbamazepine	Lamivudine	Simazine	Sulfamethoxazole	Terbuthylazine	Cinchonidine
Limit of detection	0.01	0.001	0.008	0.001	0.0001	0.001	0.0002	0.001	0.002	0.001	0.0001	0.001
WWTP D Raw In	0.122	0.014	2.82	0.008	0.002	nd	0.04	0.028	0.318	0.002	0.001	nd
WWTP D AS Clarifier	0.066	0.02	1.722	nd	0.004	0.004	0.132	nd	2.46	0.042	0.012	nd
WWTP D MBR Final	0.082	0.016	2	nd	0.004	0.004	0.118	nd	2.66	0.012	0.0122	nd
WWTP E Raw WW	0.802	nd	6	nd	0.006	0.014	0.104	0.0526	0.234	0.014	0.0028	nd
WWTP E MBR Out	0.054	0.05	1.96	nd	0.004	0.002	0.288	nd	0.362	0.05	0.0122	nd

2.3.4 Sampling Campaign 3

2.3.4.1 *Sampling*

The sampling procedure for the third sampling campaign was the same as the sampling procedure for the first and second sampling campaigns. Again only a few of the composite samples were available. The sampling was also carried out at the same time of day as the first and sampling campaigns.

2.3.4.2 *Sample analyses*

The following analyses were performed on the samples taken during the second sampling campaign:

- Macro-determinants: chemical and physical parameters (all samples)
  Ammonia, nitrate plus nitrite, DOC, TOC, EC, pH, COD, turbidity and UV_{254} absorbance.
- Perfluorinated compounds (PFCs) (all samples)
  Perfluoroheptanoic acid (PFHPA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorooctanesulfonate (PFOS), perfluorodecanoic acid (PFDA) and perfluoroundecanoic acid (PFUnDA)
- Priority CECs (all samples)
  Bisphenol A (BPA), triclosan, 17α ethinyl estradiol (EE2), acetaminophen, atrazine, imidacloprid, carbamazepine, lamivudine, simazine, sulfametoxazole, terbuthylazine and cinchonidine.

2.3.4.3 *Results of analyses for the third sampling campaign*

The results of the various analyses, as seen above, performed on the samples collected during the second sampling campaign can be seen in Table and Table (Macro-determinants chemical and physical parameters), Table 2.23 (PFCs), Table 2-25 and Table 2-24 (Priority CECs).

Table 2-21: Macro-determinants chemical and physical parameters for WWTP E and WWTP D

Analysis	Unit	WWTP D Raw	WWTP D Clarifier	WWTP D Final effluent	WWTP E Raw WW	WWTP E MBR Out
Ammonia	mg/L	27	0.99	0.94	53	0.13
Nitrate	mg/L	<0.1	2	1.7	<0.1	9.1
DOC	mg/L	63	7.4	6.9	106	7.5
EC	mS/m	58	45	44	96	56
pH	-	7	7.5	7.5	7	7.2
COD	mg/L	443	22	21	969	21
UV 254nm	Abs			0.164		

Table 2-22: Macro-determinants chemical and physical parameters for WWTP C

Analysis	Unit	WWTP C AS Raw	WWTP C MBR Raw	WWTP C AS Out	WWTP C MBR Out	WWTP C Combined Final
Ammonia	mg/L	59	68	0.24	0.06	2.9
Nitrate	mg/L	<0.1	<0.1	1.4	4.9	2.9
DOC	mg/L	63	79	9.6	7.9	9.9
EC	mS/m	106	104	82	82	86
pH	-	7.3	7.3	7.5	7.4	7.8
COD	mg/L	1147	1028	39	22	31
UV 254nm	Abs					0.22

Table 2-23: Perfluorinated compounds: Sampling campaign 3 (all units in ng/L)

Parameter	PFHPA	PFOA	PFNA	PFOS	PFDA	PFUnDA
WWTP C MBR Raw	22.68	9.62	45.38	0.62	3.39	nd
WWTP C MBR Final	20.33	5.54	43.78	nd	0.28	nd
WWTP C AS Raw	44.66	15	7.78	nd	4.16	nd
WWTP C AS Final	31.77	10.01	6.96	nd	3.68	nd
WWTP C Combined final	37.14	13.31	6.48	nd	3.39	nd
WWTP D Raw WW	26.17	6.31	3.32	nd	3.03	nd
WWTP D Clarifier	18.32	19.41	3.1	nd	2.64	nd
WWTP D Final Effluent	14.92	22.33	4.581	nd	2.19	nd
WWTP E Raw WW	39.99	13.79	6.336	nd	3.615	nd
WWTP E MBR	34.51	12.79	6.1	3.11	3.83	10.122

Table 2-24: Priority CECs for WWTP C: Sampling campaign 3 (all units in µg/L)

Parameter	Bisphenol A	Triclosan	17a-ethynyl estradiol	Acetaminophen	Atrazine	Imidacloprid	Carbamazepine	Lamivudine	Simazine	Sulfamethoxazole	Terbuthylazine	Cinchonidine
Limit of detection	0.002	0.002	0.02	0.001	0.0001	0.0006	0.002	0.0006	0.001	0.0006	0.00006	0.002
WWTP C MBR Raw	44.3	0.0417	1.16	nd	0.0111	0.39	0.391	0.0037	5.04	0.0057	0.158	nd
WWTP C AS Raw	10.8	0.0799	2.09	nd	0.0049	0.064	0.147	0.0029	0.451	nd	0.019	nd
WWTP C MBR Final	0.0232	0.0227	0.789	nd	0.0298	5.66	0.651	nd	10.1	0.0109	0.34	nd
WWTP C AS Final	0.115	0.0468	1.63	nd	0.0148	1.67	0.55	nd	4.35	0.0104	0.346	nd
WWTP C Combined Final	0.0417	0.0332	0.935	nd	0.0583	2.69	0.475	nd	21.9	0.0124	0.388	nd

Table 2-25: Priority CECs for WWTP E and WWTP D: Sampling campaign 3 (all units in µg/L)

Parameter	Bisphenol A	Triclosan	17a-ethynyl estradiol	Acetaminophen	Atrazine	Imidacloprid	Carbamazepine	Lamivudine	Simazine	Sulfamethoxazole	Terbuthylazine	Cinchonidine
Limit of detection	0.002	0.002	0.02	0.001	0.0001	0.0006	0.002	0.0006	0.001	0.0006	0.00006	0.002
WWTP D Raw In	0.611	0.0089	1.65	nd	0.0046	nd	0.0236	0.018	0.0737	0.0224	0.0011	nd
WWTP D AS Clarifier	0.0258	0.0164	0.906	nd	0.0053	0.0033	0.186	nd	0.257	0.0277	0.0132	nd
WWTP D MBR Final	0.0268	0.0114	0.776	nd	0.0052	0.004	0.194	nd	0.268	0.0256	0.0139	nd
WWTP E Raw WW	0.677	0.018	2.63	0.0177	0.0056		0.055	0.0189	0.113	ND	0.0044	nd
WWTP E MBR Out	nd	0.0386	0.507	0.0171	0.0082	0.0071	0.26	nd	0.282	0.0139	0.0587	nd

