

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

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***VOLUME I: A CONCISE RESEARCH REPORT***



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

## **VOLUME I: A CONCISE RESEARCH REPORT**

Report to the  
**Water Research Commission**

by

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

Volume I: A concise research report (**This report**)

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 (**WRC Report No. TT 742/3/17**)

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## EXECUTIVE SUMMARY

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### BACKGROUND

If not treated properly, 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. The possible presence of emerging contaminants in the final reclaimed water 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. Thus, there is uncertainty over the magnitude of risk of human exposure to emerging contaminants of concern in wastewater treated for direct potable reuse. 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 following were the aims of the project:

- a. Compile a list of emerging contaminants of concern in reclaimed potable water for Southern Africa.
- b. Identify 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.
- c. Draw up an assessment report on indicative CEC removal potential in water reclamation systems and wastewater treatment plants, potential for failures in reliability and consequent risks for direct potable water reuse.

### SCOPE OF WORK

This report comprises a summary of sections of the overall project focussing on potential occurrence contaminants of concern; list of priority compounds which should be monitored and methods for their detection and at what levels these contaminants are deemed safe for drinking water. The performance of different treatment processes for the removal of chemicals of concern was investigated at six different water treatment plants, including two water reclamation plants and three municipal wastewater treatment plants, and one drinking water treatment plant representing unintended (*de facto*) water reuse. The report also contains a plant reliability analysis, which was carried out by conducting a parametric time series analysis on the data set, identify trends, and investigate the duration of plant upsets or breakdowns. A qualitative risk assessment was also conducted to determine possible health impacts because of human exposure to the identified priority chemicals of concern. The risk assessment consisted of a multi-criteria decision analysis (MCDA) risk matrix based on the Water Safety Plan principles as proposed by the World Health Organisation, and using health impacts based on equivalent safe dose corresponding to long-term exposure.

### SUMMARY OF RESULTS

For selecting a priority list of emerging contaminants of concern for reclaimed water quality monitoring in South Africa, the following criteria was considered:

- compounds detected in South African potable waters
- compounds which are persistent and are not removed by conventional water treatment processes
- pharmaceuticals prescribed in the largest volumes in South Africa
- pesticides identified as high-risk priority pesticides in South Africa

- chemicals representing each of the groups of CECs
- chemicals representing South African prevalence (e.g. antiretroviral drugs)
- potential for human exposure
- analytical ability to detect.

The table below shows the recommended list of priority contaminants of emerging concern (CECs) for assessing water quality for direct potable reuse.

GROUP	TYPE	CHEMICALS
Industrial chemicals	Flame retardants	TDCPP and TCEP
	X-ray contrast fluid	Iopromide
	PAH	Benzo(a)pyrene
Pesticides, biocides and herbicides	Herbicide	Atrazine
	Herbicide	Terbuthylazine
	Insecticide	Imidacloprid
	Pesticide	Simazine
Natural chemicals	Stimulant	Caffeine
	Hormone	17-beta estradiol
Pharmaceuticals and metabolites	Antiretroviral drugs	Lamivudine Stavudine
	Anti-epileptic drugs	Carbamazepine
	Anti-malarial drugs	Cinchonidine Cinchonine
	Analgesic	Paracetamol
	Antibiotic	Sulfamethoxazole
Personal care products	Anti-microbial	Triclosan
Household chemicals and food additives	Plasticiser	Bisphenol-A
Transformation products	By-product	N-Nitrosodimethylamine (NMDA)

The risk assessment that was undertaken has shown that the vast majority of the contaminants are reduced to insignificant levels during the treatment process (with the exception of 17 $\alpha$ -ethinylestradiol). More research about hormones, their degradation products and possible treatment technologies are needed to better understand the risks in reclaimed water. It is suggested that further risk assessments are conducted including more contaminants as well as microbial risks. Regarding process performance and plant reliability analysis, the existing historical process data used were found to be unsuitable in its current state for deriving process monitoring and plant reliability 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).

## RECOMMENDATIONS

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 if various activities are tested. For example, different oestrogen mimicking assays and anti-androgenic activity may be included.