2.3.5 Comparison

2.3.5.1 *Perfluorinated Compounds*

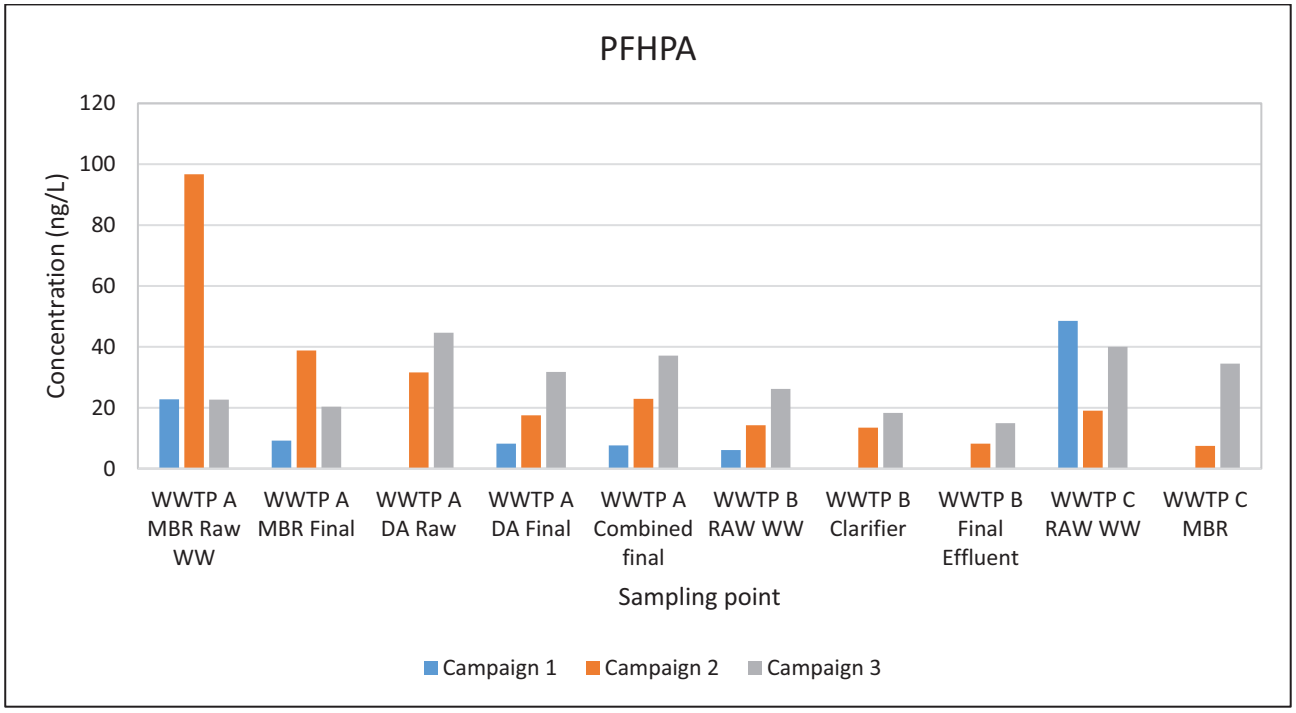

Figure 2-37: PFHPA for all the sampling campaigns for all WWTP samples

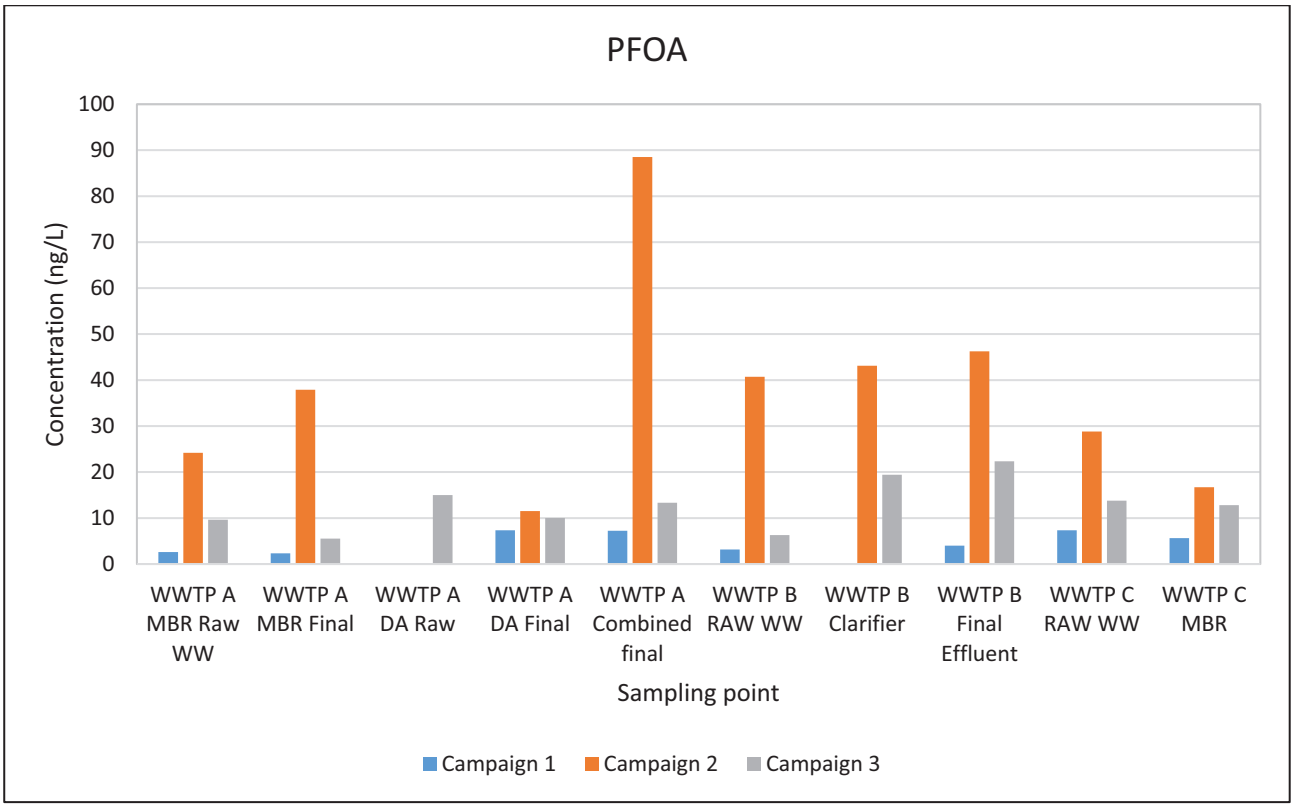

Figure 2-38: PFOA for all the sampling campaigns for all WWTP samples

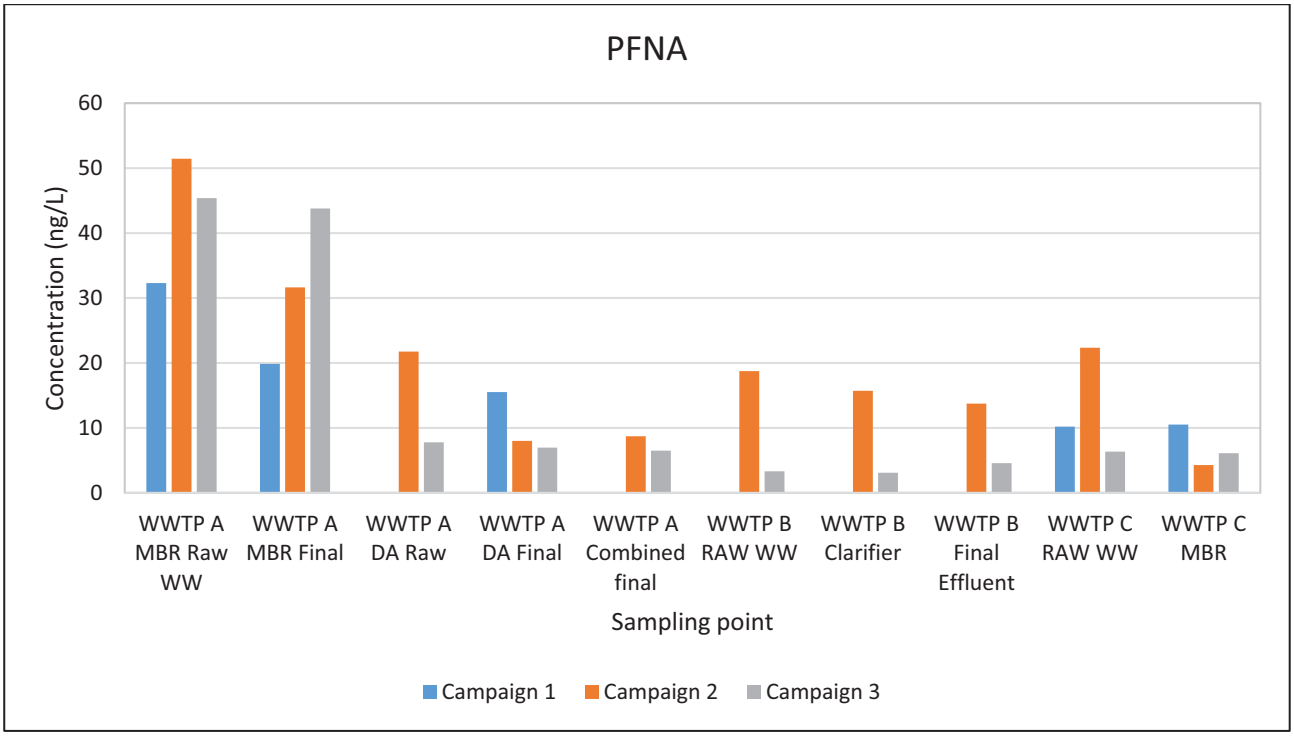

Figure 2-39: PFNA for all the sampling campaigns for all WWTP samples

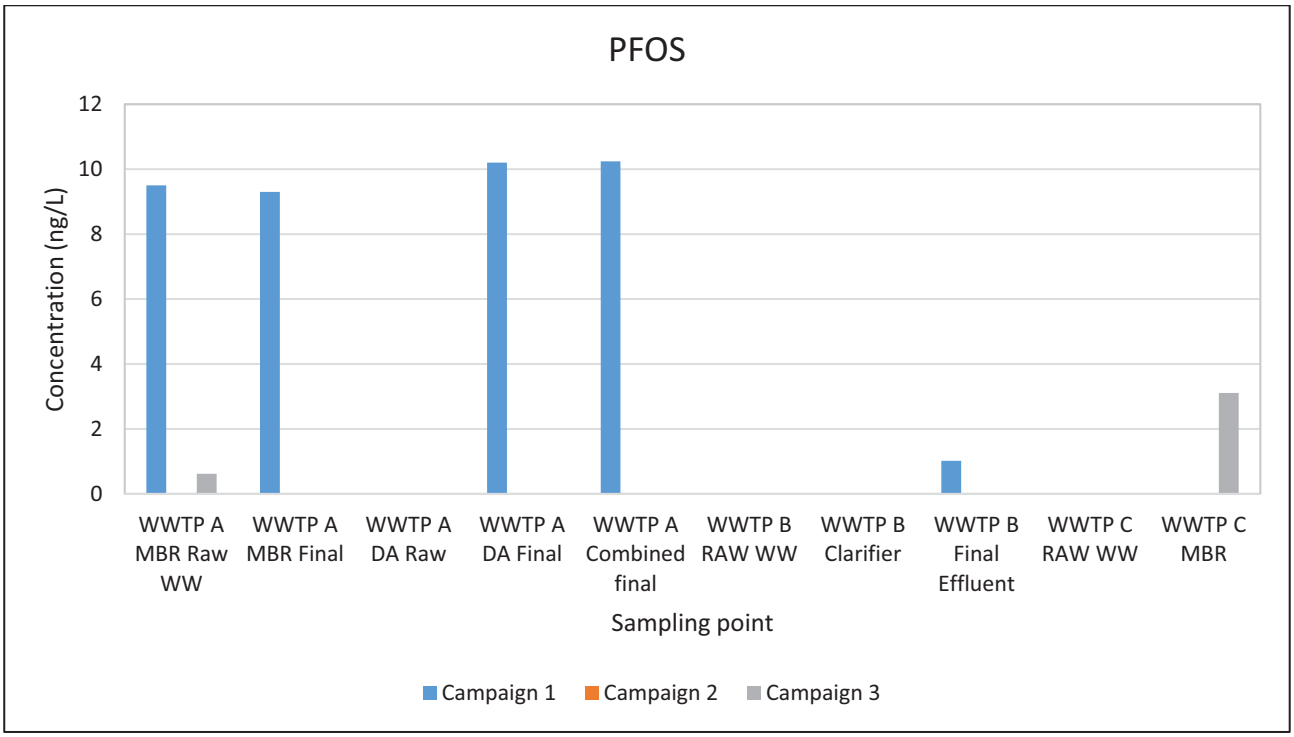

Figure 2-40: PFOS for all the sampling campaigns for all WWTP samples

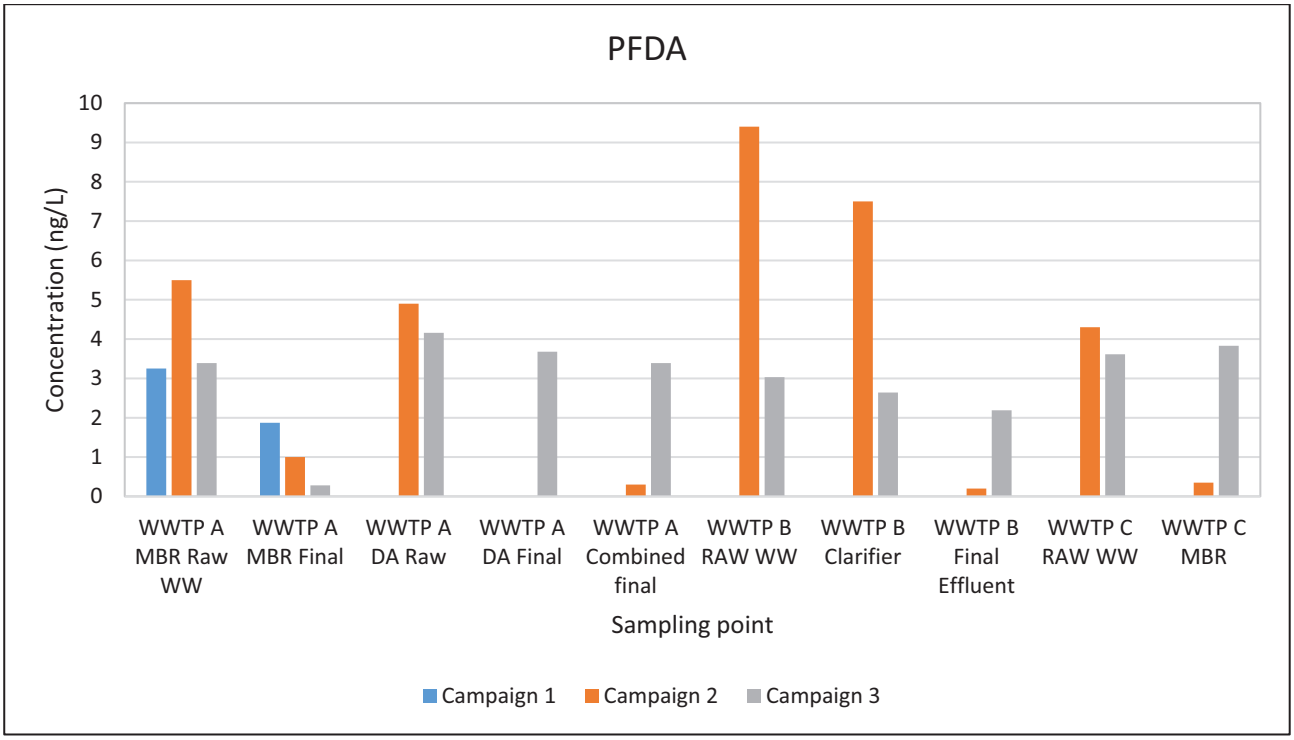

Figure 2-41: PFDA for all the sampling campaigns for all WWTP samples

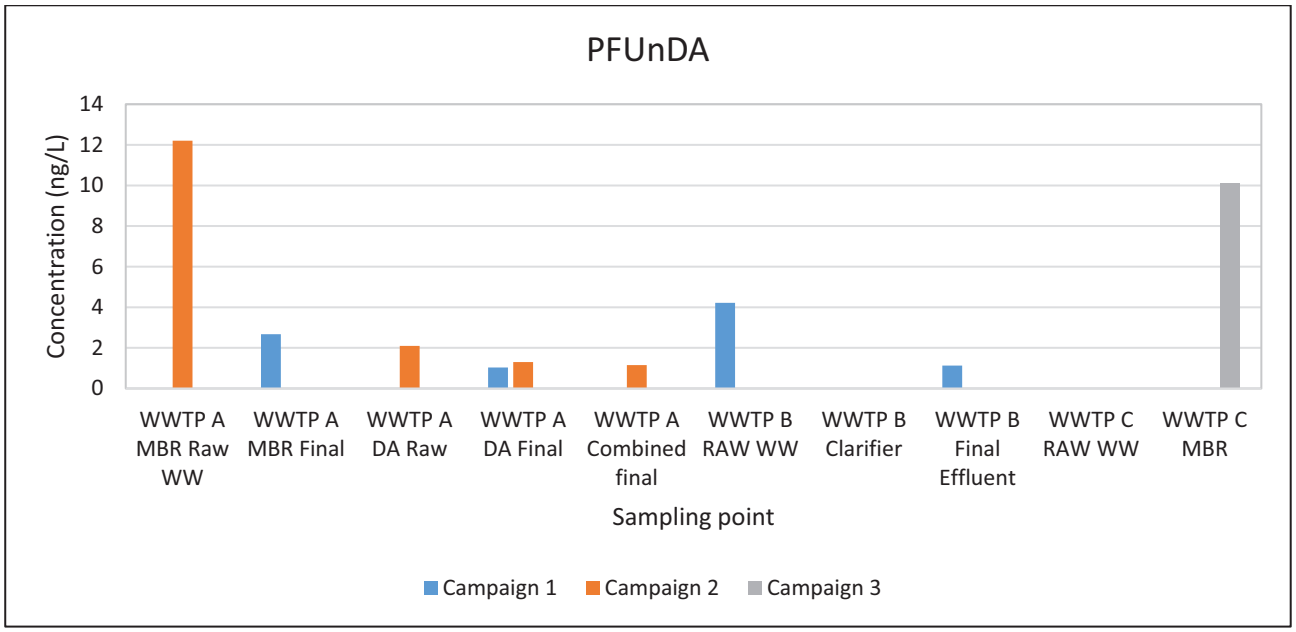

Figure 2-42: PFUnDA for all the sampling campaigns for all WWTP samples

2.3.5.2 *Priority Chemicals of Emerging Concern*

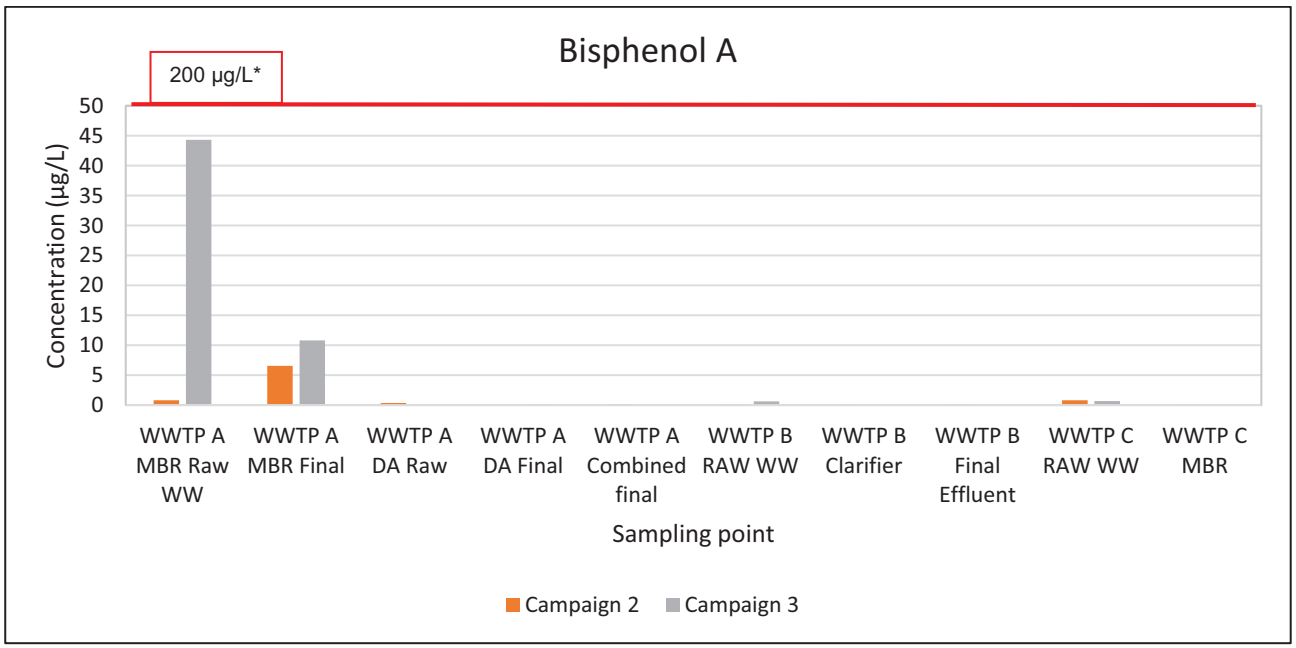

Figure 2-43: Bisphenol A for all the sampling campaigns for all WWTP samples. * Limit proposed for potable water (NRMMC, 2008 Guideline value)

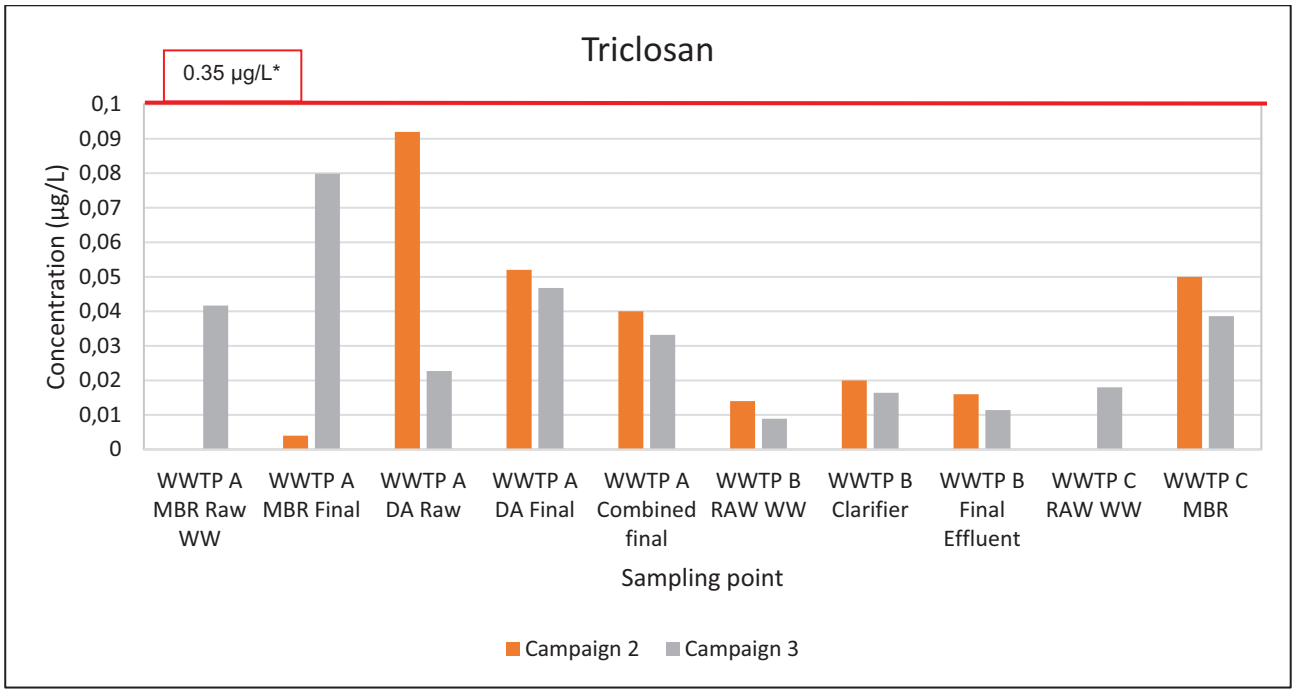

Figure 2-44: Triclosan for all the sampling campaigns for all WWTP samples. * Limit proposed for potable water (NRMMC, 2008 Guideline value)

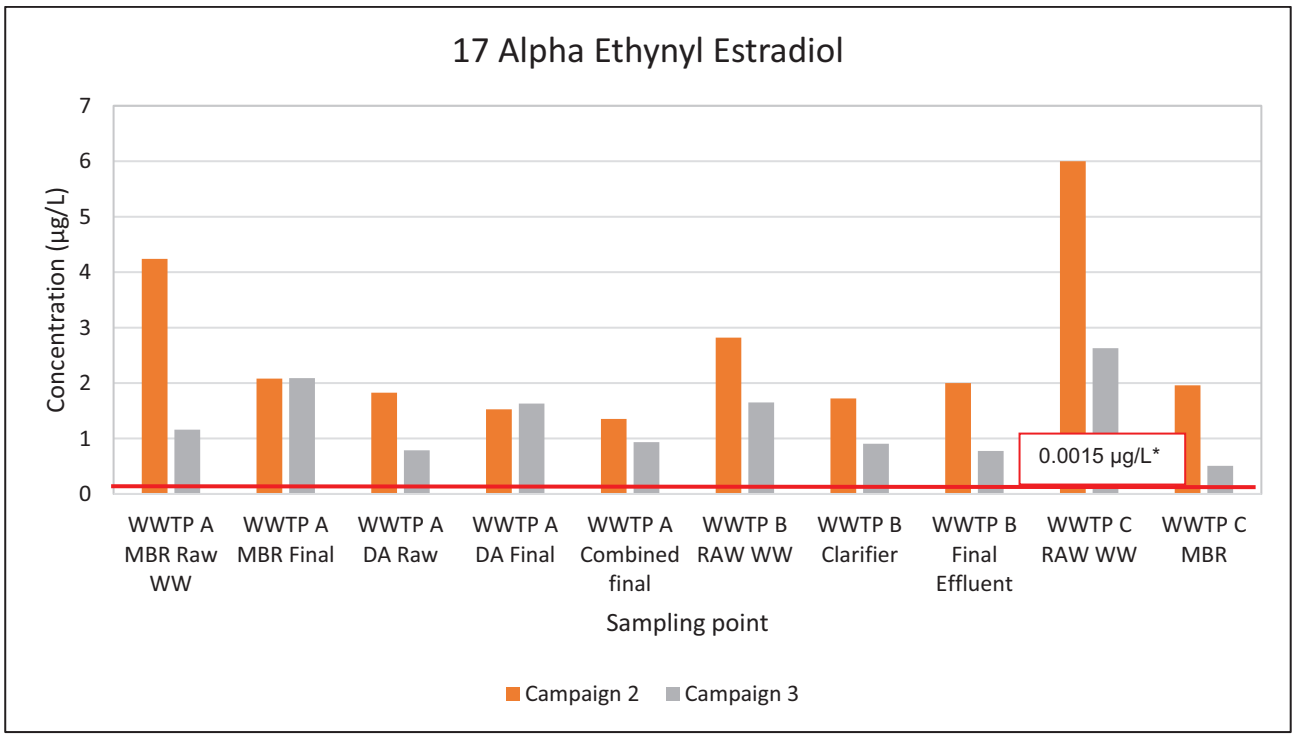

Figure 2-45: 17 Alpha Ethynyl Estradiol for all the sampling campaigns for all WWTP samples. * Limit proposed for potable water (NRMMC, 2008 Guideline value)

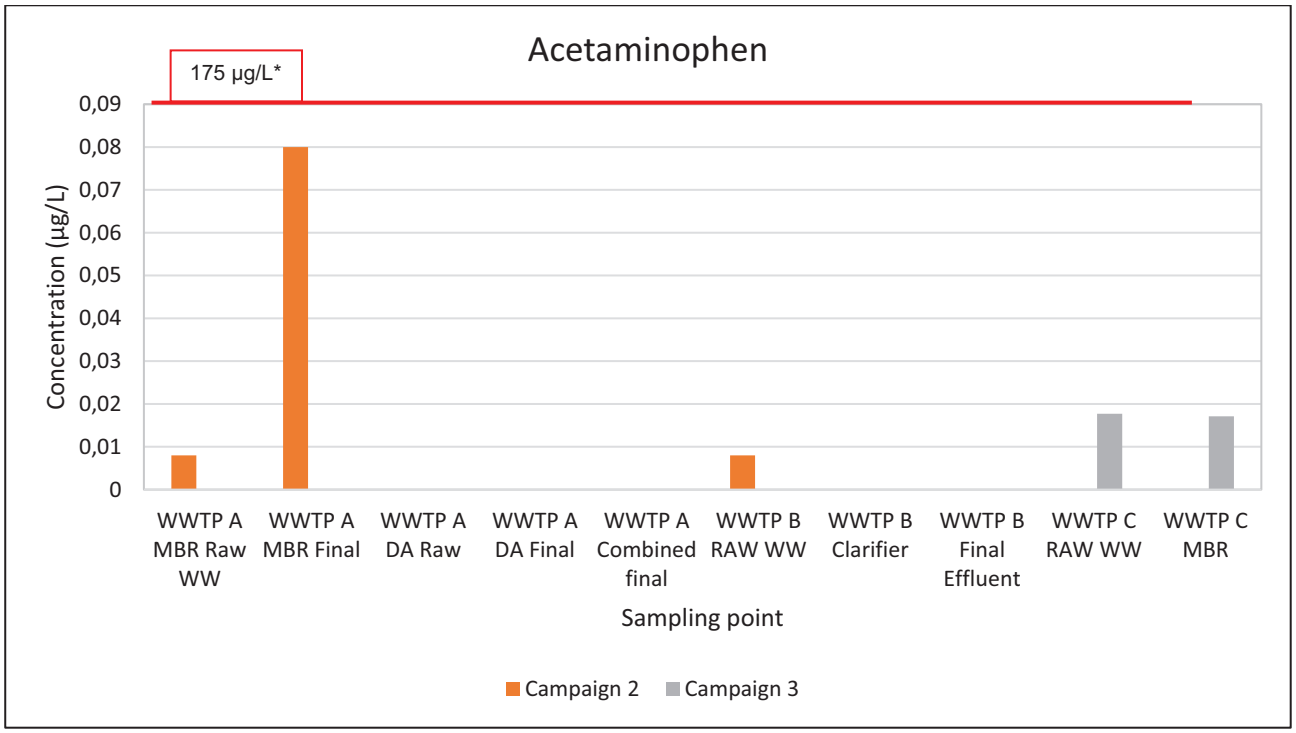

Figure 2-46: Acetaminophen for all the sampling campaigns for all WWTP samples. * Limit proposed for potable water (NRMMC, 2008 Guideline value)

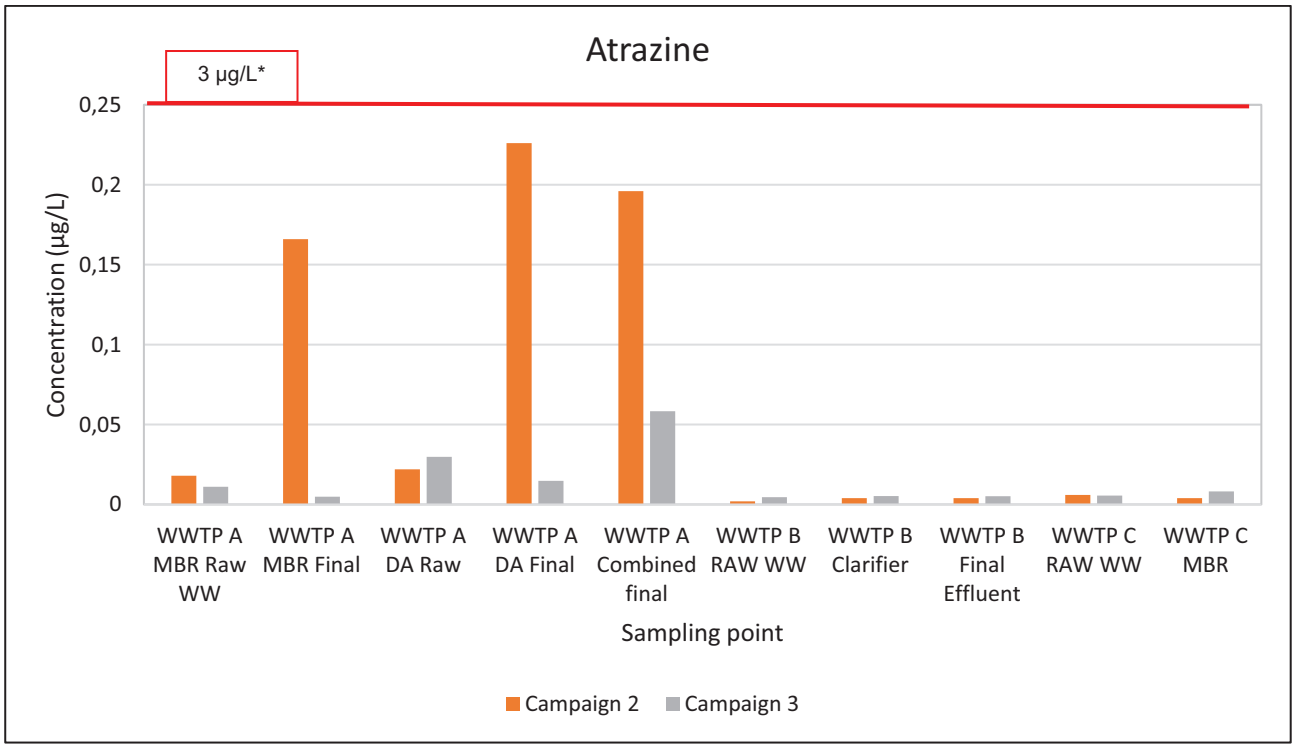

Figure 2-47: Atrazine for all the sampling campaigns for all WWTP samples. * Limit proposed for potable water (EPA, 2012 California drinking water limits)