During wide discussions within the water sector during carrying out this project, including and in particular also the DWS, the conclusion was reached that it is imperative that a national (virtual) centre for analysis of contaminants of concern (including all specialised chemical and microbiological analyses) be established, consisting of a network of laboratories. More specifically, the following is proposed:

- That a national laboratory network for advanced water quality analysis be established, and that it will have the framework of a virtual centralised facility, but consisting of regional laboratory networks in four of the provinces, namely Western Cape, Gauteng, KwaZulu-Natal and Free State.
- It is the intention that the national laboratory network for advanced water quality analysis will:
  - Facilitate regional cooperation between the laboratories.
  - Propose validated, standard operating procedures.
  - Provide competitive analysis costs (different packages) for WSPs.
  - Develop regional capacity and expertise for specialised water quality analysis.
  - Promote the exchange of scientific data and technical knowledge.
- Support (financial and institutional) by the Department of Water and Sanitation (DWS) will be crucial in ensuring the success and sustainability of the water reuse RLNs. DWS is the sector leader and as such needs to set the tone regarding the importance of credibility in water quality testing results. Private-public partnerships (PPP) could also be a viable option for this purpose, either as part of the Strategic Water Partners Network (SWPN) or similar thereto.
- A further important factor, and one that needs to be addressed from the outset, is the need for well-trained and experienced personnel and managers for the regional laboratory networks (RLNs). Follow-up projects by the WRC, WISA, Universities, Water Boards and EWSETA will be required to create and enabling climate for planning the staffing and career development in the RLNs. Capacity building initiatives in current WRC projects are already driving this strongly.



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## 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	17 $\alpha$ -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 <sub>3</sub>	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	wastewater treatment works



## CHAPTER 1: BACKGROUND

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### 1.1 INTRODUCTION

South Africa is a water stressed country, where the demand for water is fast approaching available supply. To cope with the scarcity of water and growing water supply demand, increasing attention has been given to the reclamation of water from wastewater sources for direct potable reuse. The use of treated wastewater for direct potable applications can play an integral role in meeting future water demands. However, wastewater reuse that has not been adequately treated can be a possible exposure pathway to a high number of emerging contaminants and their metabolites. 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.

A portfolio of treatment options is available to mitigate water quality issues in reclaimed water. However, most municipal wastewater treatment plants are not specifically designed to deal with the emerging contaminants found in wastewater. 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 (DPR). 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.

### 1.2 PROJECT AIMS

The following were the aims of the project:

- a. Compile a list of emerging contaminants of concern in reclaimed potable water for Southern Africa.
- b. 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.
- c. Draw up an assessment report on indicative CEC removal potential in water reclamation systems and wastewater treatment plants, potential for failures in reliability and consequent risks for direct potable water reuse.

### 1.3 SCOPE AND LIMITATIONS

It should be noted that whenever DPR is implemented, the holistic system consists of the wastewater and the advanced water reclamation plant, as well as the distribution and collection system. These are part of the multi-barrier approach towards minimizing health impacts, and should not be seen in isolation. However, for the purposes of this study, the collection and distribution systems were not included in the scope of study. For the evaluation of treatment system performance, plant reliability analysis and risk assessment, several water reclamation systems (direct potable reuse) and wastewater treatment plants (WWTPs) were selected in Southern Africa for assessment of the indicative removal capability of the wastewater treatment plants and

water reclamation systems to remove the contaminants of emerging concern. The study sites consisted of two water reclamation plants (WRPs), three municipal WWTPs and a water treatment plant (WTP), as well as information obtained from a completed WRC project carried out on pilot plant scale at the Darvill wastewater treatment plant. The following evaluations were performed on the above-mentioned plants:

- a. Evaluation of indicative potential of the water reclamation plants and the wastewater treatment plants treatment plant for removal of most of the contaminants of emerging concern in the priority list, as well as for removal of perfluorinated compounds (PFCs).
- b. Treatment system performance and plant reliability analysis for one of the two water reclamation plants, based on historical plant data.
- c. A risk assessment at one of the two water reclamation plants.

The two WRPs, three WWTPs and one WTP were sampled during three sampling programmes. The sampling programmes were not designed to determine the general performance and operation of the plants and no conclusions regarding these subjects can be made based on the results of the sampling programmes. Rather, the purpose and design of the sampling programmes were to simply determine the indicative removal potential of certain treatment processes for the priority parameters that were identified in this project. The WTP was included in the third sampling programme as a means of comparing the treatment processes' indicative removal potential with those of the WRPs and WWTPs, but also to provide some perspective as to the levels of the priority compounds that can be found in a river in comparison to that found in treated wastewater. It is important to note that, not all the plants were sampled during all three of the sampling programmes, instead, only one WRP and the three WWTPs were sampled during all three of the sampling programmes, the other WRP was sampled during the second and third sampling programmes, and the WTP was only sampled during the third sampling programme.