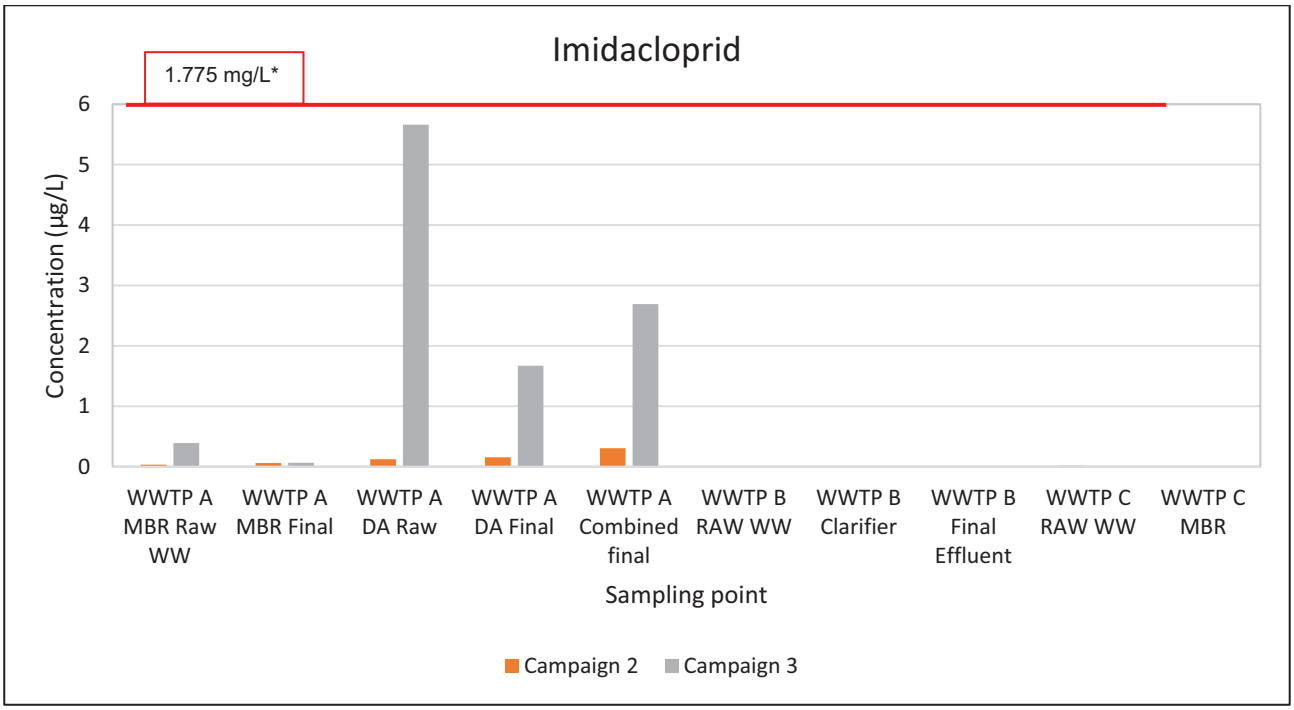

Figure 2-48: Imidacloprid for all the sampling campaigns for all WWTP samples. * Limit proposed for potable water (EPA, 2005 California drinking water limits)

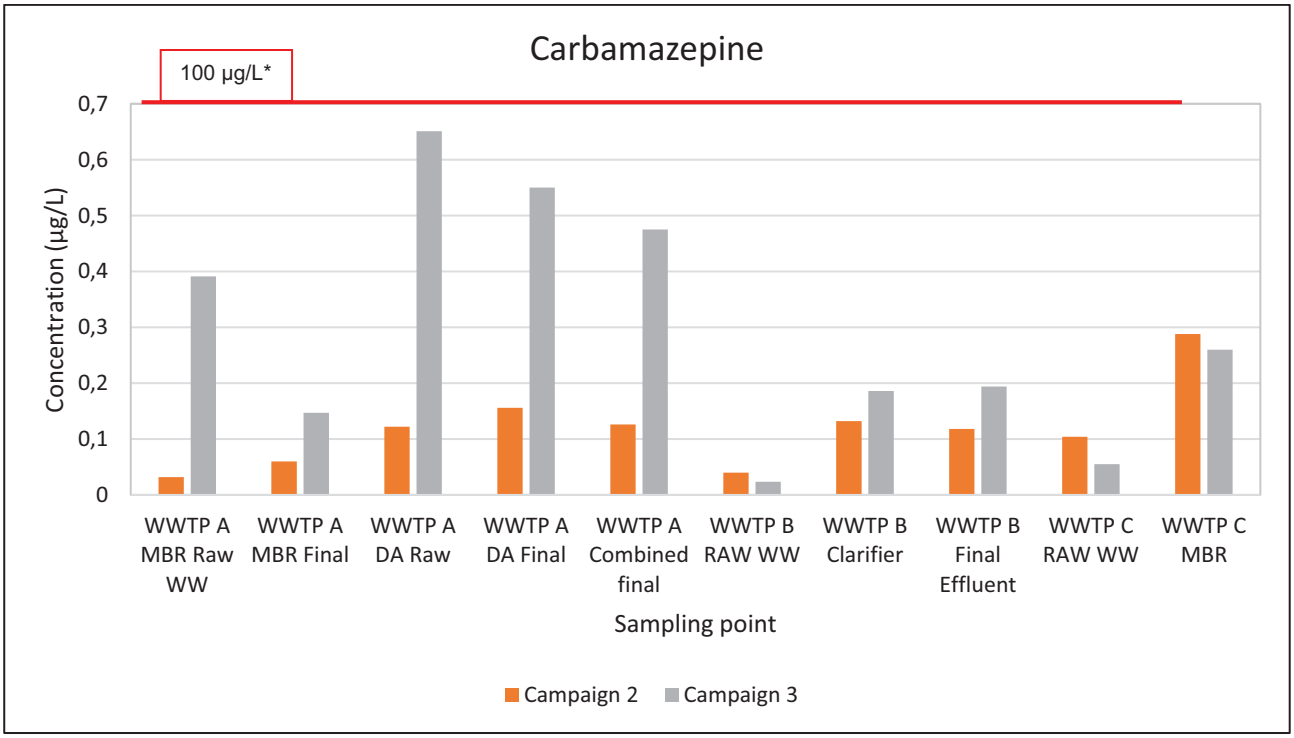

Figure 2-49: Carbamazepine for all the sampling campaigns for all WWTP samples. * Limit proposed for potable water (NRMMC, 2008 Guideline value)

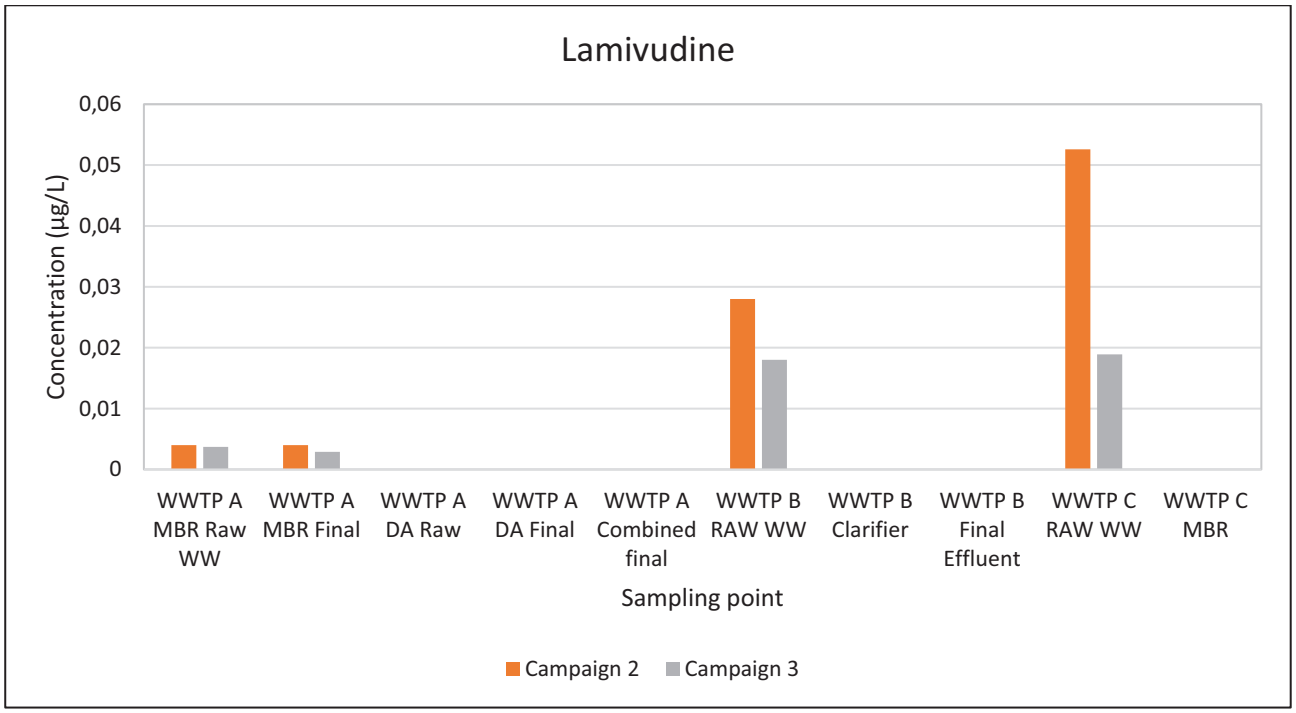

Figure 2-50: Lamivudine for all the sampling campaigns for all WWTP samples. * Limit proposed for potable water (NRMMC, 2008 Guideline value)

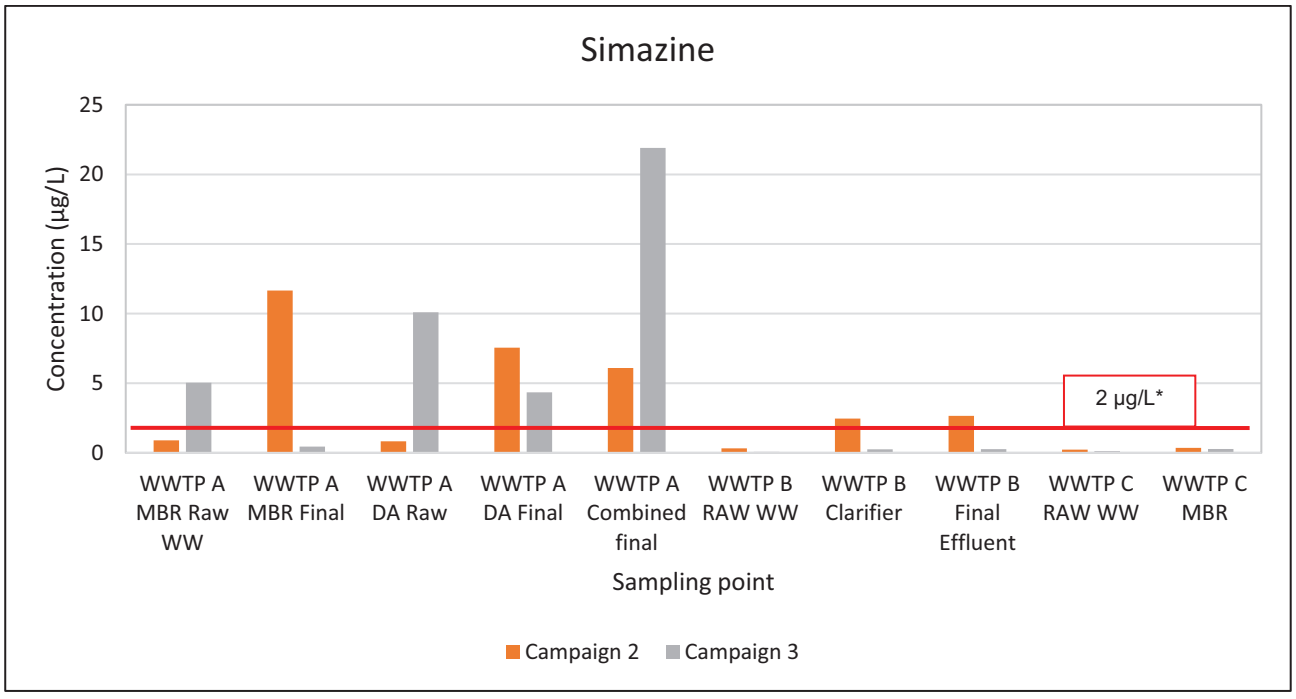

Figure 2-51: Simazine for all the sampling campaigns for all WWTP samples. * Limit proposed for potable water (WHO, 2011c Guideline value)

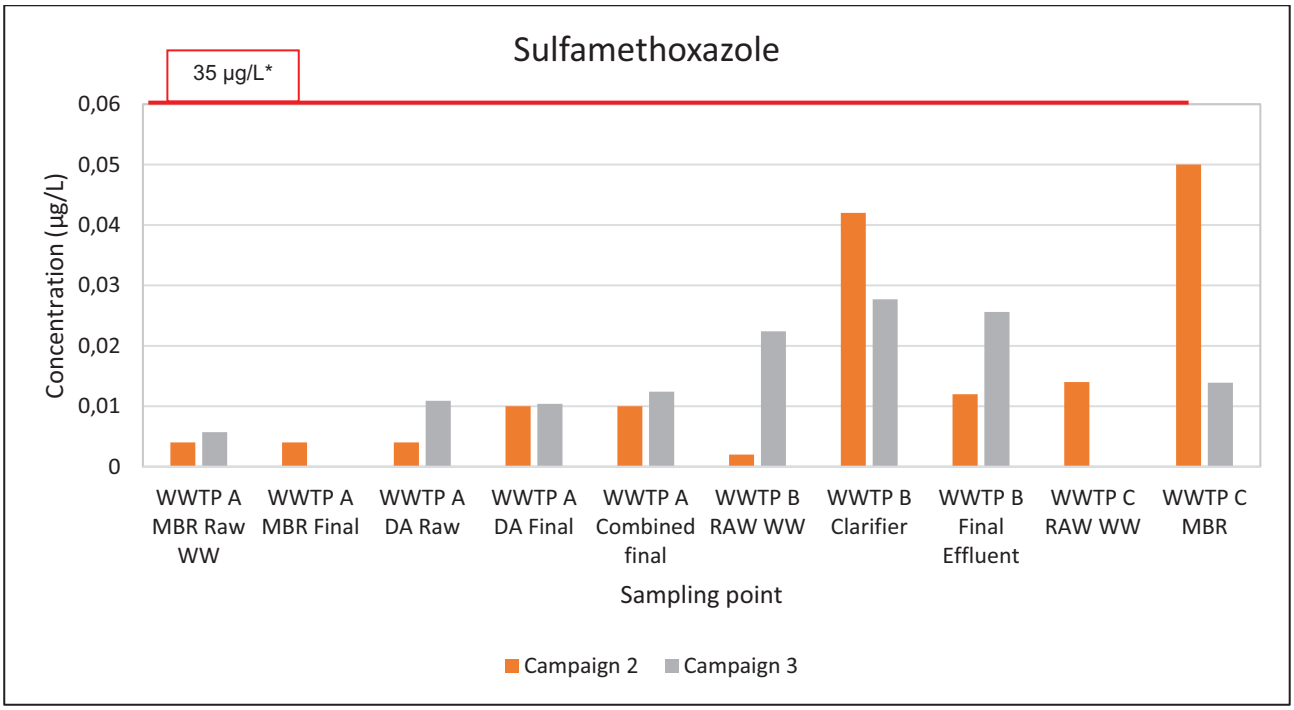

Figure 2-52: Sulfamethoxazole for all the sampling campaigns for all WWTP samples. * Limit proposed for potable water (NRMMC, 2008 Guideline value)

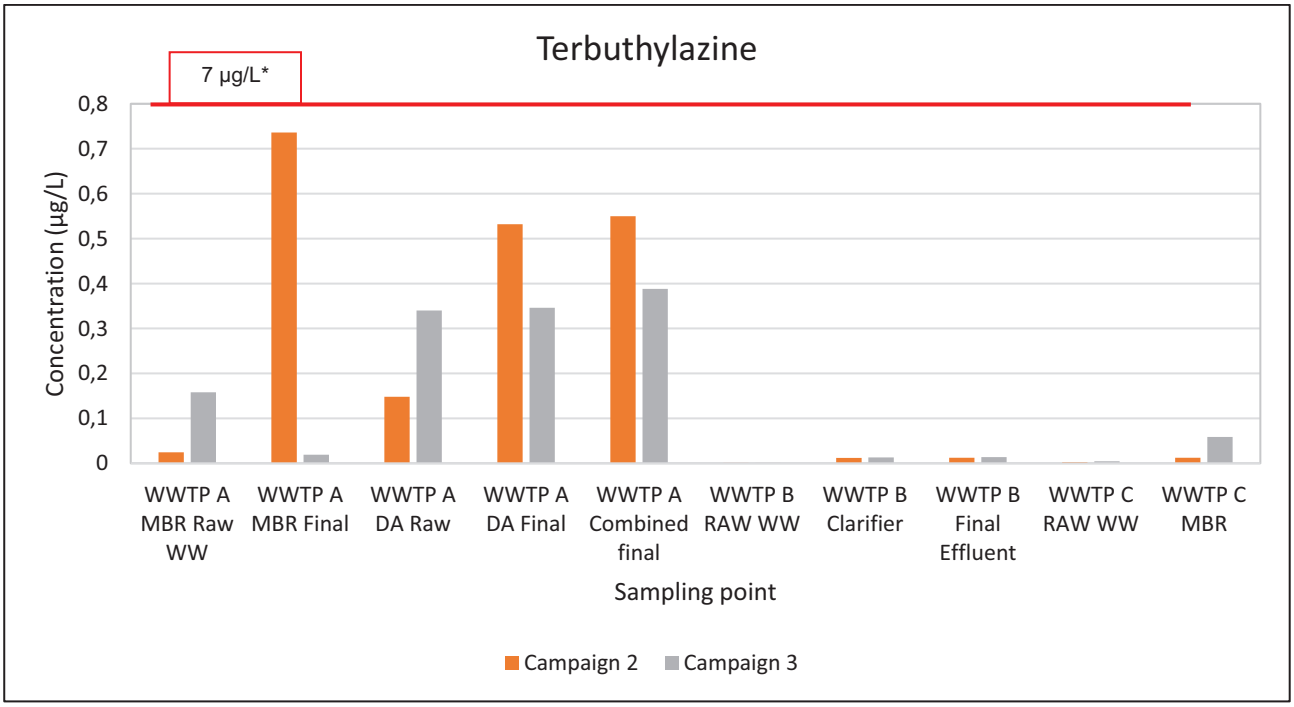

Figure 2-53: Terbuthylazine for all the sampling campaigns for all WWTP samples. * Limit proposed for potable water (WHO, 2011c Guideline value)

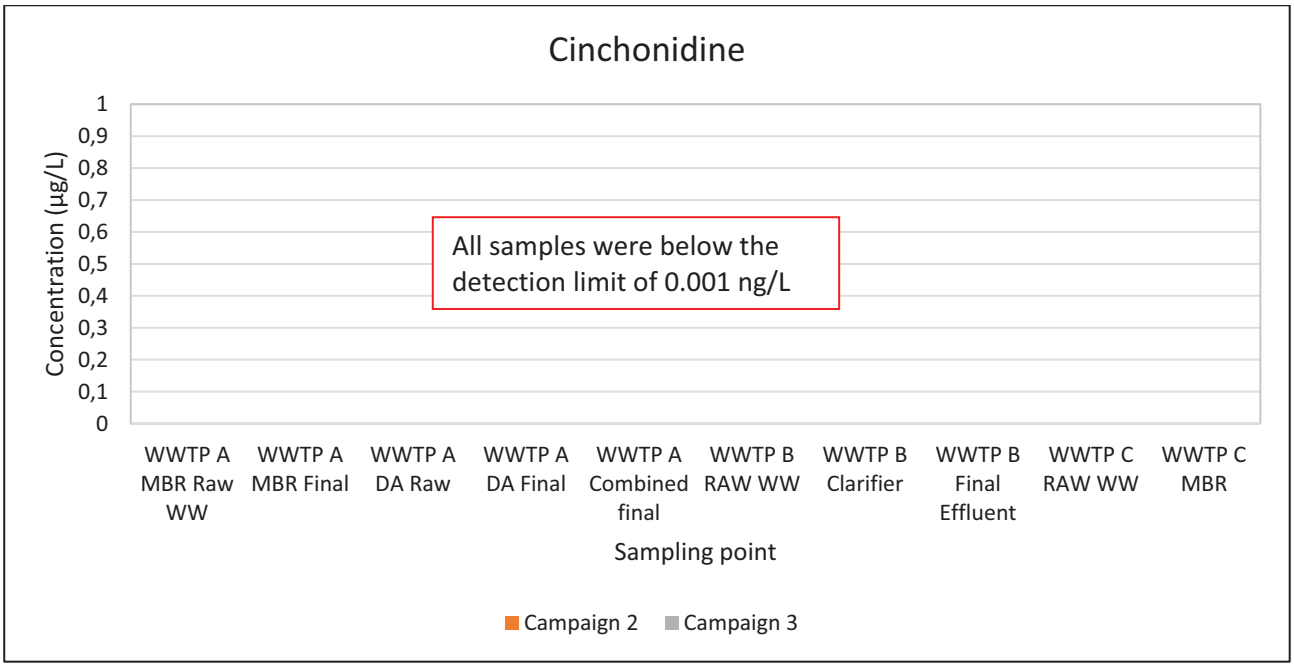

Figure 2-54: Cinchonidine for all the sampling campaigns for all WWTP samples

2.4 WATER TREATMENT PLANT ABSTRACTING WATER FROM A POLLUTED RIVER

2.4.1 Plant Description

WTP F abstracts water from a river which receives return flows from more than 20 WWTPs. The plant uses the conventional treatment processes of coagulation and flocculation, sedimentation, rapid sand filtration and chlorine disinfection.

2.4.2 Sampling Campaign 3

2.4.2.1 *Sampling*

The sampling procedure consisted of taking a single grab sample at each of the following locations:

- Berg River
- Withoogte raw water inflow
- After sand filtration
- Final water

After a sample has been taken it was immediately placed in a cooler box with ice packs in order to ensure that the samples remain at a temperature near 4°C. The majority of the samples were taken in class bottles with a foil cover underneath the lid to ensure that the sample never came in contact with any plastics that can interfere with the analyses.