## **1.4 REPORT LAYOUT**

Chapter 1 – Background on the project

Chapter 2 – Provides an overview on contaminants of emerging concern, including the different classes, sources and pathways, and detection and monitoring. Based on the assessment of laboratory capacity in South Africa, the establishment of a network of laboratories for specialised water quality analysis is proposed.

Chapter 3 – Provides a brief account of the processes followed for prioritisation of emerging contaminants of concern for reclamation systems and the list of priority compounds

Chapter 4 – Provides research findings on the indicative removal of selected priority compounds during water treatment (both reclamation and conventional water treatment systems), as well an assessment of plant treatment process performance and reliability.

Chapter 5 – Provides research findings based on water toxicity testing using bioassays and findings from risk assessment studies.

Chapter 6 – Conclusions and recommendations

## **CHAPTER 2: CONTAMINANTS OF CONCERN IN THE WATER CYCLE**

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### **2.1 INTRODUCTION**

The sources and occurrence of emerging micropollutants in the aquatic environment has been widely discussed and published in literature (Baker and Kasprzyk-Hordern, 2013). This is due to their environmental persistence, high pharmacological activities as well as psychoactive properties and other yet to be identified impacts on human, animals and aquatic species (Claessens et al., 2013). However, there is limited information regarding the environmental fate, and eco-toxicological behaviour of these compounds in the environment. Environmentalists consider water and wastewater originating from industrial, agricultural or municipal activities as potential sources of micropollutants in the environment. In addition, wastewater treatment plants, landfilling areas, and agricultural run-off are other routes through which these micropollutants enter the surface water. Despite extensive published articles and reviews on the sources, occurrence, transport and fate of emerging micropollutants in the literature, very little information exists on the pathways, particularly from sources to receptors. This is not only due to lack of adequate data, but also related to interconnectedness of the complex physicochemical characteristics of the compounds. The health effects associated with exposure of aquatic organisms to contaminants of concern, such as low sperm count, high incidence of certain cancers, the incidence of intersex fish within the water system, and others, have been documented in the literature. However, the human health effects associated with exposure to emerging contaminants have yet to be clearly established. Proper identification of contaminants of emerging concern that may have future implications on human health is considered necessary and requires attention.

### **2.2 CLASSES OF CONTAMINANTS OF EMERGING CONCERN**

#### **2.2.1 Overview**

In the recent past, the increase in the human population as well as the production and consumption of pharmaceuticals and other chemically related products have doubled and have contributed to the generation of different waste constituents originating from industries, agricultural activities, domestic operations and municipal treatment works, among others. Chemicals of emerging concern identified in reclaimed water can include the following:

- Pharmaceuticals and veterinary medicines (prescribed and over-counter drugs)
- Endocrine disrupting compounds (an exogenous compound that mimics or block hormonal functions in the body)
- Personal care products (active ingredients in cosmetics, fragrances, soap, insect repellents, toothpastes, e.g. antiseptics (triclosan/triclocarban))
- Flame retardants (active ingredient incorporated into consumer products such as electronics, plastic and children's toys)
- Perfluorinated and brominated substances (used as dirt-repellent coatings, spray for leather and textiles (Houtman, 2010; Fawell and Ong, 2012))
- Pesticides and herbicides
- Nanomaterials

## 2.2.2 Databases for contaminants of concern

Some of the more comprehensive databases for contaminants of concern are:

- IRIS (Integrated Risk Information System) database, with more than 550 compounds, available at <http://cfpub.USEPA.gov/ncea/iris/indexcfm?fuseaction=iris.showSubstanceList>.
- SIN (Substitute It Now) list with 406 compounds available at <http://www.chemsec.org/what-we-do/sin-list>.
- HSDB (Hazardous Substances Data Bank) database, with information on 5 756 compounds available at <http://sis.nlm.nih.gov/enviro/hsdbchemicalslist.html>.
- Country lists. Many countries have drawn up their own lists of CECs. A reference to some of these lists is available at [http://ec.europa.eu/environment/archives/document/pdf/bkh\\_annex\\_02\\_03.pdf](http://ec.europa.eu/environment/archives/document/pdf/bkh_annex_02_03.pdf).
- TEDX (The Endocrine Disrupting Exchange) database, with more than 1000 compounds available at <http://endocrinedisruption.org/endocrine-disruption/tedx-list-of-potential-endocrine-disruptors/overview>.
- The Household Products database with information and ingredients on 14 000 consumer brands in the USA, available at <http://hpd.nlm.nih.gov>.

The USEPA has a CECs Removal Database consisting of published scientific studies on the removal of CECs from water and wastewater. The database is available at <http://water.USEPA.gov/scitech/swguidance/ppcp/results.cfm>. A report on Treating Contaminants of Emerging Concern: A Literature Review Database (August 2010) is available at the website, providing examples for municipal wastewater and treated effluent.

## 2.3 SOURCES AND PATHWAYS

### 2.3.1 General overview

Table 2-1 summarises the potential sources of chemicals of emerging concern in the environment. Generally, the main sources of contaminants of emerging concern in the water cycle are as follows:

- Several investigations have confirmed the presence of pharmaceuticals and their byproducts in municipal wastewater and of course in drinking-water. The level of these compounds in water varies from country to country depending on individual consumption patterns, rate of production, specific sales and practices, metabolism rate, WWTPs capacity and removal efficiency, as well as environmental persistence (Luo et al., 2014).
- Emerging micropollutants enter the freshwater system via point and diffuse sources. Conventional WWTPs are not specifically designed to remove these compounds. Within the WWTPs, some of these compounds are completely broken down by biological processes, while highly persistent ones pass through the treatment plants and enter the surface water. WWTP treated effluent and untreated urban wastewater have been identified as a channel through which these compounds enter the surface water, groundwater and even drinking water (Radjenovic et al., 2008).
- High concentrations of biologically active compounds have been found in drinking water. The higher the population consumption rate, the greater the concentration of the contaminants found present in the water cycles (Fawell and Ong, 2012).
- Pharmaceuticals may enter the environment via human excretion, disposal of expired drugs, agricultural activities as shown in Figure 2-1 below. Barnes et al. (2008) detected an appreciable amount of pharmaceuticals such as ciprofloxacin, erythromycin, codeine, carbamazepine, ibuprofen, salicylic acid in surface and drinking water at low concentrations.
- Hospital wastewater is another source through which contaminants such as disinfectants and musks, radioactive elements, heavy metals, and iodised contrast media get introduced into the aquatic system (Verlicchi et al., 2010; Watkinson et al., 2009).

- The use of veterinary medicines, landfill leachates, leaking of septic tank and sewer systems have been identified as other sources of EMs in USA and some parts of Europe (Bartelt-Hunt et al., 2010).
- Manufacturing industries equally contribute a substantial amount of unregulated pollutants into our water ways (Larsson, 2008).
- Other sources include pesticide application, animal manure and livestock activities.
- Compounds also enter aquatic environments through recreational and domestic activities such as swimming, showering, bathing or clothes washing.
- Buska et al. (2009) identified contaminants such as hormones, pharmaceuticals and flame retardant in the wells closer to landfill sites. More than 80 pharmaceuticals and personal care products detected according to Heberer, (2002) originated from reclaimed water used for artificial groundwater recharge.
- Accidental spills could also be another source of EMs in the aquatic ecosystems.
- EMs also enter the environment via physical and chemical breakdown during disposal and recycling operations within wastewater treatment plants (WWTPs).

**Table 2-1: Sources of emerging micropollutants in the aquatic environment**

CATEGORY	IMPORTANT CLASSES	MAJOR SOURCES (DISTINCT)	MAJOR SOURCES (NON-EXCLUSIVE)
Pharmaceuticals	NSAIDs, lipid regulator, anticonvulsants, antibiotics, $\beta$ -blockers and stimulants	Domestic wastewater (from excretion), hospital effluents	Sources that are not exclusive to individual categories include: <ul style="list-style-type: none"> <li>• Industrial wastewater (from product manufacturing discharges)</li> <li>• Landfill leachate (from improper disposal of used, defective or expired items)</li> </ul>
Personal care products	Fragrances, disinfectants, UV filters, and insect repellents	Domestic wastewater (from bathing, shaving, spraying, swimming, etc.)	
Steroid hormones	Estrogens	Domestic wastewater (from excretion), run-off from CAFOs and aquaculture	
Surfactants	Non-ionic surfactants	Domestic wastewater (from bathing, laundry, dishwashing, etc.), industrial wastewater (from industrial cleaning discharges)	
Industrial chemicals	Plasticizers, fire retardants	Domestic wastewater (from leaching out of the material)	
Pesticides	Insecticides, pesticides and fungicides	Domestic wastewater (from improper cleaning, run-off from gardens, lawns and roadways, etc., agricultural runoff)	