2.4.2.2 *Sample analyses*

The following analyses were performed on the water treatment plant during the third sampling campaign:

- Macro-determinants: chemical and physical parameters (all samples)
  Ammonia, nitrate plus nitrite, DOC, TOC, EC, pH, COD, turbidity and UV_{254} absorbance.
- Perfluorinated compounds (PFCs) (all samples)
  Perfluoroheptanoic acid (PFHPA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorooctanesulfonate (PFOS), perfluorodecanoic acid (PFDA) and perfluoroundecanoic acid (PFUnDA)
- Priority CECs (all samples)
  Bisphenol A (BPA), triclosan, 17α ethinyl estradiol (EE2), acetaminophen, atrazine, imidacloprid, carbamazepine, lamivudine, simazine, sulfametoxazole, terbuthylazine and cinchonidine.

2.4.2.3 *Results of analyses for the third sampling campaign*

The results of the various analyses, as seen above, performed on the samples collected at the river and water treatment plant during the third sampling campaign can be seen in Table 2-26 (macro-determinants chemical and physical parameters), Table 2-27 (PFCs) and Table 2-28 (Priority CECs).

Table 2-26: Macro-determinants chemical and physical parameters: Sampling campaign 3

Analysis	Unit	Bergriver	WTP F Inlet	Filtration	Final water
Sulphate	mg/L	3.7			
Nitrate + Nitrite	mg/L	0.4			
DOC	mg/L	3.1	3.8	2.8	2.8
TOC	mg/L	3.9			
EC	mS/m	8	18	22	22
pH		7.1	7.4	9.5	8.0
COD	mg/L	11			
Turbidity	NTU	57	33	1.3	1.1
UV absorbance (254nm)	Abs	0.331	0.218	0.08	0.077

Table 2-27: Perfluorinated compounds (PFCs) (all units in ng/L)

Parameter	PFHPA	PFOA	PFNA	PFOS	PFDA	PFUnDA
Berg River	48.53	50.23	7.43	nd	2.68	nd
WTP F Inlet	34.51	31.19	3.85	nd	2.48	nd
Filtration	24.58	21.09	16.21	nd	6.783	nd
Final water	19.365	16.39	16.34	nd	2.413	nd

Table 2-28: Priority CECs: Sampling campaign 3 (all units in µg/L)

Parameter	Bisphenol A	Triclosan	17 Alpha Ethynyl Estradiol	Acetaminophen	Atrazine	Imidacloprid	Carbamazepine	Lamivudine	Simazine	Sulfamethoxazole	Terbuthylazine	Cinchonidine
Limit of detection	0.002	0.002	0.02	0.001	0.0001	0.0006	0.002	0.0006	0.001	0.0006	0.00006	0.002
Bergriver	ND	ND	0.0997	ND	0.0026	ND	0.0224	ND	0.0461	ND	0.0096	ND
WTP F Inlet	ND	ND	0.0327	ND	0.0036	ND	0.0222	ND	0.0502	ND	0.0166	ND
Filtration	ND	ND	0.0582	ND	0.0029	ND	0.0223	ND	0.0361	ND	0.0125	ND
Final water	ND	ND	0.0374	ND	0.0024	ND	0.0158	ND	0.0342	ND	0.0096	ND

2.5 SUMMARY

The target compounds, PFCs, BPA and acetaminophen were identified and quantified in the collected wastewater samples. Of all the targeted perfluorinated compounds, PFHpA, PFOA, PFNA, and PFUnDA were found to be the dominant PFCs detected in the raw wastewater influent of all the WWTPs.

The highest concentration of PFOs was found in WWTP C (10.0-9.5 ng/ℓ), which receives inflow from both municipal, industrial and landfill leachates. There is a noticeable decrease in the PFCs concentration (except for PFOA, PFOS and PFNA) from influent to effluent through the treatment processes. Increases in the concentration of some PFCs after activated sludge treatment was noted in WRP A (during and after initial chlorination) and WWTP E and WWTP C. Chularueangaksorn et al. (2012) attributed the increase to bioaccumulation/adsorption of PFCs from new inflow of wastewater onto the activated sludge, which are subsequently released downstream.

Increase in concentrations of PFOA, PFNA and PFOS were found in the WWTPs effluents. Sinclair and Kannan (2006) and Chularueangaksorn et al. (2012) also obtained similar results of increase PFOA and PFOS concentrations in effluent. It was suggested that degradation of some PFC precursors through treatment process can form additional PFOA and PFOS source.

This study indicates that the available treatment process in WRP A was able to effectively remove more than 80% of targeted PFCs in the wastewater. The largest percentage of total PFCs removal was found in WRP A (97%), followed by WWTP E (65%), WWTP D (54%) and WWTP C (52%).

CHAPTER 3: PLANT RELIABILITY ANALYSIS

3.1 INTRODUCTION

Reliability in the context of water treatment process units is defined as the probability of adequate performance; the percent of the time that effluent concentration meets requirements (Niku et al., 1979).

$$Reliability = 1 - P(failure) = 1 - P(effluent\ concentration > requirements)$$

The probability of failure is dependent on the distribution of the effluent concentration. Thus, to determine reliability, accurate estimates of the distributions of the effluent concentrations are required. Future reliability can be predicted based on past effluent concentration distributions, subject to the assumption that process operating conditions in the future remain the same as the past. Calculated reliability must be interpreted relative to minimal reliability requirements. Minimal reliability requirements can be related to the cost of operating the treatment plant:

$$Total\ cost = Initial\ cost + Operational\ cost + Cost\ of\ failure \times P(failure)$$

A trade-off present in the total cost calculation: the cost of adverse effects of failure on the one hand, and the extra initial and operational costs for a more reliable process on the other hand. Another way to interpret reliability: If a treatment plant is designed to allow no more than one violation per year, then its reliability should be 99.7% or greater.

Reliability can be summarised per process unit, per constituent, in terms of two key parameters:

- The **expected percentage of compliance** $1 - \alpha_C$ (the percentage of time the value of the exit concentration of a constituent is less than the specified standard, X_S). The calculation of this value is referred to as **Algorithm 1**.
- The **design value** (μ_X) as compared to the actual mean value (m_X) of the exit concentration of a constituent from a process unit, given a required probability of failure α_S. The calculation of this comparison is referred to as **Algorithm 2**.

3.1.1 Algorithm 1: calculated expected percentage of compliance $1 - \alpha_c$

The required inputs to this algorithm are the following:

- Historical data for variable under consideration, x.
- Specified standard, X_s.

The calculation procedure is as follows:

- Calculate the mean (m_x) and standard deviation (s_x) of the historical data x.
- Determine whether x conforms to a parametric distribution, specifically log-normal or normal distributions, by making use of the Kolmogorov-Smirnov test (NIST/SEMATECH, 2013).
    - The mean (m_x) and standard deviation (s_x) values are used to create a surrogate log-normal distribution represented by its cumulative distribution function $F_{log\text{-}normal}(m_x, s_x)$, as well as a surrogate normal distribution function $F_{normal}(m_x, s_x)$.
    - The variable x is then separately tested against the surrogate distributions $F_{log\text{-}normal}(m_x, s_x)$ and $F_{normal}(m_x, s_x)$ using the Kolmogorov-Smirnov test at a confidence level of 95%.

- After this test, x is classified as having one of the following three distributions: log-normal, normal, or empirical (non-parametric).

- The expected percentage of compliance ($1-\alpha_c$) is calculated by making use of the properties of the determined distribution.
  - For log-normal distributions, the following calculations are done:
    - The coefficient of variation (CV) is calculated:
$$CV = \frac{s_x}{m_x}$$
    - The test statistic is calculated:
$$Z_{1-\alpha_c} = \frac{\ln X_s - [\ln m_X - 0.5\ln(CV^2+1)]}{\sqrt{\ln(CV^2+1)}}$$
    - The probability of failure α_c is determined from standard normal variate tables.
    - Note that the above approach is used when it is not easy to determine the inverse cumulative distribution function F^{-1} for the log-normal distribution. If this functionality is available, then α_c is calculated as follows:
$$\alpha_c = F^{-1}_{log-normal}(m_x, s_x, X_s)$$
  - For normal distributions, the procedure is:
    - The inverse cumulative distribution function F^{-1} for normal distributions is generally easily obtained with most statistical software packages:
$$\alpha_c = F^{-1}_{normal}(m_x, s_x, X_s)$$
  - For empirical distributions, the procedure is:
    - Given that the empirical cumulative distribution function $F_{empirical}$ is presented in terms of $\{x, F_{empirical}(x)\}$ pairs, $1-\alpha_c$ can be determined by interpolation with X_s as the input.

3.1.2 Algorithm 2: calculating design value μ_x

The required inputs to this algorithm are the following:

- Historical data for variable under consideration, x.
- Specified (acceptable) probability of failure α_s.

Calculation methodology:

- Calculate the mean (m_x) and standard deviation (s_x) of the historical data x.
- Determine whether x conforms to a parametric distribution, specifically log-normal or normal distributions (see method in Algorithm 1).
- The design value μ_x is calculated by making use of the properties of the determined distribution.
  - For log-normal distributions:
    - The coefficient of variation (CV) is calculated:
$$CV = \frac{s_x}{m_x}$$
    - The test statistic $Z_{1-\alpha_s}$ corresponding to the specified probability of failure α_s is determined from standard normal variate tables.
    - The coefficient of reliability (COR) is calculated:
$$COR = \sqrt{CV^2+1} \times e^{\left\{-Z_{1-\alpha_S}\sqrt{\ln(CV^2+1)}\right\}}$$
    - The design value μ_x is calculated:
$$\mu_x = (COR)X_s$$
  - For normal distributions and empirical distributions, the above formulation does not hold. It was only determined whether the design mean should be larger or smaller than the actual mean, based on the expected percentage of compliance calculated in algorithm 1.

- If actual compliance is smaller than specified compliance $(1 - \alpha_c) < (1 - \alpha_x)$:
  - Design mean must be decreased.
- If actual compliance is greater than specified compliance $(1 - \alpha_c) > (1 - \alpha_s)$:
  - Design mean can be relaxed (increased).

3.2 DATA COLLECTION

In terms of plant data, the following requirements were stipulated in the proposal for this project:

- "Specification (by client) of discharge standards and design concentrations per process unit, per constituent."
- Only variables for which discharge standards were provided, were considered in the reliability analysis.

Table 3-1 shows an example of the process streams (before and/or after process units) and constituents for which discharge standards for the Goreangab water reclamation plant (Windhoek) as defined by the client, and that had sufficient data for the required distribution calculations. Daily measurements spanning from 01/01/2009 to 18/02/2015 were available, with some missing data instances as well.

3.3 ASSUMPTIONS

The following assumptions are made about the data:

- **Measurement data are representative of all expected process operating conditions.**
  The estimation of expected reliability requires that future process conditions are similar to past process conditions. All process operating conditions, including (and especially) extreme conditions, must be present in the historical sensor data.

- **Measurement data are collected in an unbiased fashion.**
  The estimation of expected reliability requires an accurate representation of frequencies of measurements. Therefore, the collection of measurement data should be consistent, and independent of the type of process operating conditions. I.e., measurements for poor conditions should not be discarded or not recorded at all.

If these assumptions are not valid, it will have a detrimental effect on the accuracy and utility of the reliability analysis.

3.4 DISTRIBUTION CHECKING

The original reliability analysis specified by Niku et al. (1979) assumes log-normal distributed data. The first check on the data is thus on what distribution the various variables exhibit. For this purpose, the Kolmogorov-Smirnov test (NIST/SEMATECH, 2013a) was used. First, the parameters of the assumed distributions were calculated (i.e. mean and variance). Secondly, a log-normal and normal distribution corresponding to these parameters were calculated. Finally, the Kolmogorov-Smirnov test was applied to compare the actual data to the calculated distributions. If the actual data did not match either the log-normal or normal distributions, the empirical distribution was used for further calculations. The results of the distribution checking step are shown in Table 3-2. Of the 28 variables considered, only 6 variables showed log-normal distributions, and no variables showed normal distributions.

Table 3-1: An example of process streams and constituents for compliance

Process Unit	Variable	Unit	WINGOC			SANS 241	This study	
			1st Alarm Operational Target	2nd Alarm Operational Target	Max Process Failure Conditions		Alarm Operational Target	Max Process Failure Conditions
Raw Mix In	Turbidity	NTU			10			
DAF Outlet (Combined)	Turbidity	NTU	1.5	5	8		1.5	5
Sandfilter combined outlet	Turbidity	NTU	0.2	0.35	0.5		0.2	0.35
	Manganese (Mn)	mg/L			0.03		0.03	0.05
	Iron (Fe)	mg/L			0.05			0.05
Ozone Contact Outlet	Residual O3	mg/L			0.15			
	Dissolved organic carbon	mg/L						15
	Chemical oxygen demand	mg/L						25
	Heterotrophic Plate Count	cfu/ml					80	100
	Total coliform	cfu/100ml						0
BAC Outlet	Manganese (Mn)	mg/L					0.01	0.025
	Iron (Fe)	mg/L						0.05
GAC Outlet (Combined)	UV 254	ABS_CM						0.06
	Total organic carbon	mg/L					2	5
	Dissolved organic carbon	mg/L					2	5
Ultrafiltration combined outlet	Turbidity	NTU					0.15	
Final Water	Turbidity	NTU			0.2		0.1	0.2

Process Unit	Variable	Unit	WINGOC			SANS 241	This study	
			1st Alarm Operational Target	2nd Alarm Operational Target	Max Process Failure Conditions		Alarm Operational Target	Max Process Failure Conditions
	Free chlorine	mg/L			0.9-1.2		1.2	1.5
	Total dissolved solids	mg/L				1200		1000
	Conductivity	mS/m				170		150
	Sulphate (SO4)	mg/L				250		200
	Ammonia (NH3-N)	mg/L				1.5		0.1
Final Water	Chloride (Cl)	mg/L				300		250
	Sodium (Na)	mg/L				200	100	400
	Nitrate (NO3)	mg/L_N				11		10
	Nitrite (NO2)	mg/L_N				0.9		0.05
	Iron (Fe)	mg/L_Fe				0.3	0.05	0.1
	Manganese (Mn)	mg/L_Mn				0.1	0.01	0.025
	Total organic carbon	mg/L				10		
	Dissolved organic carbon	mg/L					0.01	0.05

Table 3-2: Results from distribution checking (log-normal distribution indicated in orange, insufficient samples indicated in red)

Process Unit	Variable	Unit	Sample Size	Unique Values	Distribution
Raw Mix In	Turbidity	NTU	2299	1439	Empirical
DAF Outlet (Combined)	Turbidity	NTU	2296	1390	Empirical
Sandfilter combined outlet	Turbidity	NTU	2300	373	Empirical
	Manganese (Mn)	mg/L	515	40	Empirical
	Iron (Fe)	mg/L	514	46	Empirical
Ozone Contact Outlet	Residual O3	mg/L	550	99	Lognormal
	Dissolved organic carbon	mg/L	588	272	Lognormal
	Chemical oxygen demand	mg/L	592	65	Empirical
	Heterotrophic Plate Count	cfu/ml	661	232	Empirical
	Total coliform	cfu/100ml	569	3	Empirical
BAC Outlet	Manganese (Mn)	mg/L	290	6	Empirical
	Iron (Fe)	mg/L	295	11	Empirical
GAC Outlet (Combined)	UV 254	ABS_CM	595	39	Empirical
	Total organic carbon	mg/L	1	1	
	Dissolved organic carbon	mg/L	597	158	Empirical
Ultrafiltration combined outlet	Turbidity	NTU	2074	202	Empirical
Final Water	Turbidity	NTU	3118	248	Empirical
	Free chlorine	mg/L	1160	162	Empirical
	Total dissolved solids	mg/L	1424	32	Empirical
	Conductivity	mS/m	3110	1523	Empirical
	Sulphate (SO4)	mg/L	69	30	Lognormal
	Ammonia (NH3-N)	mg/L	302	2	Empirical

	Chloride (Cl)	mg/L	69	26	Lognormal
	Sodium (Na)	mg/L	65	62	Lognormal
	Nitrate (NO3)	mg/L_N	300	86	Empirical
	Nitrite (NO2)	mg/L_N	300	8	Empirical
	Iron (Fe)	mg/L_Fe	2065	179	Empirical
	Manganese (Mn)	mg/L_Mn	2051	117	Empirical
	Total organic carbon	mg/L	71	21	Lognormal
	Dissolved organic carbon	mg/L	595	145	Lognormal

This is different to the expectation created by Niku et al. (1979) and Oliveira and Van Sperling (2008), i.e. presence of log-normal distributions. The following reasons could be offered for this difference:

- The authors above considered only the final effluent discharge measurements. Intermediate quality measurements after process units may show different characteristics.
- The variables considered by Oliveira and Van Sperling (2008) are: BOD (biochemical oxygen demand), COD (chemical oxygen demand), TSS (total suspended solids), TN (total nitrogen), TP (total phosphorous) and FC (fecal or thermotolerant chloroforms). There is overlap between these variables and the variables considered in this study, but there are also other variables present in this study (e.g. UV, free chlorine, etc.) which may show different fundamental behaviour.
- The authors above considered continuous wastewater treatment plants. The water reclamation plant considered in this study may not function continuously (e.g. raw inflow may be diverted to alternate effluent if the raw inflow is too difficult to treat). This could alter the expected distributions as well.
- The measurement instrument limits and reporting standards could also affect the apparent distribution: if a measurement instrument cannot measure values beyond certain limits, this can alter expected distributions.

The valid sample sizes and unique values for the different variables are also reported in Table 3-2. The issue of missing data is important in reliability calculations: since reliability calculations are based on the characteristics of a distribution, the distribution (parametric or non-parametric/empirical) estimate must be accurate. An accurate distribution estimate cannot be obtained from a small sample size, or a sample with only a small number of unique values. For this purpose, only variables with more than 30 samples (a rule-of-thumb threshold), and more than 20 unique values, were considered.

Given the sample size and uniqueness requirements, 24 variables were appropriate to investigate further in terms of reliability.

3.5 CALCULATION OF RELIABILITY

Two sets of results are presented: the expected percentage of compliance, and the design mean (in comparison to the actual mean).

3.5.1 Expected percentage of compliance

Table 3-3 presents the compliance results. Overall, 14 of the 24 variables considered showed compliance above 80% for all standards. The importance of compliance violation is up to expert interpretation by plant engineers and other relevant parties.

Table 3-3: Expected percentage of compliance results (poor performance indicated)

Process Unit	Variable	WINGOC			SANS 241	2212	
		1st Alarm Operational Target	2nd Alarm Operational Target	Max Process Failure Conditions		Alarm Operational Target	Max Process Failure Conditions
Raw Mix In	Turbidity			99.11			
DAF Outlet (Combined)	Turbidity	88.93	98.03	99.35		88.93	98.03
Sandfilter combined outlet	Turbidity	93.00	98.88	99.25		93.00	98.88
	Manganese (Mn)			95.61		95.61	97.77
	Iron (Fe)			74.65			74.65
Ozone Contact Outlet	Residual O3			11.44			
	Dissolved organic carbon						100.00
	Chemical oxygen demand						95.69
	Heterotrophic Plate Count					71.65	74.05
	Total coliform	Too few samples					
BAC Outlet	Manganese (Mn)	Too few samples					
	Iron (Fe)	Too few samples					
GAC Outlet (Combined)	UV 254						99.12
	Total organic carbon	Too few samples					
	Dissolved organic carbon					92.80	99.84
Ultrafiltration combined outlet	Turbidity					98.62	
Final Water	Turbidity			98.90		95.61	98.90
	Free chlorine			37.30		46.94	78.66
	Total dissolved solids				92.91		68.29
	Conductivity				41.98		32.07
	Sulphate (SO4)				94.35		82.90
	Ammonia (NH3-N)	Too few samples					

Process Unit	Variable	WINGOC			SANS 241	2212	
		1st Alarm Operational Target	2nd Alarm Operational Target	Max Process Failure Conditions		Alarm Operational Target	Max Process Failure Conditions
Final Water	Chloride (Cl)				97.70		84.32
	Sodium (Na)				35.43	0.00	100.00
	Nitrate (NO3)				71.00		59.88
	Nitrite (NO2)	Too few samples					
	Iron (Fe)				99.46	96.17	98.87
	Manganese (Mn)				98.74	48.42	97.69
	Total organic carbon				99.96		
	Dissolved organic carbon					0.00	0.00

3.5.2 Design mean (in comparison to actual mean)

The following tables present the design mean results. The results are given for α_s = 0.05 and for 0.01, corresponding to 95% compliance (Table 3-4) and 99% compliance (Table 3-5), respectively. For empirically distributed variables, ">" suggests that the design mean can be made larger (more lenient), and "<" implies the design mean should be made smaller (more stringent). Since this analysis is closely related to the expected percentage of compliance analysis, similar trends are observed. Overall, this analysis highlights possible problem areas that may require tighter control. As an example of how to interpret these tables, consider the following two examples:

3.5.2.1 *Example 1: DAF outlet (combined): Turbidity [Empirical distribution example]*

The actual mean value from historical data is 1.19. The standard for the first alarm operational target is 1.5. Based on the calculated empirical distribution for this variable, the expected compliance to the first alarm operational target is 88.93%. Therefore, the current operation of the process unit is not sufficient to ensure 95% compliance to the first alarm operational target. In order to enable 95% compliance to the specified target, one of three interventions should be considered: 1) Assume variance of process unit will stay the same, and reduce design mean value (signified by "<" sign); this translates in stricter operation. 2) Decrease the variance of the process unit, while operating at the current design mean value (not indicated in Table). 3) Decrease the variance of the process unit, and reduce the design mean value (not indicated in Table).