Figure 2-1 depicts generic pathways to receptors. It is imperative to understand and identify individual pathways into freshwater system as this will help to predict the associated future health risk. Although the concentrations of EM in the environmental matrices are very low, ranging between ngL-1 and µgL-1, a continuous exposure especially of aquatic species may have harmful effects while effects on human remain to be proven.

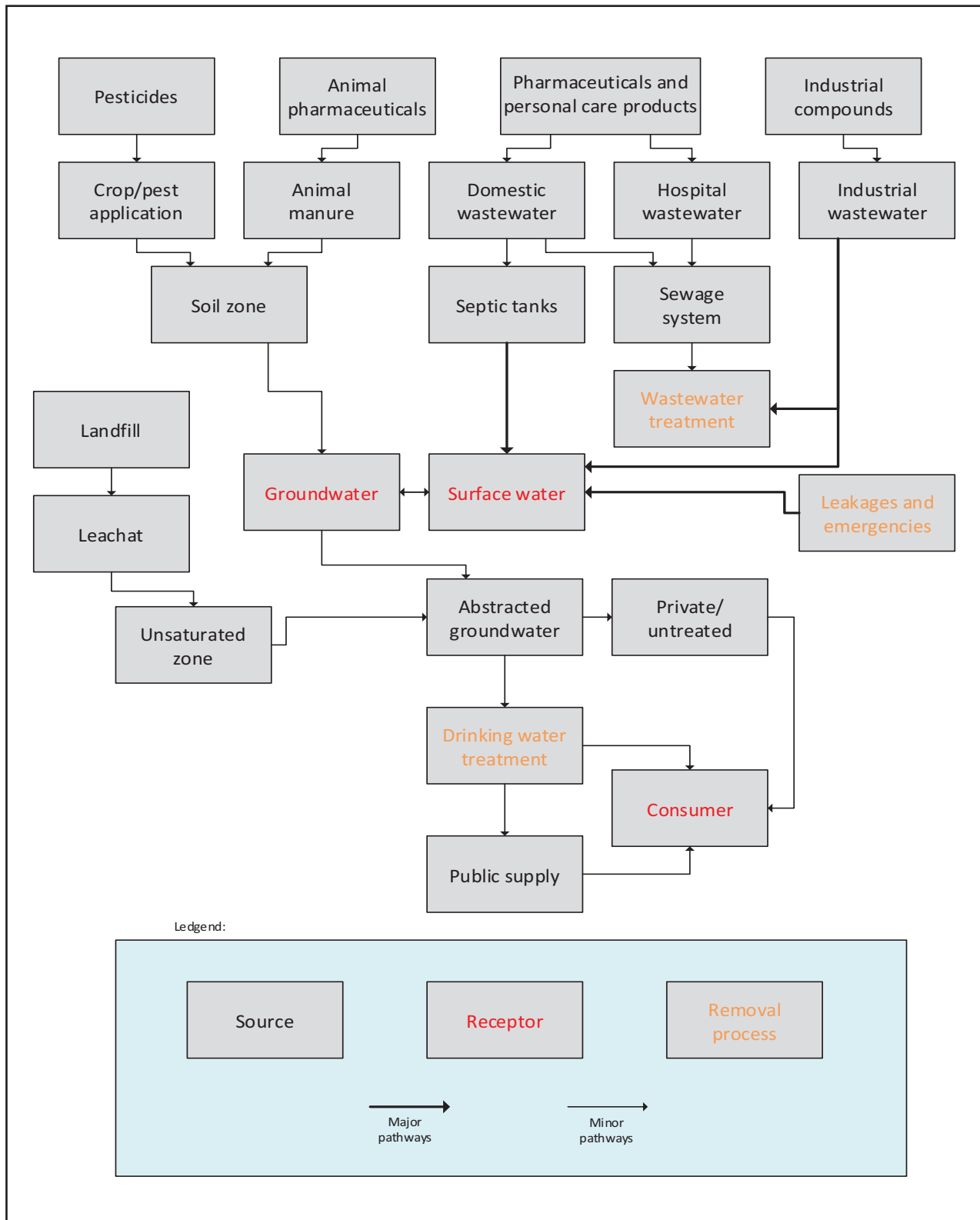


Figure 2-1: Potential sources and pathways of some emerging to receptors and aquatic environment (Reference: Stuart et al., 2012)