3.5.2.2 *Example 2: Final water: Sodium (Na) [Lognormal distribution example]*

The actual mean value from historical data is 212.07. The standard for the SANS 241 target is 200. Based on the calculated lognormal distribution for this variable, the expected compliance to the SANS 241 target is 35.43%. Therefore, the current operation of the process unit is not at all sufficient to ensure 95% compliance to the SANS 241 standard. In order to enable 95% compliance to the specified target, the mean adjustment intervention (see previous example) can be specified explicitly (since the lognormal distribution is valid): the design mean value for the process unit should be reduced to 162.09. Assuming constant variance, this change in design mean value should result in 95% compliance in future, subject to sufficient representation by the collected process data used to determine the lognormal distribution parameters.

Table 3-4: Design mean results for 95% compliance (stricter design means indicated)

Process Unit	Variable	Actual Mean	WINGOC			SANS 241	2212	
			1st Alarm Operational Target	2nd Alarm Operational Target	Max Process Failure Conditions		Alarm Operational Target	Max Process Failure Conditions
Raw Mix In	Turbidity	2.23			>			
DAF Outlet (Combined)	Turbidity	1.19	<	>	>		<	>
Sandfilter combined outlet	Turbidity	0.16	<	>	>		<	>
	Manganese (Mn)	0.02			> (Slightly)		> (Slightly)	>
	Iron (Fe)	0.04			<			>
Ozone Contact Outlet	Residual O3	0.23			0.095			
	Dissolved organic carbon	3.89						10.90
	Chemical oxygen demand	14.46						> (Slightly)
	Heterotrophic Plate Count	1428.60					<	<
	Total coliform	0.01	Too few samples					
BAC Outlet	Manganese (Mn)	0.01	Too few samples					
	Iron (Fe)	0.03	Too few samples					
GAC Outlet (Combined)	UV 254	0.02						>
	Total organic carbon	1.20	Too few samples					
	Dissolved organic carbon	1.47					<	>
Ultrafiltration combined outlet	Turbidity	0.08					>	
Final Water	Turbidity	0.08			>		> (Slightly)	>
	Free chlorine	1.27			< (Tighter Variance)		<	<
	Total dissolved solids	975.58				<		<
	Conductivity	850.82				<		<
	Sulphate (SO4)	152.32				149.13		119.30

Process Unit	Variable	Actual Mean	WINGOC			SANS 241	2212	
			1st Alarm Operational Target	2nd Alarm Operational Target	Max Process Failure Conditions		Alarm Operational Target	Max Process Failure Conditions
Final Water	Ammonia (NH3-N)	0.15	Too few samples					
	Chloride (Cl)	211.10				225.20		187.66
	Sodium (Na)	212.07				162.09	81.05	324.18
	Nitrate (NO3)	9.48				<		<
	Nitrite (NO2)	0.12	Too few samples					
	Iron (Fe)	1.97				>	>	>
	Manganese (Mn)	0.14				>	<	>
	Total organic carbon	1.43				4.28		
	Dissolved organic carbon	1.40					0.0069	0.035

Table 3-5: Design mean results for 99% compliance (stricter design means indicated)

Process Unit	Variable	Actual Mean	WINGOC			SANS 241	2212	
			1st Alarm Operational Target	2nd Alarm Operational Target	Max Process Failure Conditions		Alarm Operational Target	Max Process Failure Conditions
Raw Mix In	Turbidity	2.23			> (Slightly)			
DAF Outlet (Combined)	Turbidity	1.19	<	<	> (Slightly)		<	<
Sandfilter combined outlet	Turbidity	0.16	<	< (Slightly)	> (Slightly)		<	< (Slightly)
	Manganese (Mn)	0.02			<		<	<
	Iron (Fe)	0.04			<			<
Ozone Contact Outlet	Residual O3	0.23			0.077			
	Dissolved organic carbon	3.89						9.46
	Chemical oxygen demand	14.46						<
	Heterotrophic Plate Count	1428.60					<	<
	Total coliform	Too few samples						
BAC Outlet	Manganese (Mn)	Too few samples						
	Iron (Fe)	Too few samples						
GAC Outlet (Combined)	UV 254	0.02						> (Slightly)
	Total organic carbon	Too few samples						
	Dissolved organic carbon	1.47					<	>
Ultrafiltration combined outlet	Turbidity	0.08					<	
Final Water	Turbidity	0.08			< (Slightly)		<	< (Slightly)
	Free chlorine	1.27			< (Tighter variance)		<	<
	Total dissolved solids	975.58				<		<
	Conductivity	850.82				<		<
	Sulphate (SO4)	152.32				117.35		93.88
	Ammonia (NH3-N)	Too few samples						

Process Unit	Variable	Actual Mean	WINGOC			SANS 241	2212	
			1st Alarm Operational Target	2nd Alarm Operational Target	Max Process Failure Conditions		Alarm Operational Target	Max Process Failure Conditions
	Chloride (Cl)	211.10				198.56		165.46
	Sodium (Na)	212.07				148.03	74.02	296.06
	Nitrate (NO3)	9.48				<		<
	Nitrite (NO2)	Too few samples						
	Iron (Fe)	1.97				>	<	< (Slightly)
	Manganese (Mn)	0.14				<	<	<
	Total organic carbon	1.43				2.77		
	Dissolved organic carbon	1.40					0.0059	0.029

3.6 SUMMARY

Reliability analysis, as any data analyses, is sensitive to the quality and quantity of measurements available. Quality refers to data originating from calibrated instruments, taken consistently and without bias, for a long enough historical period to reflect all possible process conditions. Quantity refers to the number of samples used in the analysis: although a bare minimum of 30 values could be used to estimate a distribution, such a small sample size would not guarantee the previously mentioned quality requirements, and would also result in a large uncertainty of the estimated reliability.

The reliability analysis proposed in the project proposal was adapted to be used for non-log-normal distributions, as the majority of variables considered in this study was not log-normally distributed. The calculations should be able to be implemented in standard spreadsheet software such as Excel.

In general, the variables tested showed an expected percentage of compliance of less than 99%, including the most critical variables (i.e. final water quality). The significance of this finding should be determined by process experts.

Since the practical application of reliability analysis is only as good as the data on which it is based, it would be worthwhile to conduct a rigorous data collection campaign, specifically for the purpose of estimating good distribution models for reliability analysis. Such a rigorous data collection campaign would have the following properties:

- Consistent measurements.
  Measurements should be taken in the same manner, at the same time, by the same calibrated instruments, to prevent unnecessary bias.
- Validated measurements.
  Measurements must be validated by experts, such that impossible values and data logging values are avoided.
- Annotated measurements.
  Measurements should be annotated, as far as practical, by a description of the overall prevailing conditions. For example, whether the process is at normal operating conditions, higher flow rates than normal, more contaminated inlet water, just after maintenance occurred, etc. Annotations allow for sensible data pre-processing, and also can be used as a check for representativeness.
- Representative measurements.
  Reliability analysis considers the performance of a plant or process unit for all possible conditions, including failures. If measurements under failure conditions are excluded, this will bias the reliability analysis such that the expected compliance is overly optimistic.
- Large sample sizes.
  The larger the sample size used to estimate a distribution function (given that all possible conditions are represented), the more accurate the reliability analysis will be.

A future direction for reliability analysis is to consider how process unit reliabilities affect other process unit reliabilities, and in turn, the reliability of the entire plant under consideration. For this, multivariate and conditional distribution fitting would be required, which would require rigorous data collection at a high data quality.

CHAPTER 4: HUMAN HEALTH RISK ASSESSMENT

4.1 BIO-ASSAYS FOR TESTING EFFICIENCY OF WATER TREATMENT

4.1.1 Overview

There has been increasing concern regarding substances in the environment that could impact on the endocrine systems of man and animals. The cost of monitoring the entire spectrum of potential EDCs in water and water related media would be prohibitive and it is not possible to estimate the potential health risks of endocrine disruptors based on the chemical composition alone. Biological methods are becoming progressively more popular as screening tools because the chemical nature of an environmental sample is not usually known. The effects of chemical mixtures cannot necessarily be based on their concentrations, so bioassays are used to assess the potential effects of complex mixtures of endocrine disrupting chemicals.

A battery of bio-assays was included in the study to illustrate their use in assessing water quality. These included the Ames mutagenicity test, the Daphnia acute toxicity test and the YES (yeast estrogen screen) test, to test for oestrogenic activity. This provides a broad indication of effluent quality and is often recommended as screening tests for wastewater reuse. The Ames and Daphnia methods are included in the America Standard Methods for the Examination of Water and Wastewater (APHS, 2011). The YES test is included in the Global Water Research Coalition overview of sources and biological methods for measuring EDC (GWRC, 2003). The assay is robust and can be successfully applied as a screen for environmental water and sediment samples, is suitable for a high volume of samples and is also relatively quick (Beresford et al., 2000). It is based on measuring oestrogenic activity relative to the most potent oestrogenic compound, namely 17ß-oestradiol. The relative potency EEQs for oestrogenic activity are shown in Table 4-1 (Legler et al., 1999; Ghijsen and Hoogenboezem, 2000) and as they represent relative potencies they are unit less.

Table 4-1: Substance Relative potency to 17 ß-oestradiol

17ß-oestradiol	1
Oestrone	$5.8X10^{-2}$
17 α-oestradiol	$1.6X10^{-2}$
Bisphenol A	$7.8X10^{-6}$
di-n-butylphthalate	$1.8\ X10^{-8}$
Dimethyl phthalate	$1.1X10^{-5}$
n-nonyl phenol	$3.8X10^{-5}$
n-octyl phenol	$1.4X10^{-6}$
o,p-DDT	$9.1X10^{-6}$
Dieldrin	$2.4X10^{-7}$

4.1.2 Bioassay Pilot Tests

Three bioassays recommended by the OECD and GWRC, representing different trophic levels to provide an overall assessment of water quality, are presented in the sections following. The tests include the Ames mutagenicity test, the Daphnia toxicity test and the oestrogenicity activity test.

In total the two WRPs, three WWTPs and one WTP) were sampled for the bioassay testing. In all instances, the samples were taken in pre-washed 1 litre glass bottles (except for the macro-determinants samples that were taken in 500 mL plastic bottles). The samples were placed in cooler bags with ice and ice packs to remain at 4 degrees C during transportation to the laboratories. Since some of the analyses performed on the samples are advanced, multiple laboratories were used, each with a different speciality. The following analyses were performed on the samples:

- Macro-determinants: chemical and physical parameters (all samples)
  Ammonia, nitrate plus nitrite, DOC, TOC, EC, pH, COD, turbidity and UV_{254} absorbance.
- Perfluorinated compounds (PFCs) (all samples)
  Perfluoroheptanoic acid (PFHPA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorooctanesulfonate (PFOS), perfluorodecanoic acid (PFDA) and perfluoroundecanoic acid (PFUnDA)
- Priority CECs (all samples)
  Bisphenol A (BPA), triclosan, 17α ethinyl estradiol (EE2), acetaminophen, atrazine, imidacloprid, carbamazepine, lamivudine, simazine, sulfametoxazole, terbuthylazine and cinchonidine.
- Ames mutagenicity test (only raw and final samples)
- Oestrogen mimicking test (only raw and final samples)

4.1.2.1 *Ames mutagenicity test*

The Ames test was developed to test mutagenic materials in water soluble extracts of sediment, air, chemicals, food components, cosmetics, waste waters and potable waters (Ames et al., 1975). The principle of this bacterial reverse mutation test is that it detects mutations which reverse mutate the test strains and restore the functional capability of the bacteria to synthesize an essential amino acid. The revertant bacteria are detected by their ability to grow in the absence of the amino acid required by the parent test strain. It has been shown that many chemicals that are positive in this test also exhibit mutagenic activity in other tests.

In this study, the EPBI Muta-ChromoPlate™ was used to test for mutagenicity in the wastewater and drinking water influents and effluents. The test makes use of a 96-well microplate version of the *Salmonella typhimurium* Ames Test. The strain *S. typhimurium* TA98 was used to screen the samples. A minimal medium containing histidine and biotin to allow for a few cell divisions is used. Positive (2-Nitrofluorene) and negative controls are included and the measurement of the background reverse mutation rate is compared to the rates following exposure to test samples. If samples have twice the number of reverse mutations compared to the background mutation rate it is considered to be mutagenic. An additional bacterial strain that mimics human metabolic activation (TA 98 p450) for those chemicals that may become mutagenic subsequent to metabolic activity was also tested. Diluted samples (1 in 10) were included to reduce potential toxic effects. Toxicity was observed in raw wastewater (Figures 4-1 to 4-6), with reductions observed in most wastewaters. Where no mutagenic activity was observed it is likely that it was masked by the toxicity.

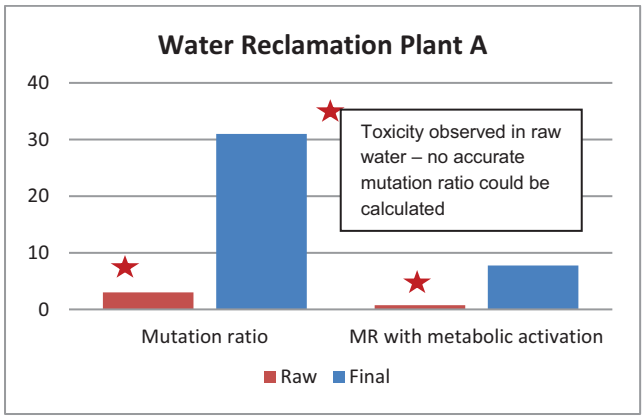

Figure 4-1: Mutagenicity Results for WRP A

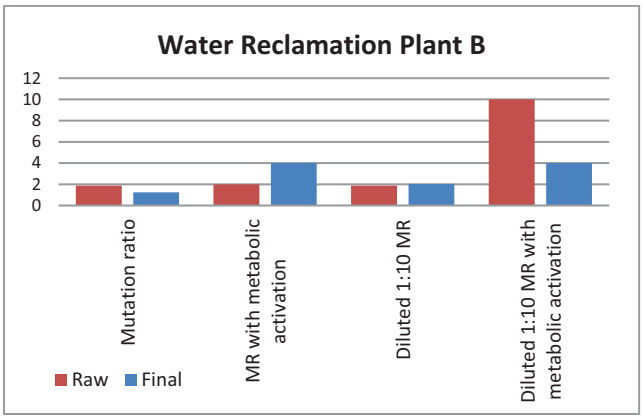

Figure 4-2: Mutagenicity Results for WRP B

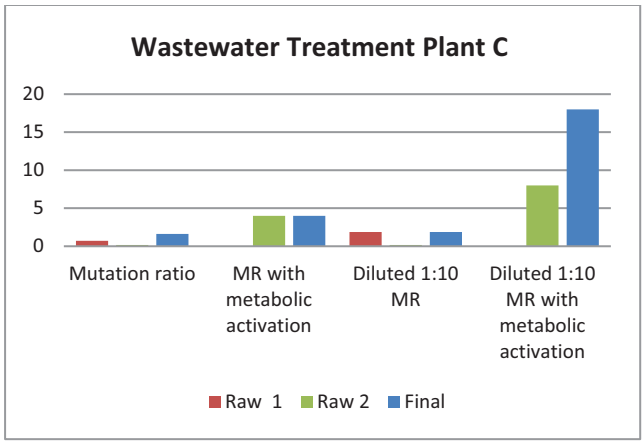

Figure 4-3: Mutagenicity Results for WWTP C

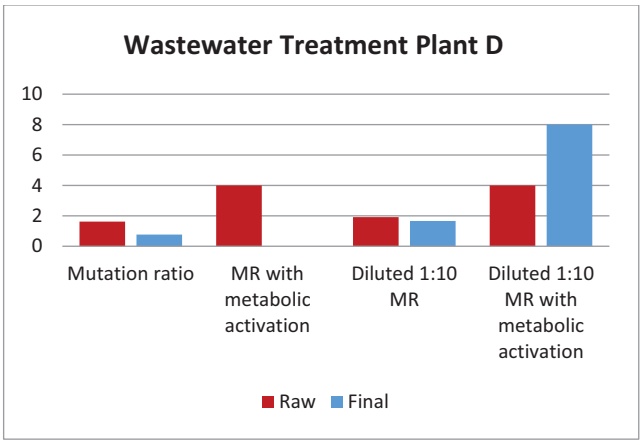

Figure 4-4: Mutagenicity Results for WWTP D

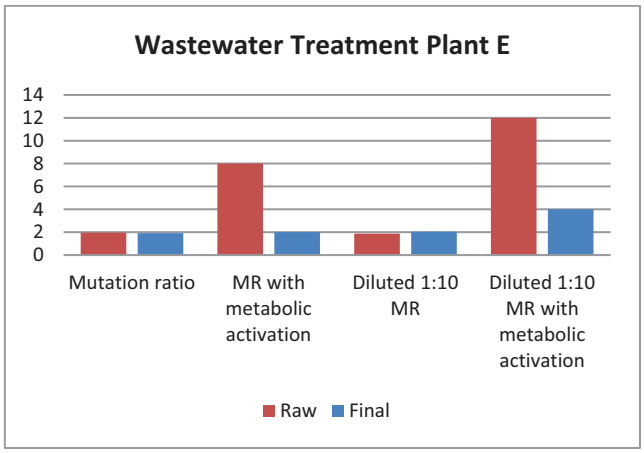

Figure 4-5: Mutagenicity Results for WWTP E

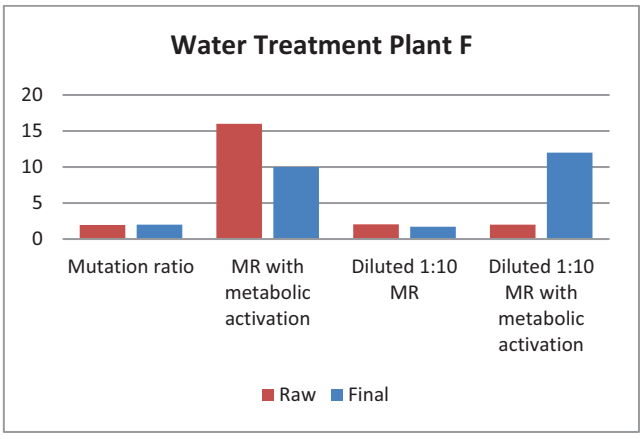

Figure 4-6: Mutagenicity Results for WTP F

4.1.2.2 *Daphnia 24-48 hour toxicity test*

Daphnia (freshwater water fleas), and Daphnia magna specifically, is prescribed in the Organisation for Economic Co-operation and Development Guidelines for the Testing of Chemicals, Tests No. 202 Acute Immobilisation Test (OECD, 2004). Daphnia are excellent organisms to use in bio-assays because they are sensitive to changes in water chemistry and are simple and inexpensive to culture in an aquarium. Young daphnids are exposed to a range of concentrations of the test samples for a period of 48 hours. Dead and immobilized Daphnia are recorded at 24 hours and 48 hours and compared with control values.

All wastewaters showed 100% toxicity (results are not included in the figure) with improvements in effluents shown in Figure 4-7. Drinking waters elicited high toxicity levels (WRP A and B). The presence of chlorine in treated drinking water and wastewater effluents will cause toxicity, illustrating the need to neutralise the chlorine used to disinfect the water, prior to testing.

Daphnia Toxicity Assay of Water and Wastewater Samples

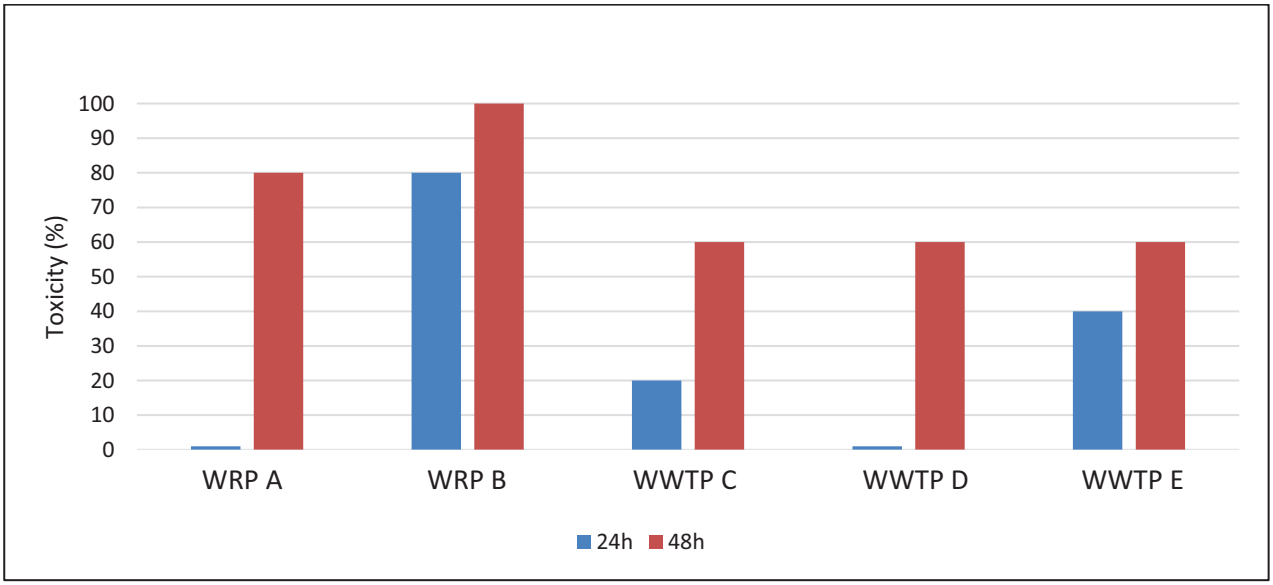

Figure 4-7: Daphnia toxicity results for sampling campaign 3

4.1.2.3 *YES Oestrogenicity Activity Test*

In vitro screening of wastewater samples collected from selected water treatment works were tested for oestrogen receptor agonistic activity. The water samples were tested for oestrogen receptor agonistic activity associated with the water sample extracts and evaluated using the Yeast Estrogen Screen (YES) described by Routledge and Sumpter (1996) and Sohoni and Sumpter (1998). Oestrogen receptor agonism is calculated using turbidity corrected absorbance values (Sohoni and Sumpter, 1998) and expressed as % relative to the maximal 17β-Estradio (E2) response (De Jager et al., 2011). Estradiol equivalent (EEQ) concentrations are calculated using E2 dose response curve regression equations derived per assay plate (Grover et al., 2011).

Estradiol equivalent (EEQ) concentrations (ng/L) of water samples collected from selected waste water treatment works were calculated with a limit of detection (LOD) of 1,7 ng/L.

Oestrogenic activity decreased in all wastewater treatment works with final effluents being below detection limits Figure 4-8. The above bio-assays have illustrated the improvements in wastewater quality following treatment through the various treatment works, and the results have shown how these bio-assays are able to be used to monitor the water quality.

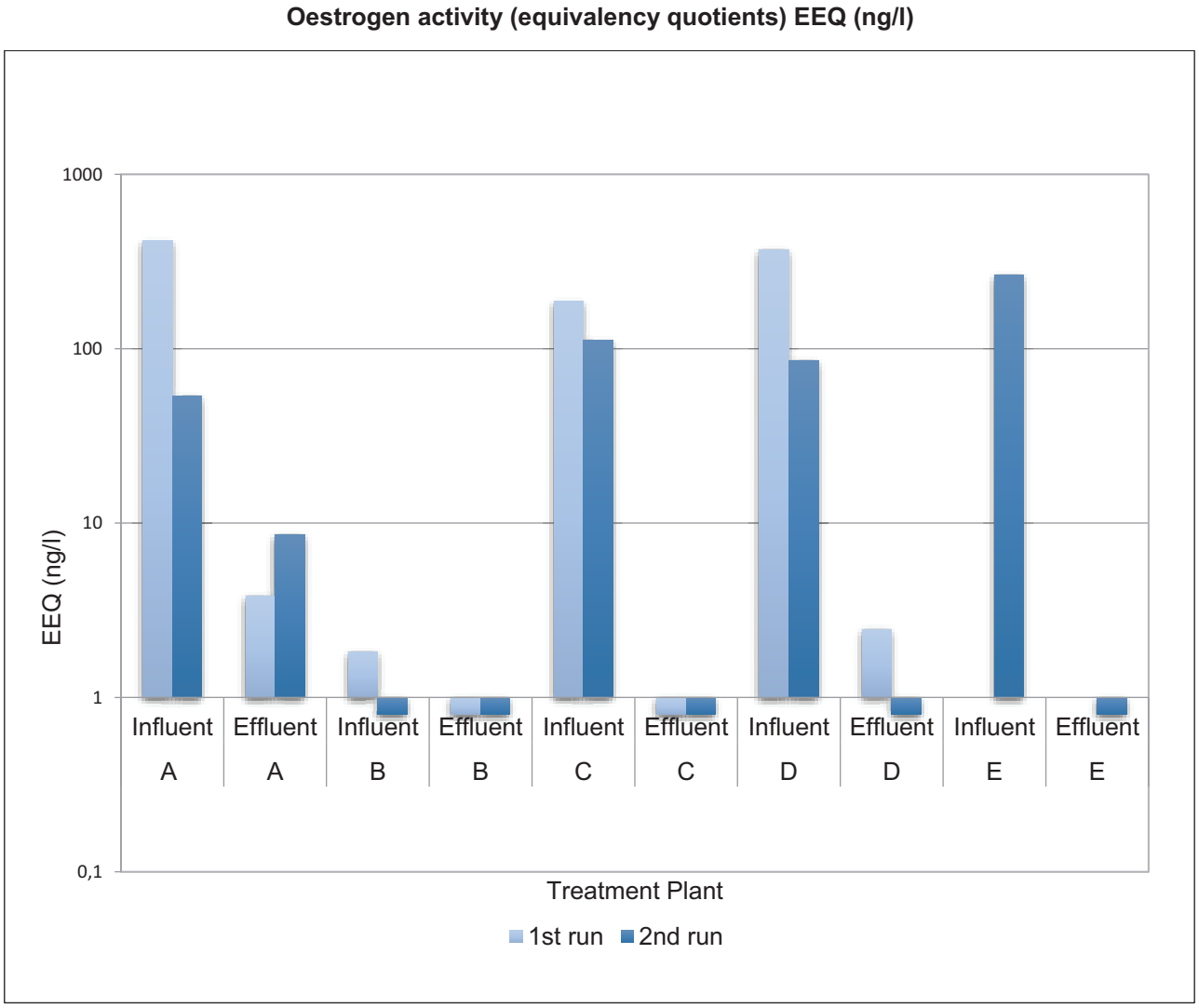

Figure 4-8: Oestrogen activity removal at water treatment plants (sampling campaign 3)

4.2 HUMAN HEALTH RISK ASSESSMENT STUDIES

4.2.1 Overview

Water Reclamation Plant A was selected for this study and the study was undertaken during April-June 2015. The human health risk assessment studies were undertaken by the post-graduate students from the Chalmers University of Technology (Sweden) under the supervision of Chris Swartz (Project Leader on this WRC project) (see Falk and Ohlin, 2015). The objective of the risk assessment was to identify chemical risks from hazards in the WRP A system that may lead to adverse human health effects for the community from identified contaminants of emerging concern and to suggest measures method undertaken at to reduce the unacceptable risks. The specific aims were to:

- Determine which processes in the WRP A system are able to reduce the identified contaminants of emerging concern in the inflow.
- Determine which hazards in the system may reduce the ability to remove identified contaminants of emerging concern.
- Establish what risks are caused by these hazards.
- Identify the most feasible measures to reduce the unacceptable risks.

A risk matrix was used to visualise the severity of several hazards and their probability of occurrence, while a multi criteria decision analysis (MCDA) approach was used for ranking countermeasures (Falk and Ohlin, 2015).

4.2.2 Assumptions

An important aspect to keep in mind is that this study is based on the assumption that the concentration of the CECs is constant in the inflowing wastewater. In reality, these concentrations vary due to precipitation, season and other factors. Furthermore, the concentration and the number of detected contaminants could change due to the activities in the town i.e. new industries connecting to the wastewater system or outbreaks of new diseases leading to increased usage of certain pharmaceuticals among the population connected to the WWTP. When implementing a reclaimed water system, it is important to take the activities within the community into account as well as possible future changes. It was assumed that the population of the community gets all of their daily intake (2 litre) from the municipal drinking water system. This leads to an overestimation of the exposure from the contaminants in the drinking water since people generally consume other kinds of liquids during the day. When calculating the long-term exposure an intake of the same water is assumed throughout the whole life. Since most people do not get their water from the same water supply system during their whole life this assumption might be misleading. However, it gives an indication on whether the levels of contaminants in the water are acceptable or not.

4.2.3 Selection of model CECs and analysis

Table 4-2 shows a list of prioritised CECs that were possible to analyse with standardised methods. 17 β-estradiol was not possible to analyse and was therefore substituted by the similar hormone 17α-ethinylestradiol (EE2). For this risk assessment study, caffeine was excluded as it is not toxic but an indicator. Sampling 1 was done in April 2015 and qualitative analyses for each of the contaminants were made on eight sampling points along the plant. Four of these samples were considered more important due to the location of where they were

taken, ie at intake, after WWTP, after RO and at the final effluent. In May 2015, follow-up sampling (Sampling 2) was done at the 4 locations described above, and quantitative analysis were done in order to obtain concentrations of the contaminants to be used as input in the risk matrix. Quantitative analysis of Iopromide, Stavudine and Cinchonine was not done as they were not detected during the qualitative screening step. Table 4-3 and **Error! Reference source not found.** show the results from the quantitative sampling. The concentrations are decreasing while traveling through the treatment train for the majority of the contaminants, which was expected. Imidacloprid is the most remarkable exception with a higher concentration in the outflow compared to the inflow. The concentration for sulfamethoxazole and simazine is also increasing along the treatment train. Cinchonidine has a concentration below the detection limit, as well as the majority of the samples for paracetamol.

Table 4-2: List of CECs analysed for risk assessment (Falk and Ohlin, 2015).

Group	Contaminant	Sampling 1 Detection	Sampling 2 Quantitative
Industrial Chemicals	Iopromide	-	
Pesticides, biocides and herbicides	Atrazine	+	✓
	Terbutylazine	+	✓
	Imidacloprid	+	✓
	Simazine	+	✓
Natural Chemicals	Caffeine	+	
	EE2	+	✓
Pharmaceuticals and metabolites	Lamivudine	+	✓
	Stavudine	-	
	Carbamazepine	+	✓
	Cinchonidine	+	✓
	Cinchonine	-	
	Paracetamol	+	✓
	Sulfamethoxazole	+	✓
Personal Care products	Triclosan	+	✓
Household chemicals and food additives	Bisphenol A	+	✓

Table 4-3: Concentration of contaminants

CEC	Intake *[µg/L]*	After WWTP *[µg/L]*	After RO *[µg/L]*	Effluent *[µg/L]*
EE2	2.53	2.38	0.154	0.13
Atrazine	0.0003	0.0006	0.0003	0.0001
Bisphenol A	0.5	0.179	0.029	0.015
Carbamazepine	0.402	1.08	0.94	0.72
Cinchonidine	<0.002	<0.002	<0.002	<0.002
Imidacloprid	<0.001	<0.001	0.003	0.002
Lamivudine	0.007	0.001	0.001	0.0003
Paracetamol	0.359	<0.001	<0.001	<0.001
Simazine	0.004	0.028	0.018	0.014
Sulfamethoxazole	0.014	0.022	0.01	0.013
Terbuthylazine	0.003	0.004	0.001	0.001
Triclosan	0.35	0.05	0.008	0.002

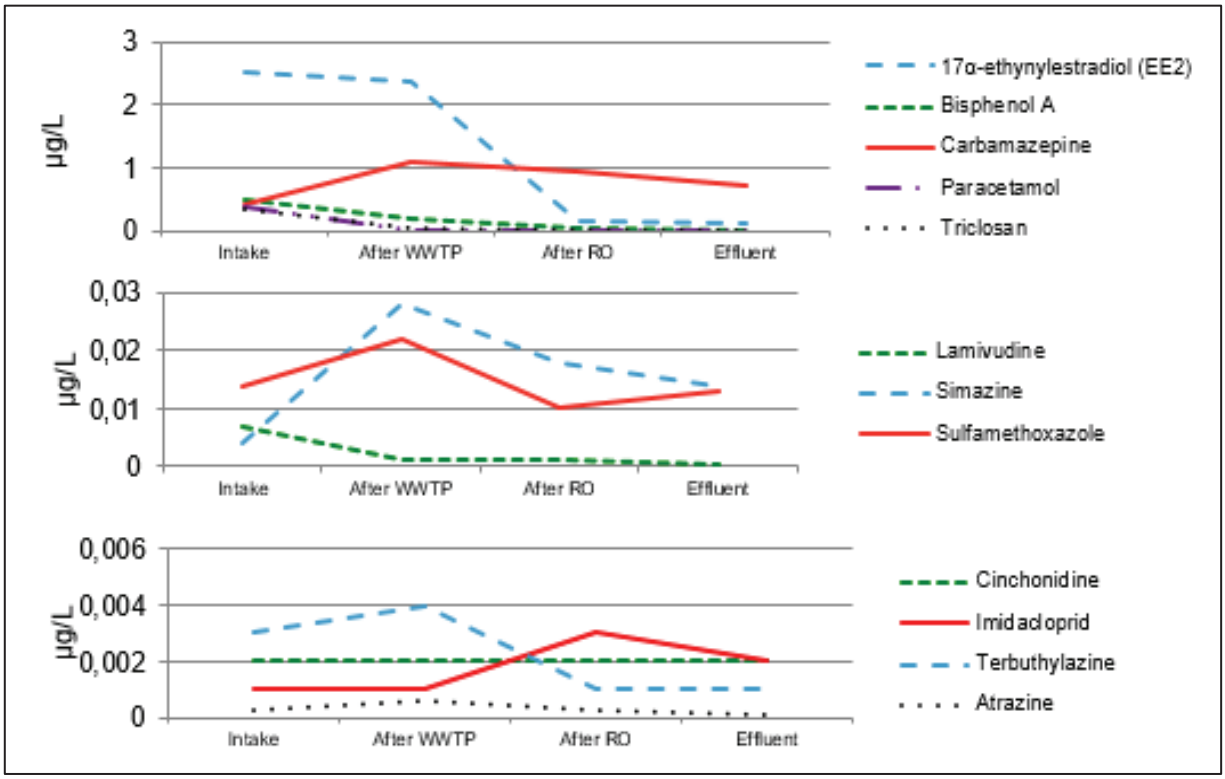

Figure 4-9: Results from quantitative analysis

4.2.4 Creating a risk matrix

4.2.4.1 *What is a risk matrix?*

A risk matrix can be used to visualise the severity of several hazards with the probability scale located at the y-axis and the consequence scale at the x-axis (David & Wilkinson, 2009). Figure 4-9 shows an example of a risk matrix. The risk priority number is given by the consequence multiplied by the probability (WHO & IWA, 2009).

Probability						
5	*Almost certain*	5	10	15	20	25
4	*Likely*	4	8	12	16	20
3	*Moderate*	3	6	9	12	15
2	*Unlikely*	2	4	6	8	10
1	*Rare*	1	2	3	4	5
		Insignificant	*Minor*	*Moderate*	*Major*	*Catastrophic*
		1	2	3	4	5

Consequence

Unacceptable
ALARP region
Acceptable

Figure 4-10: Example of a risk matrix.

Table 4-4 shows the levels of consequence and probability used in this study, adapted from WHO (2005) and NRMMC (2008). Based on the risk priority number, the risks can be considered to be unacceptable, acceptable or "As Low As Reasonable Practicable" (ALARP), which means that they are acceptable if it is unreasonable due to technical or economic reasons to reduce them.

Table 4-4: Levels of probability and consequences (WHO, 2015 and NRMMC, 2008)

Level	Probability		Consequence	
	Descriptor	**Description (WHO, 2005)**	**Descriptor**	**Description (NRMMC, 2008)**
5	Almost certain	Once per day	Catastrophic	Major impact for large population
4	Likely	Once per week	Major	Major impact for small population
3	Moderate	Once per month	Moderate	Minor impact for large population
2	Unlikely	Once per year	Minor	Minor impact for small population
1	Rare	Once every five years or has never occurred	Insignificant	Insignificant or not detectable

4.2.4.2 *Identifying the hazards*

Hazards that could lead to health risks due to exposure to the selected CECs were classified as follows:

A. Insufficient treatment in the WWTP
B. Insufficient treatment in the WRP (excluding advanced oxidation)
C. Insufficient treatment in the advanced oxidation process
D. Ingestion of water from the brine channel
E. Contaminants constantly present in the drinking water

Hazards A, B and C are related to occasional technical failures in the treatment systems. For these hazards, the probability for any event leading to a decreased water quality was used. This also results in the use of the highest probability for all events found in one hazard. For instance, if both electrical failure as well as foam building occur in the WWTP, then the probability for both events together will be used in the hazard connected to failure in the WWTP (Hazard A). Information on the frequency of failures was obtained from field visits and interviews.

Hazard D is related to contaminants in the brine channel. The probability of unintentional ingestion, Hazard D, was assigned based on how often one person in estimated to be bathing in the brine channel. This was found by interviewing employees at the WWTP.

Hazard E - The CECs that are always present in the effluent and therefore constantly consumed by the population through the drinking water are included in Hazard E. Hazard E was assigned the highest probability due to the constant exposure of ICECs from the drinking water.

4.2.4.3 *Assigning probabilities and consequences*

Hazard A - the estimated rate of occurrence of Hazard A, any failure in the WWTP, was assumed to be once per week and thus given a probability value 4.

Hazard B - the probability of a failure leading to an increased concentration of CECs in the WRP effluent (potable water) was considered very low. Hazard B was thereby assigned the probability value 1.

Hazard C – since the system is operated and maintained by experts off-site and due to the low risk of failures, the probability for Hazard was also set at 1.

Hazard D - unintentional ingestion during bathing, is assumed to occur in average once per week. Thus, Hazard D was therefore assigned the probability value 4.

Hazard E - Since the sampled concentrations are assumed to be constant and the exposure occurs on daily basis, the probability for Hazard E was assigned the probability number 5.

4.2.4.4 *Assigning consequences*

The consequence was calculated as shown below:

$$consequence\ (C) = \frac{concentration\ (c)}{reference\ value\ (RV)}$$

Concentrations

When identifying the concentrations for the hazards connected to Hazards A, B and C, the worst-case scenario was used by assuming that no treatment of the CEC is possible in the corresponding processes during the hazard (Falk and Ohlin (2015). The treatment efficiencies obtained from the sampling results were used to calculate the expected removal after the potential failure (Table 4-5). For

Hazard D, ingestion was assumed when people from the community used the brine channel for bathing. All contaminants removed from the WRP are assumed to end up in the brine streams where the flow is approximately 1/5 of the total inflowing wastewater. The concentration was therefore calculated as the sum of the removal in the WRP times five.

For Hazard E, it was assumed that the consumers get 30% of their daily intake of water from WRP A, thus, the long-term exposure through drinking water is therefore calculated with the factor 0.3. No dilution is assumed for short-term exposure, due to the possibility that only water from the WRP is consumed during a failure.

Table 4-5: Input for calculation of consequences for the different hazards.

	A	B	C	D	E
Hazard	*Insufficient treatment in the WWTP*	*Insufficient treatment in the WRP (excluding advanced oxidation)*	*Insufficient treatment in the advanced oxidation process*	*Unintentional ingestion of water from brine channel*	*Contaminants constantly present in the drinking water*
Reference value	Short-term exposure	Short-term exposure	Short-term exposure	Ingestion during bath	Long-term exposure
Concentration during Hazard	Concentration in influent times part left after removal in WRP	Concentration before WRP times part left after removal in advanced oxidation	Concentration before advanced oxidation	Removal in WRP times 5	Effluent times 0.3

Calculating reference values (RV)

NRMMC (2008) recommends the use of the following guideline values for contaminants in reclaimed drinking water during long-term exposure:

- ADI and TDI, usually calculated by applying a safety factor to a concentration corresponding to the No Observed Adverse Effect Level (NOAEL) (WHO, 2011b).
- S-ADI, used for pharmaceuticals and derived by using the therapeutic dose divided by a safety factor (NRMMC, 2008).
- TTC that divides the chemicals into toxicity groups, which gives them a representative dosage and includes a safety factor (NRMMC, 2008).

These dosages can be summarised under the concept *equivalent safe dose* with the unit µg contaminant/kg body weight/day. Table 4-6 shows the equivalent safe doses, classes and safety factors. When calculating the reference value for long term exposure from contaminated drinking water a body weight of 70 kg and an intake of two litres of water per day were made according to NRMMC (2008). Thus, the reference value was calculated as follows:

$$Reference\ Value\left[\frac{ug}{litre}\right] = Equivalent\ Safe\ Dose\left[\frac{\mu g\ per\ day}{kg\ body\ weight}\right] \times \frac{70\ kg\ body\ weight}{2\ litre\ per\ day}$$

The reference value for ingestion during bathing (Table 4-7) was therefore calculated as shown below:

$$Reference\ Value\left[\frac{ug}{litre}\right] = Equivalent\ Safety\ Dose\left[\frac{\mu g\ per\ day}{kg\ body\ weight}\right] \times \frac{13\ kg\ body\ weight}{0.09\ litre\ /7day}$$

Table 4-6: Equivalent safe doses, classes and safety factors.