### 2.3.2 International studies

The presence of emerging micropollutants in reclaimed water has become a global issue of considerable environmental concern (Deblonde et al., 2011; Lapworth et al., 2012). Several new environmental contaminants, both regulated and unregulated, have been identified in wastewater and reclaimed water due to lack of effective treatment technology strategies and thus become ubiquitous substances in the environment (Fent, 2008). Pharmaceutical and personal health care products include over-the-counter and prescription drugs such as antibiotics, analgesics, blood lipid regulators, natural and synthetic hormones,  $\beta$ -blockers, anti-diabetics, antihypertensive and products that are used in everyday life such as surfactants and their degradation products (Yu et al., 2011; Ternes and Siegrist, 2004). The ingredients of soaps and/or detergents, perfumes, skin and hair products and dental care products are part of this diverse group of compounds. There is some evidence that certain emerging contaminants could affect human and environmental health. For example, the veterinary use of diclofenac, which is a human pharmaceutical used as an anti-inflammatory treatment, was found to be responsible for the massive decline in populations of vulture species in certain areas of Asia (Oaks et al., 2004); the veterinary drug ivermectin, which is used to treat parasitic infections in livestock, has been shown to affect the growth of aquatic invertebrates at concentration lower than those that are expected to occur in the aquatic environment (Garric et al., 2007); ethinylestradiol, one of the active ingredients in the contraceptive pill, has been associated with endocrine disruption in fish (Lange et al., 2001); and there is concern that long-term exposure to antibiotic pharmaceuticals, used in human and veterinary medicine, may be contributing to the selection of resistant bacteria in the environment which may have significant implications for human health (Boxall et al., 2003).

Some of the other international studies on occurrence of contaminants of concern are listed below:

- Swartz and colleagues (2008) utilized bioassay techniques to identify emerging contaminants in the reclaimed water obtained from the wastewater reclamation plant in Windhoek. The study demonstrated the presence of nonylphenol, estrone, ethinylestradiol, bisphenol-A, microcystin in Gammams raw and Goreangab raw water. The concentrations were however different with respect to season and the treatment technique adopted.
- Claessens et al. (2013) reported that persistent pharmaceuticals such as trimethoprim, ibuprofen, salicylic acid, lipid regulator bezafibrate,  $\beta$ -blockers propranolol and carbamazepine are widely found at low or higher concentration in reclaimed water depending on the population and consumption pattern.
- Bolong et al. (2009) reported the occurrence level of EDCs such as Nonylphenol, Estrone (E1), Estradiol (E2) Ethinylestradiol (EE2) in municipal wastewaters, surface and drinking in Germany, United Kingdom and Japan respectively. However, the concentration level varied due to difference in the WWTPs performance, population and consumption pattern.
- Persistent pharmaceuticals identified in the environment include: paracetamol and atenolol (Yamamoto et al., 2007).
- Huerta-Fontela et al. (2010) submitted that the effective removal of emerging contaminants in WWTPs is considered a critical environmental component required for the protection and sustenance of water quality status. Thus, proper understanding of the various variables within the WWTPs is a fundamental key point that determines whether a contaminant will be retained, bioaccumulate or perhaps persistent in the environment (Gros et al., 2010).
- Deblonde et al. (2011) identified and quantified emerging pollutants such as phthalates, Bisphenol-A, PCBs, polyaromatic hydrocarbons, pharmaceuticals in the wastewater influents and effluents.
- Hanh et al. (2012) have demonstrated that despite the prohibition of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) twenty years ago, most of these substances are still being detected at high concentration in wastewater and reclaimed water.
- The presence of emerging organic contaminants in reclaimed water meant for potable use has over time become a considerable source of environmental concern due to their environmental persistence and high biological activity (Baker and Kasprzyk-Hordén et al., 2013; Claessens et al., 2013).



- Now, research is focused on the persistent emerging contaminants that interfere with the endocrine system (Gavrilescu et al., 2014).