Contaminant	Equivalent safe dose *(µg/kg body weight/day)*	Class	Reference (class)	Safety factor	Reference (safety factor)
EE2	4.3×10^{-5}	S-ADI	(NRMMC, 2008)	10000	(NRMMC, 2008)
Atrazine	10	ADI	(WHO, 2011a)	100	(WHO, 2011a)
Bisphenol A	50	TDI	(NRMMC, 2008),	5000	(EFSA, 2006)
Carbamazepine	2.8	S-ADI	(NRMMC, 2008)	1000	(NRMMC, 2008)
Cinchonidine	1.6	S-ADI *	(Petrik, et al., 2014)	1000	(Petrik, et al., 2014)
Imidacloprid	60	ADI	(EFSA, 2013)	100	(EFSA, 2013)
Lamivudine	2	S-ADI *	(Petrik, et al., 2014)	1000	(Petrik, et al., 2014)
Paracetamol	50	ADI	(NRMMC, 2008),	100	(EMA, 1999)
Simazine	0.52	TDI	(WHO, 2011a)	1000	(WHO, 2011a)
Sulfamethoxazole	10	ADI	(NRMMC, 2008)	100	(NRA, 2000)
Terbuthylazine	2.2	TDI	(WHO, 2011a)	100	(WHO, 2011a)
Triclosan	1.5	TTC**	(NRMMC, 2008)	100	(NRMMC, 2008)

* Calculated from therapeutic dose

** Class III

Table 4-7: Reference values for long term, short term and ingestion during bathing

	Reference value	Long-term exposure *[µg/L]*	Short-term exposure *[µg/L]*	Ingestion during bath *[µg/L]*
1	EE2	0,001505	15	0,002
2	Atrazine	350	35000	482
3	Bisphenol A	1750	8750000	2407
4	Carbamazepine	98	98000	135
5	Cinchonidine	56	56000	77
6	Imidacloprid	2100	210000	2889
7	Lamivudine	70	70000	96
8	Paracetamol	1750	175000	2407
9	Simazine	18	18200	25
10	Sulfamethoxazole	350	35000	482
11	Terbuthylazine	77	7700	106
12	Triclosan	53	5250	72

Calculating the consequences

Table 4-8 shows the calculated consequences, considering the concentrations and reference values. A consequence of 1 corresponds to consumption equal to the reference value, whereas, a consequence <1 represents a concentration below the reference values (Falk and Ohlin, 2015). From Table 4-8, it is clear that for most of the CECs (except for **EE2**), the concentration was below the reference value.

Table 4-8:Calculated consequences for Hazards A, B, C, D and E.

	Consequence ***(Probability)***	**A** ***(4)***	**B** ***(1)***	**C** ***(1)***	**D** ***(4)***	**E** ***(5)***
1	EE2	<1	<1	<1	259	26
2	Atrazine	<1	<1	<1	<1	<1
3	Bisphenol A	<1	<1	<1	<1	<1
4	Carbamazepine	<1	<1	<1	<1	<1
5	Cinchonidine	<1	<1	<1	<1	<1
6	Imidacloprid	<1	<1	<1	<1	<1
7	Lamivudine	<1	<1	<1	<1	<1
8	Paracetamol	<1	<1	<1	<1	<1
9	Simazine	<1	<1	<1	<1	<1
10	Sulfamethoxazole	<1	<1	<1	<1	<1
11	Terbuthylazine	<1	<1	<1	<1	<1
12	Triclosan	<1	<1	<1	<1	<1

NOTE:

The method of using the largest probability for any failure, as well as using the consequences of nothing being treated in the specific treatment steps, results in an overestimation of the risks. Since the risk assessment resulted in very low risks, despite the overestimation, the risks can be considered extremely low. If future studies with the same method would result in higher risks, a more thorough investigation on the expected removal should be made. Since all the risks connected to failures inside the plant were very low in this study there was no need for analysing the potential sub-failures in the hazards. This would have been necessary with higher risks during treatment failures, both to better evaluate causes of the risks but also for deciding which countermeasures that most effectively can remove them. Some processes in the treatment system experience decreased treatment efficiency during decreased water quality of the incoming water: failure in one system could therefore lead to less sufficient treatment later in the treatment train. Moreover, if a large portion of a contaminant is removed in the beginning of the treatment train it might be inaccurate to assume that the treatment in the next step would be of the same ratio as when a larger portion would be in the feed water. This may instead lead to an underestimation of the treatment efficiency. Due to these problems, the obtained expected treatment rates should be compared to rates from similar studies in literature in case the risk assessment shows potential risks from hazards resulting from process failures. To assume long-term exposure when calculating the risk during unintentional exposure during bathing in the brine channel led to an overestimation of the risk since this refers to a lifetime's exposure. The children bathing in the channel will most likely not be exposed though this pathway when they are grown up due to the changed lifestyle. To assume short-term exposure would, on the other hand, be an underestimation since employers at the WWTP claim that the same individuals revisit every weekend, leading to repeated exposure.

4.2.4.5 *The risk matrix*

Table 4-9 shows the probability and consequence scales corresponding to the levels. The probability scale was obtained by multiplying the probability by a factor of 3, while for the consequence scale, the consequence numbers are multiplied by three for each level (see Falk and Ohlin, 2015).

Table 4-9: Probability and consequence scales

Probability			Consequence		
Scale	**P**	**Description (WHO, 2005)**	**Scale**	**Interval C=c/RV**	**Description (NRMMC, 2008)**
16	5	Once per day	**81**	C ≥ 1000	Major impact for large population
8	4	Once per week	**27**	100 ≤ C < 1000	Major impact for small population
4	3	Once per month	**9**	10 ≤ C < 100	Minor impact for large population
2	2	Once per year	**3**	1≤ C < 10	Minor impact for small population
1	1	Once every five years or has never occurred	**1**	1 > C	Insignificant or not detectable

The risk-tolerability levels were identified by plotting the product of the assigned probabilities and consequences (Figure 4-11).

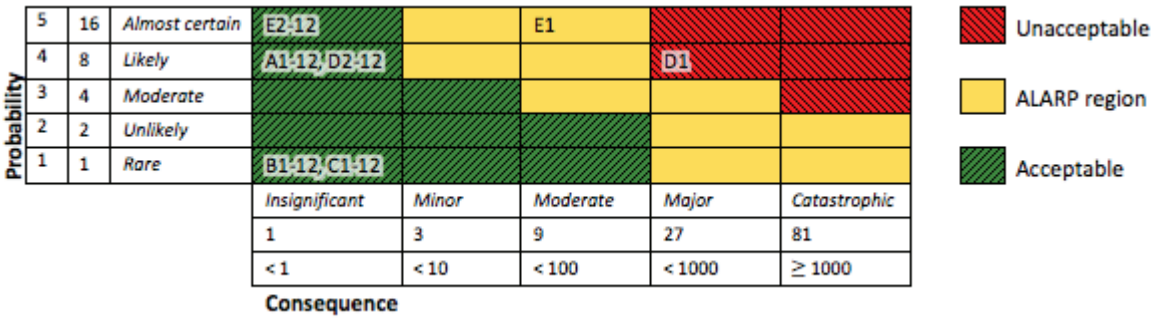

Figure 4-11: Risk matrix with location of risks.

Table 4-10 shows the risk profile and level for each of the Hazards. The risk priority number is given by the consequence scale multiplied by the probability scale (WHO & IWA, 2009). The results display that two risks have high risk priority numbers. Risk E1 that corresponds to the constant presence of EE2 in the effluent gets the risk priority number 144 and is located in the ALARP region of the risk matrix. Furthermore, risk D1, the risk of children swimming in the brine channel and ingesting the contaminant EE2, has the risk priority number of 216 and is located in the unacceptable area of the risk matrix. In order to decrease the overall risks of the system the focus was laid on decreasing these two risks by recommending countermeasures.

Table 4-10: Risk priority numbers and levels for Hazards A, B, C, D and E

Risk	Risk priority number	Risk Level
B1-12, C1-12	1	Low
A1-12, D2-12	8	Low
E2-12	16	Low
E1	144	Medium
D1	216	High

4.2.5 Countermeasures for the identified risks

4.2.5.1 *Using the Multi Criteria Decision Analysis (MCDA)approach*

Multi-Criteria Decision Analysis (MCDA) is a set of decision-making techniques used for ranking options in a structured way by using a set of criteria (DCLG, 2009). In drinking water applications, the criteria of risk reduction and cost of each countermeasure usually used (see Figure 4-11) (Lindhe, et al., 2013).

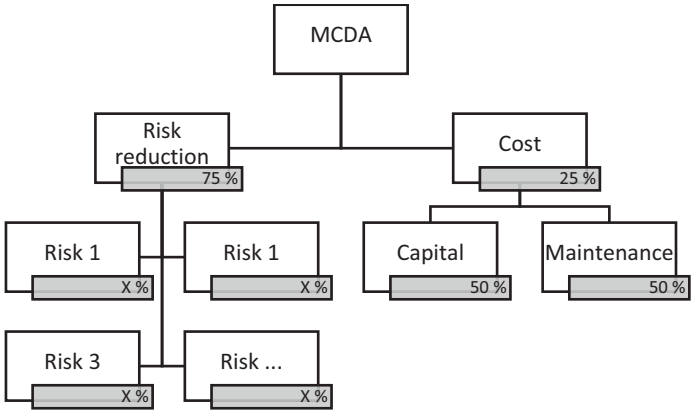

Figure 4-12: Structure of a MCDA.

The criteria are further ranked based on their importance for the result. The risk reduction may for example be considered more important than the cost of a countermeasure. After obtaining the results from the MCDA, a sensitivity analysis can be done to see how the ranking of the criteria affect the final score (DCLG, 2009). This increases the credibility of the MCDA and the most influential criteria can be further evaluated.

4.2.5.2 *MCDA analysis for WRP A*

An MCDA was performed to evaluate which countermeasures were most suitable. Ozonation (see Huber, et al., (2003); Huber, et al., (2004) and Pauwels, et al., (2006) and GAC (see de Ruddera, et al. (2004) and Bodzek and Dudziak (2006)) are known to be effective for therefore the technologies chosen as countermeasures. In addition, building a wall around the brine channel to constrain unauthorised people to enter was therefore chosen as the third countermeasure.

Risk reduction

An ozone dosage of 1 g/m^3 has shown to degrade more than 90% of the EE2, and an increased ozone dosage to 3 g/m^3 resulted in an EE2 concentration under the detection limit with more than 99.8 per cent removal (Hashimoto, Takahashi, & Murakami, 2006). With an ozone dosage of approximately 2 g/m^3 as chosen in this case was the removal assumed to be 95 per cent. The location of the ozone process is usually prior to the filtration (US EPA, 2015a). The ozone was therefore placed after the WWTP but before the sand filtration in the treatment train. The removal rate of EE2 by GAC was set to more than 99.8%, based on the most frequent mentioned treatment efficiency in the literature. The GAC was also placed after the WWTP in the same location as the ozone. This was because of the common use of GAC for filtration (US EPA, 2015b). It is not recommended to place the GAC before the flocculation though, since this would require frequent backwashing. Based on the EE2 removal, corresponding to the additional processes and their location, were new concentrations obtained as can be seen in Table 4-11.

Table 4-11: Input data for risk reduction

Countermeasure	EE2 Removal	Location	Calculated concentration of EE2 during bath	Calculated concentration of EE2 in effluent
Ozonation	>95 %	After WWTP	0.56	0.0065
GAC	>99.8 %	After WWTP	0.02	0.000026

The countermeasure of building a wall will only affect the probability of people bathing in the brine channel, which was assumed to decrease to level 1 on the probability scale. The wall will however not affect the consequence of exposure during an event of bathing and the probability of exposure from EE2 will not be affected by implementing ozone or GAC. Figure 4-13 visualises the risks location in the risk matrix after implementing the countermeasures.

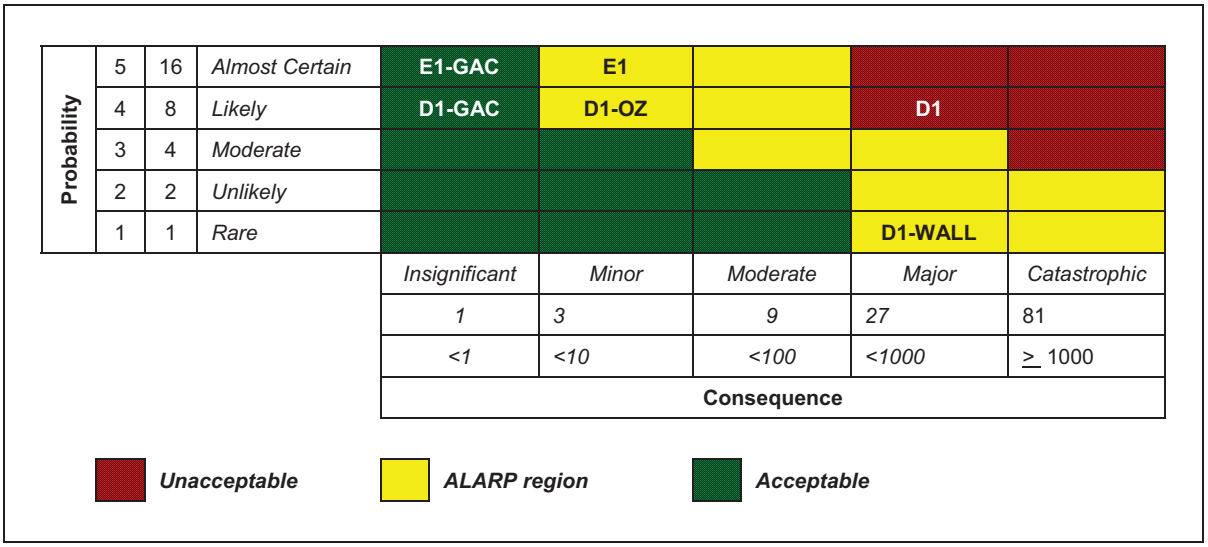

Figure 4-13: Risk reduction visualised on risk matrix.

Note:

GAC = new locations of risks if implementing GAC.

OZ = new location of risks if implementing ozonation.

WALL = new locations of risks after building a wall (only one risk is affected in this case).

The new risk priority numbers and the level changes in the risk matrix are presented in Table 4-12.

Table 4-12: Risk reduction priority numbers

Measure	D1 (EE2 In effluent)				E1 (Ingestion of EE2 during bath in brine)			
	C	P	New risk priory number	Level Change	C	P	New risk priority number	Level Change
Ozonation	13	4	*216-24*=192	◆→▲	1	5	*144-4*=96	▲→▲
GAC	<1	4	*216-8*=208	◆→●			*144-16*=128	▲→●
Wall	259	1	*216-27*=189	◆→▲			-	▲→▲

Cost

The inflowing water to a future ozonation process was assumed to be close to pH 7.0, and the need of a pH regulator was therefore excluded in the cost. By using calculations based on Munther et al. (2006), an annuity of 10 per cent during 15 years was done. The calculation for the maintenance cost originates from the average cost throughout 15 years. An average flow of 55 m^3/hour for WRP A was assumed compared to the 40 m^3/hour used by Munther et al. (2006), resulting in an approximately 50 per cent higher cost for this ozonation process. Reflecting the inflation, the approximate capital cost in year 2015 was 400 000 EUR (R5 720 000) and the maintenance cost 6 000 EUR/month (R85 800). According to an environmental consultant in water treatment the capital cost for a similar GAC treatment process was approximately 200 000 EUR in Sweden (around R2 860 000). The maintenance cost was approximately 130 000 EUR per month (R1 859 000), mainly to buy the activated carbon needed for the process. The cost of the wall around the drinking water treatment plant was approximately 12 500 EUR (R179 000) and was 2 metres high and 250 metres long. A wall around the brine channel would be about 820 metres long. With the same price per metre this wall would have a capital cost of approximate 40,000 EUR (R572 000) based on the assumption of cost from the superintendent regarding the already built wall. The assumed maintenance cost for the wall during the first 15 years is assumed to be close to zero. Table 4-13 summarises the costs for the countermeasures.

Table 4-13: Cost for the countermeasures

Countermeasures	Capital cost (Euro)	Capital cost (Rand)	Maintenance cost (Euro/year)	Maintenance cost (R/year)
Ozonation	400 000	5 720 000	6000	85 800
GAC	200 000	2 860 000	130 000	1 859 000
Wall	40 000	572 000	0	0

A MCDA model was built up, as shown in Figure 4-14. The risk reduction of Hazard E1, contaminants in the effluent, was ranked as three times more important than the risk reduction of Hazard D1, bathing in the brine channel. This ranking is so since Hazard E1 affects the whole community through the drinking water while Hazard D1 only affects the children bathing in the prohibited brine channel.

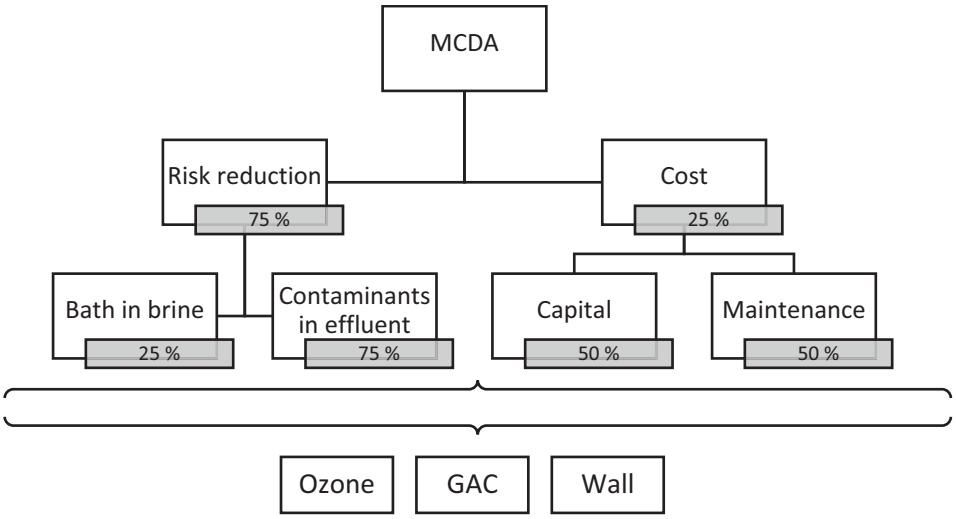

Figure 4-14: Structure of MCDA for WRP A countermeasures

The risk reductions and the costs (Table 4-12 and Table 4-13) were put into the MCDA model and a result was obtained (see Figure 4-15). The calculation of the scores of the countermeasures in the MCDA was done in the software Web-HIPRE. The result shows that the most suitable countermeasure is to implement a process with GAC. This is mainly due to the risk reduction of risk E1 (contaminant EE2 in the drinking water). The sensitivity analysis below shows the influence that the ranking of the criteria has on the result in the MCDA.

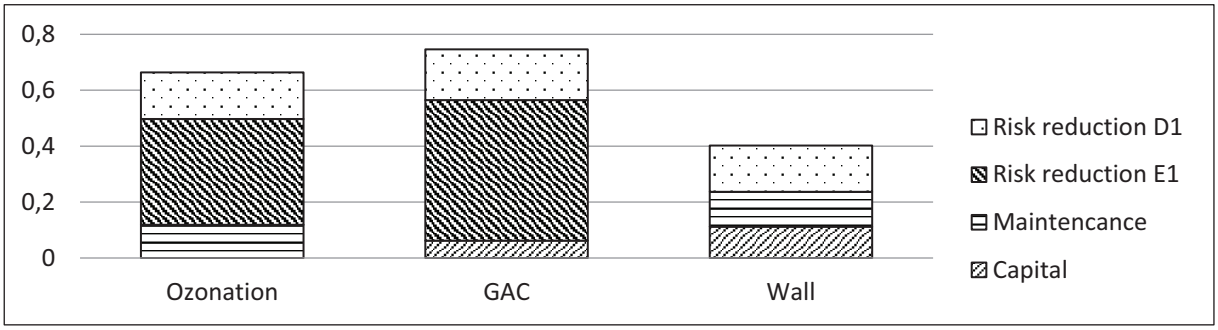

Figure 4-15: Result from MCDA

Figure 4-16 shows the result of the MCDA depending on how the risk reduction is ranked in relation to the cost. The risk reduction had the influence of 75 per cent and the cost 25 per cent, giving GAC the highest score. All the countermeasures would have received approximately the same score if the risk reduction on the other hand would have been considered as equally important as the cost (50 per cent). The sensitivity graph in Figure 4-17 shows how the result of the MCDA varies depending on the inter-ranking of the risk reduction of risk E1 (EE2 constantly in effluent) versus risk D1 (children getting exposed to EE2 through brine channel). In the MCDA the risk reduction of E1 was ranked to have a 75 per cent influence on the result while the risk reduction of D1 had 25 per cent influence. It can be seen in the Figure 4-16 that GAC receives the highest score unless the risk reduction of E1 is ranked to have less than 25 per cent of the total influence of the risk reduction.

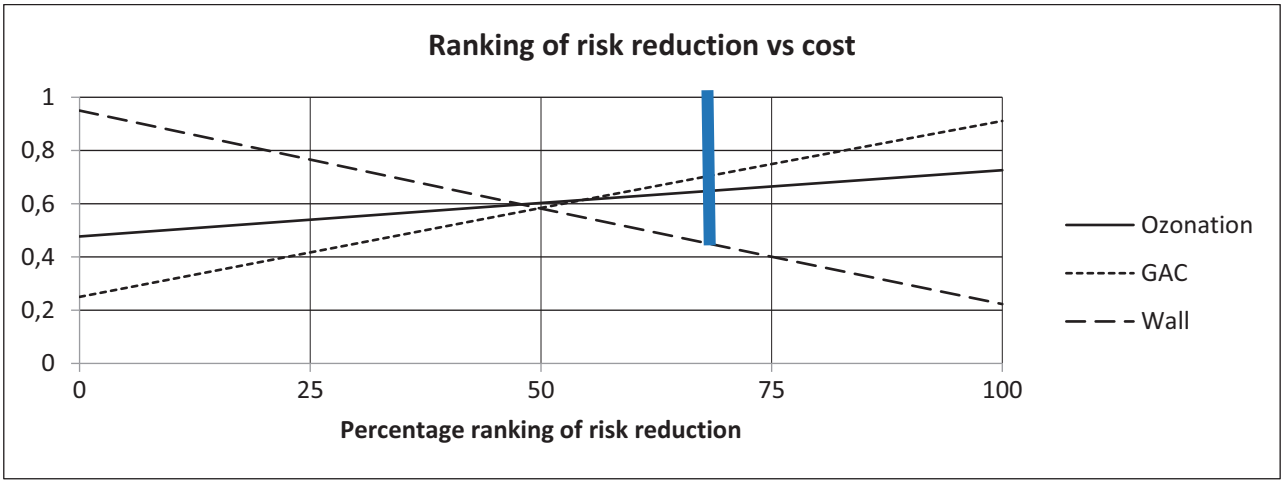

Figure 4-16: Sensitivity plot for ranking of risk reduction in relation to cost. The risk reduction was ranked to 75 per cent in MCDA

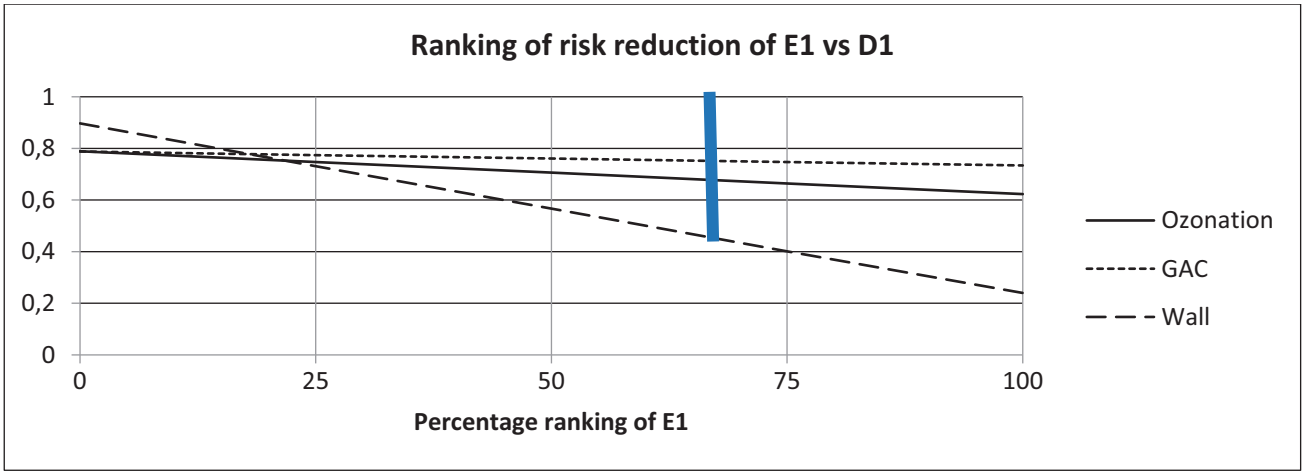

Figure 4-17: Sensitivity plot for ranking of risk reduction of E1 (EE2 constantly in effluent) in relation to D1 (children getting exposed to EE2 through brine channel). E1 was ranked to 75 per cent in the MCDA.

The influence ranking variation of the capital cost versus the maintenance cost to the result of the MCDA can be seen in Figure 4-18. The capital cost is ranked to be equally influential to the result as the maintenance cost in the MCDA. If the capital cost would have the influence of 25 per cent or less, the countermeasure of ozonation would receive the highest score.

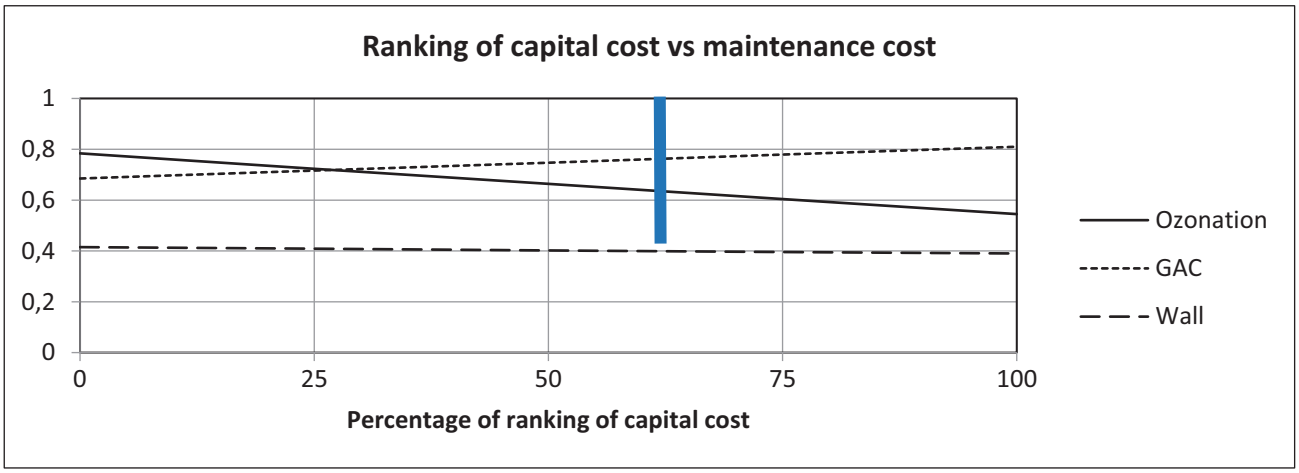

Figure 4-18: Sensitivity plot for ranking of capital cost in relation to maintenance cost. The maintenance cost was ranked to 50 per cent in the MCDA.

4.3 SUMMARY OF RESULTS

By studying the obtained risk matrix, the most severe risks were identified. To minimise these risks, countermeasures were suggested. The impact of each countermeasure led to new probabilities and consequences for the hazards and thereby new risk priority numbers. When an additional treatment step was chosen as a countermeasure its' expected removal and location in treatment train were found in the literature. These facts were used to introduce the treatment step in the calculations to get the expected final removal with it included. Thereby, new concentrations could be obtained in order to calculate the new consequences.

The basis for the MCDA was that the risk reduction is more important than the cost when choosing countermeasures. The sensitivity analysis showed that an equal rating of the risk reduction and the cost would have led to another result, which means that this ranking was essential for the results. However, this ranking was done due to the fact that a countermeasure can only be a good investment if it leads to a high risk reduction and the same cannot be said for a low cost. The treatment efficiency found in scientific studies was given a high significance in the MCDA due to the high ranking of the risk reduction, which may be problematic due to the small selection of relevant literature about treatment technologies for the rare hormone EE2. Furthermore, the few existing reports in the area do have a big variation of their results.

The risk reduction for the hazard related to high concentrations of EE2 in the drinking water was ranked higher than decreasing the risk of exposure during illegal bathing in the brine channel. This, due to the fact that the high concentrations in the effluent can affect the whole population and the swimming activities only concern a small group during a more limited time of their life. This ranking was also made due to the general population's inability to choose alternative sources of drinking water, compared to the intentional illegal activity.

The sensitivity analysis did, however, show that the same result of the MCDA would have been obtained even if the risk reduction of the two hazards had been equally rated.

It was difficult to find realistic investment and operation costs to use in the MCDA for the countermeasures. This was due to the disinclination from companies to give price information about their products, but also because of the uncertainty of the price picture in South Africa compared to other parts of the world. It was further considered very uncertain to use cost estimation that was older than a couple of years. Some prices were adjusted according to inflation but the fact remains that these kinds of technologies develop dramatically during a short period of time. It could therefore be inadequate to get price pictures from outdated reports due to the fast development of technologies. The maintenance cost also varies due to the ozonation dosage and expected carbon consumption, which was hard to estimate due to the limited literature in this field.

Ozonation and GAC, the technologies used as countermeasures in the MCDA, have scientifically shown good treatment efficiency for EE2 but could be perceived as expensive. A cheaper option than these technologies could therefore be to implement a pilot scale sized electrochemical treatment process using electrolysis. Electrolysis has proven to give a sufficient treatment of EE2 and has several benefits, including low maintenance cost. This technology was not included in the MCDA due to the limited ability to find this technology on the commercial market in South Africa, but could be very interesting to evaluate in future studies.

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1 INDICATIVE CEC REMOVAL POTENTIAL OF THE DIFFERENT TREATMENT PLANTS

This study indicates that the available treatment process in WRP A was able to effectively remove more than 80% of targeted PFCs in the wastewater. The largest percentage of total PFCs removal was found in WRP A (97%), followed by WWTP C (65%), WWTP B (54%) and WWTP A (52%). Of all the targeted perfluorinated compounds, PFHpA, PFOA, PFNA, and PFUnDA were found to be the dominant PFCs detected in the raw wastewater influent of all the WWTPs. The highest concentration of PFOs was found in WWTP A (10.0-9.5 ng/ℓ), which receives inflow from both municipal, industrial and landfill leachates. There is a noticeable decrease in the PFCs concentration (except for PFOA, PFOS and PFNA) from influent to effluent through the treatment processes. Increases in the concentration of some PFCs after activated sludge treatment was noted in WRP A (during and after initial chlorination) and WWTP C and WWTP A. Chularueangaksorn et al. (2012) attributed the increase to bioaccumulation/adsorption of PFCs from new inflow of wastewater onto the activated sludge, which are subsequently released downstream. The concentrations of BPA and ACE in the four WWTP influents ranged from 1.32-210 µg/L and nd-175 µg/L respectively. There was a major decrease in the effluent concentration through the different treatment processes, indicating that these compounds are effectively removed by the treatment processes. Removal efficiency for BPA in WRP A, WWTP C, WWTP B, and WWTP B are 98.5%, 99.7, 93.4%, and 86.5%, respectively. Removal efficiency of Acetaminophen is 100% (WRP A), 95.6% (WWTP C), 100% (WWTP A), and 95.8% (WWTP B). The concentrations of BPA are this study (WRP A and C) are closely related to value reported by Olujimi et al. (2013) in Cape Gate WWTP, Cape Town.

5.2 STATISTICAL ANALYSIS OF PROCESS PERFORMANCE AND PLANT RELIABILITY

5.2.1 Process performance analysis

Overall, the current historical process data is not suited as is for deriving process monitoring models. However, there is scope, given rigorous data collection programmes, for univariate monitoring of key quality variables (slow sample rates), or multivariate monitoring of operational variables (fast sample rates).

5.2.2 Plant reliability analysis

Reliability analysis, as any data analyses, is sensitive to the quality and quantity of measurements available. Quality refers to data originating from calibrated instruments, taken consistently and without bias, for a long enough historical period to reflect all possible process conditions. Quantity refers to the number of samples used in the analysis: although a bare minimum of 30 values could be used to estimate a distribution, such a small sample size would not guarantee the previously mentioned quality requirements, and would also result in a large uncertainty of the estimated reliability. Since the practical application of statistical analysis is only as good as the data on which it is based, it would be worthwhile to conduct a rigorous data collection programme,

specifically for the purpose of estimating good distribution models for reliability and performance analyses. Such a rigorous data collection programme would have the following properties:

- Consistent measurements
- Validated measurements
- Annotated measurements
- Representative measurements
- Large sample sizes.

A future direction for statistical analysis is to consider how process unit reliabilities affect other process unit reliabilities, and in turn, the reliability of the entire plant under consideration. For this, multivariate and conditional distribution fitting would be required, which would require rigorous data collection at a high data quality.

5.3 HUMAN HEALTH RISKS

There has been increasing concern regarding substances in the environment that could impact on human health. Biological methods are becoming more popular as screening tools to assess the effects of chemical mixtures A battery of bio-assays was included in the study to illustrate their use in assessing water quality. These included the Ames mutagenicity test, the Daphnia acute toxicity test and the YES (yeast estrogen screen) test, to test for oestrogenic activity. This provided a general indication of effluent quality and is often recommended as screening tests for wastewater reuse. The bio-assays showed the improvements in wastewater quality following treatment through the various treatment works, and the results showed how these bio-assays are able to be used to monitor the water quality.

It is recommended that a battery of bio-assays representing different trophic levels be included in a monitoring programme if direct reuse of wastewater is known to occur either intentionally or unintentionally. Different bio-assays can be selected as long as various activities are tested. For example, different oestrogen mimicking assays and anti-androgenic activity may be included.

Findings from health risk assessment studies revealed the need to manage two risks. The first risk corresponds to the constant presence of 17α-ethinylestradiol (EE2) in the final effluent. Furthermore, the risk of children swimming in the brine channel and ingesting the contaminant EE2, has the risk priority number of 144 and is located in the unacceptable area of the risk matrix. As water reclamation processes were found to not treat the water to a satisfying level with respect to EE2, countermeasures were recommended. Electrochemical removal could be a good option in a pilot project for the plant in the future, but more research needs to be completed for an appropriate design and implementation of this process. Ozonation and GAC are therefore the technologies chosen as countermeasures due to the reasons stated above.

In addition, building a wall was suggested to constrain unauthorised people from reaching the brine channel. A fence has earlier been built and rebuilt several times around the area but has been stolen and is therefore not a good option to prevent the children from the community to enter. A wall was previously built around the drinking water treatment plant in the town and has been effective according to the superintendent.

REFERENCES

1. Adolfsson-Erici, M., Pettersson, M., Wahlberg, C. and Asplund, L. (2005). Östrogena ämnen i avloppsvatten, slam och lagrad urin. Stockholm: Svenskt Vatten AB.
2. Ames, B.N., McCann, J. and Yamasaki, E. (1975). Methods for Detecting Carcinogens and Mutagens with the Salmonella/Mammalian-Microsome Mutagenicity Test. Mutation Res., 31, 347-364.
3. Asano, T., Burton, F., Leverenz, H., Tsuchihashi, R. and Tchobanoglous, G. (2007). Water Reuse; Issues, Technologies and Applications. New York: Metcalf and Eddy.
4. Beresford, N., Routledge, E.J., Harris, C.A. and Sumpter, J.P. (2000). Issues arising when interpreting results from an in vitro assay for estrogenic activity. Toxicology and Applied Pharmacology 162: 22-33.
5. Bodzek, M. and Dudziak, M. (2006). Elimination of steroidal sex hormones by conventional water treatment and membrane processes. Desalination, 198, 24-32.
6. Chiang, L.H., Russell, E.L., Braatz, R.D. 2001. Fault detection and diagnosis in industrial systems. Advanced Textbooks in Control and Signal Processing. Springer.
7. Chopra, A., Kumar Sharma, A. and Kumar, V. (2011). Overview of Electrolytic treatment: An alternative technology for purification of wastewater. Applied Science Research, 3(5), 191-206.
8. Daughton, C., Ternes, T. December 1999. Pharmaceuticals and personal care products in the environment; agents of subtle change? Environmental Health Perspectives, v 107, n 6, p 907-938
9. De Jager, C., Aneck-Hahn, N.H., Barnhoorn, I.E.J., Bornman, M.S., Pieters, R., Van Wyk, J.H. and Van Zijl, C. (2011) The compilation of a toolbox of bio-assays for detection of estrogenic activity in water. WRC Report No. 1816/1/10. Water Research Commission, Pretoria.
10. De Ruddera, J., Van de Wiele, T., Dhooge, W., Comhaire, F. and Verstraete, W. (2004). Advanced water treatment with manganese oxide for the removal of 17a-ethynylestradiol (EE2). Water Research, 38, 184-192.
11. Drewes, J.E., Hemming, J.D.C., Schauer, J.J. and Sonzogni, W.C. 2006. Removal of Endocrine Disrupting Compounds in Water Reclamation Processes. Water Environment Research Foundation. ISBN 184339-758-7
12. Falk, D. and Ohlin A. (2015) Chemical risk assessment in the potable water reclamation system in Beaufort West, South Africa: identified contaminants of emerging concern affecting human health. Master of Science Thesis in the Master's programme Infrastructure and Environmental Engineering. Chalmers University of Technology, Gothenburg, Sweden
13. Grover, D.P., Balaam, J., Pacitto, S. Readman, J.W., White, S. and Zhou, J.L. (2011). Endocrine disrupting activities in sewage effluent and river water determined by chemical analysis and in vitro assay in the context of granular activated carbon upgrade. Chemosphere, 84: 1512-1520.
14. GWRC (2003). Endocrine Disrupting Compounds An overview of the sources and biological methods for measuring EDCs Prepared by: Kiwa Water Research (Netherlands).

15. Huber, M., Canonica, S., Park, G.-Y. and Von Gunten, U. (2003). Oxidation of Pharmaceuticals during Ozonation and Advanced Oxidation Processes. Environmental Science and Technology, 37(5), 1016-1024.

16. Huber, M., Ternes, T. and Von Gunten, U. (2004). Removal of Estrogenic Activity and Formation of Oxidation Products during Ozonation of 17α-Ethinylestradiol. Environmental Science and Technology, 38(19), 5177-5186.

17. Johnson, A. and Sumpter, J. (2001). Removal or endocrine-disrupting chemicals in activated sludge treatment works. Environmental Science and Technology, 35(24), 4697-4703.

18. Julies, E.M., Pool, E.J., Faul, A.K. and Amutenya, C. 2013, Endocrine disrupting chemicals in various wastewater treatment and reclamation plants in Namibia. Department: Biological Sciences, University of Namibia, International Water Association Reuse specialist conference, Windhoek, Namibia, October 2013.

19. Koh, Y., Chiu, T., Boobis, A., Cartmell, E., Scrimshaw, M. and Lester, J. (2008). Treatment and Removal Strategies for Estrogens from Wastewater. Environmental Technology, 29(3), 247-267.

20. Lee, B.-C., Kamatab, M., Akatsuka, Y., Takeda, M., Ohno, K., Kamei, T. and Magara, Y. (2004). Effects of chlorine on the decrease of estrogenic chemicals. Water Research, 38(3), 733-739.

21. Metcalf & Eddy, 2006. Water Reuse: Issues, Technologies, and Applications. McGraw-Hill, New York.

22. Metcalf, G., Pillay, L., Murutu, C., Chiburi, S., Gumede, N. 2013. Wastewater Reclamation for Potable Reuse. Water Research Commission, Project No. K5/1894.

23. Moriyama, K., Matsufuji, H., Chino, M. and Takeda, M. (2004). Identification and behavior of reaction products formed by chlorination of ethynylestradiol. Chemosphere, 55(6), 839-847.

24. Napier-Munn, T.J. 2014. Statistical methods for mineral engineers. How to design experiments and analyse data. JKMRC Monograph Series in Mining and Mineral Processing: No. 5. JKMRC.

25. Niku, S., Schroeder, E.D., Samaniego, F.J. (1979). Performance of activated sludge processes and reliability-based design. Journal of the Water Pollution Control Federation. 50(12), 2841-2857.

26. NIST/SEMATECH. (2013). Engineering Statistics Handbook: 1.3.5.16. Kolmogorov-Smirnov Goodness-of-Fit Test. http://www.itl.nist.gov/div898/handbook/eda/section3/eda35g.htm

27. OECD (2004) Guidelines for the Testing of Chemicals, Section 2 Effects on Biotic Systems. Test No. 202: Daphnia sp. Acute Immobilisation Test". OECD Guidelines for the Testing of Chemicals. Organisation for Economic Co-operation and Development. ISBN 9789264069947.

28. Oliveira, S.C., Von Sperling, M. (2008). Reliability analysis of wastewater treatment plants. Water Research. 42, 1182-1194.

29. Pauwels, B., Deconinck, S., and Verstraete, W. (2006). Electrolytic removal of 17α-ethinylestradiol (EE2) in water streams. Journal of Chemical Technology and Biotechnology, 81, 1338-1343.

30. Purdom, C., Hardiman, P., Bye, V., Eno, N., Tyler, C. and Sumpter, J. (1994). Chemistry and Ecology. i Estrogenic Effects of Effluents from Sewage Treatment Works (ss. 275-285). Taylor and Francis.

31. Racz, L. and Goel, R. (2009). Fate and removal of estrogens in municipal wastewater. Journal of Environmental Monitoring, 58-68.

32. Routledge, E. and Sumpter, J. (1996). Estrogenic activity of surfactants and some of their degradation products assessed using a recombinant yeast screen. Environmental Toxicology and Chemistry 15: 241-248.

33. Snyder, S.A., Adham, M.R., Redding, A.M., Cannon, F.S., DeCarolis, J., Oppenheimer, J., Wert, E.C., Yoon, Y., 2005. Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals. ScienceDirect, Desalination 202, 156-181.

34. Sohoni, P. and Sumpter, J.P. (1998). Several environmental oestrogens are also anti-androgens. Journal of Endocrinology 158: 327-339.

35. Ternes, T.A., Janex-Habibi, M., Knacker, T., Kreuxinger, N., Siegrist, H. 2004. Assessment o Technologies for the Removal of Pharmaceuticals and Personal Care Products in Sewage and Drinking Water Facilities to Improve the Indirect Potable Water Reuse. EU Projects, European Union, Contract No. EVK1-CT-2000-00047 http//www.eu-poseidon.com


9781431209569