Thus, the occurrence of these priority pollutants varies from region to region and could depend on the number of drugs consumed by the population, toxicity and persistency of the compounds once released into the aquatic environment.

### **2.3.3 South African studies**

Research on the occurrence and potential health impact of CECs have also been carried out in South Africa, and especially during the past decade. In 2005, Burger developed a strategic research plan, in which the occurrence of EDCs in South African water systems was investigated (Burger, 2005). One of the first lists of priority compounds (for effects on both humans and animals) was subsequently compiled, which included a set of inclusion criteria for EDCs. In a WRC research project to verify analytical methods for testing the levels of PPHCPs in treated drinking water and sewage, Osunmakinde et al. (2013) found varying concentrations of these compounds, which included hypertension medication, antiretrovirals, analgesics and antibiotics, as well as hormones from natural and contraceptive sources. In another WRC project, Patterton (2013) did a scoping study on known and emerging contaminants influencing drinking water quality, screening in seven cities over four seasons 618 compounds. 32 compounds were detected, which included the following pesticides: terbutylazine, imidacloprid and simazine. Ncube et al. (2012) suggested a protocol for the selection and prioritisation of contaminants in drinking water in which Rand Water, RSA, was used as a case example. A priority list of organic contaminants was identified which could then be used by Rand Water to optimise their resources and efficiency without compromising of public health. Monitoring was done at five sample sites in the Rand Water drinking water value chain during both dry and wet seasons. A list with 130 contaminants was finally produced (after reducing it from the original list of around 600 contaminants, and the contaminants were grouped into six classes, consisting of industrial chemicals, pesticides, disinfection by-products, polymeric residues, cyanotoxins and PPCPs. More detail on this classification and prioritisation can be found in Chapter 3 of this report.

## **2.4 DETECTION AND MONITORING OF EMERGING CONTAMINANTS**

### **2.4.1 Overview**

The need for analysis of CECs is a global topic. Concerns on emerging contaminants have been identified by various scientific conferences and a series of publications has been released on the presence of these compounds in the environment. There have been analytical challenges in the analysis of emerging contaminants; this is not only due to the complexity of the compounds' chemical properties, but also due to the low concentrations, matrices complexity of the contaminants (Petrovic et al., 2003), thermal lability and high polarity (Yang et al., 2007). The availability of precise analytical methods that can be effective for measurement at low concentration levels (ng/l or lower) is the requirement for accurate risk assessment of contaminants and for the monitoring of the water (surface, drinking, and wastewater) quality. This section focuses on the analytical techniques currently employed in South Africa to detect and quantify CECs in aqueous systems. The costs of advanced water quality analysis, such as EDCs and emerging contaminants relevant to both water purification and water reclamation, is limiting for proper monitoring and risk management at such plants. Furthermore, only a few laboratories can perform the specialized analyses required for monitoring of treatment process efficiency to minimize risks and health impacts.

## 2.4.2 Quantifying concentrations of CECs in water

In the last couple of years, there has been significant in analytical techniques for analysing emerging micro-pollutants. However, the identification and perhaps quantification of these xenobiotics in the environment depends solely on the availability and accessibility of advanced analytical facilities. These analytical facilities include: high performance liquid chromatography (HPLC), high performance liquid chromatography coupled with mass spectrometry (HPLC-MS), liquid chromatography mass spectrometry (LC-MS), liquid chromatography mass spectrometry coupled with mass spectrometry (LC-MS/MS), gas chromatography mass spectrometry, Nuclear Magnetic Resonance (NMR), amongst others. Screening (presence/absence) tests are also available. Test kits are also available for plants to purchase and use in their own laboratories. Table 2-2 shows the testing procedure for three tests kits that are typically used to perform advanced water quality tests. Laboratories can screen samples at a fixed cost and then do further quantitative analyses for compounds found in the samples at an additional cost. Table 2-3 shows a list of parameters that are included in the WHO's guidelines for drinking water that can be screened by many the laboratories.

**Table 2-2: Tests kits for advanced analyses available in South Africa**

KIT	SAMPLING
Microcystin	5 Individual tests
ELISA for Estradiol	Approximately 80 samples/tests. Must be performed at the same time.
Ames test for Mutagenicity	16 tests to be performed at the same time

**Table 2-3: WHO parameter list for screening**

PARAMETERS			
Acrylamide	1,2-Dichloropropane	Terbutylazine	Nickel
Alachlor	1,3-Dichloropropene	Tetrachloroethene	Nitrate (as NO <sub>3</sub> <sup>-</sup> )
Aldicarb	Dichlorprop	Toluene	Nitrite (as NO <sub>2</sub> <sup>-</sup> )
Aldrin and Dieldrin	Dimethoate	Trifluralin	Selenium
Antimony	Bromodichloromethane	Hexachlorobutadiene	Uranium
Arsenic	Bromoform	Isoproturon	1,2-Dichlorobenzene
Atrazine	Endrin	Trihalomethanes (Total THMs)	1,4-Dichlorobenzene
Barium	Carbofuran	MCPA	Dichloroethane
Benzene	Ethylbenzene	Xylenes	Dichloroethene
Benzo[a]pyrene	Fenoprop		Dichloromethane
Boron	Carbon tetrachloride	Mecoprop	Simazine
Bromate	Chlordane	Mercury	Sodium dichloroisocyanurate
Cadmium	Chloroform	Methoxychlor	Sodium dichloroisocyanurate (as Cyanuric acid)
Chlorate	Chlorotoluron	Metolachlor	Styrene
Chlorine	Chlorpyrifos	Microcystin-LR	2,4,5-T
Chlorite	Cyanazine	Molinate	
Chromium	2,4D	Monochloroacetate	

PARAMETERS			
Copper	2,4DB	Nitrilotriacetic acid (NTA)	
Cyanide	DDT and metabolites	N-Nitrosodimethylamine (NDMA)	
Fluoride	Di(2-ethylhexyl)phthalate	Pendimethalin	
Lead	Dibromochloromethane	Pentachlorophenol	
Manganese	1,2-Dibromo-3-chloropropane	Permethrin	

## 2.5 WATER QUALITY LABORATORIES IN SOUTH AFRICA

### 2.5.1 Situational context

In a study by Balfour et al. (2011), nearly 100 laboratories were surveyed. The geographic spread of the laboratories correlated to their testing capability has provided a useful tool in establishing if there are sufficient laboratories across the country, and where additional credible laboratories need to be established. The results also showed a high occurrence of financial reasons for non-accreditation (25%). The initial financial implications of attaining ISO 17025 accreditation were reported to be severe. The maintenance of equipment, procurement of stock, method validation, technician competency per method, and record keeping are vital in achieving ISO 17025 accreditation. It appeared that training was a priority for most laboratories. A total of 79% of laboratories had conducted training needs assessments, but the main concern lay with those laboratories with little or no training at all. A total of 77% of laboratories acknowledged the availability of assistance both internally and externally, and 79% stated that their organisation can train personnel from their facilities to assist them in methodology training. The basic laboratory information from the study is useful to determine geographic spread, to analyse where there are sufficient laboratories and where additional laboratories should be established. It is also useful to look at the geographic spread of the laboratories that have SANAS accreditation to establish the number of accredited labs per province as well as any trends regarding accreditation or participation in proficiency testing schemes. Overall, findings from the study by Balfour et al. (2011), indicated deficiencies in the analytical capabilities of laboratories in South Africa. There is, therefore, a need for the establishment of a national laboratory network for specialised water quality analysis in South Africa, to be funded by central government (Department of Water and Sanitation).

### 2.5.2 Need for a national laboratory network for advanced water quality analysis

Good analytical facilities are essential ingredients of research and overall rating of a University. Research involving emerging micro-pollutants is relatively new and as such modern analytical facilities are required for method development and identification in water samples. The recalcitrant toxic contaminants in wastewater are present in µg/L to ng/L level and therefore require good analytical facilities to be able to detect them in environmental samples. It is proposed that a national facility for advanced water quality analysis will be established, and that it will have the framework of a virtual centralised facility, but consisting of regional laboratory networks in four of the provinces, namely:

- Western Cape
- Gauteng

- KwaZulu-Natal
- Free State/North West

In WRC Report No. 1853/1/11 on “Aquatic toxicity testing in South Africa: Status of aquatic toxicity testing in South Africa” (Chapman et al., 2011), it was recommended that a network be created between toxicity testing laboratories in South Africa, with administrative and financial support from the Department of Water and Sanitation. The researchers adapted this approach from Loko (2008). The focus of the proposed network was to improve the sustainability and quality of aquatic toxicity testing in South Africa. More specifically, the aims were to ensure the comparability and validity of aquatic toxicity testing of South African laboratories, to encourage data integrity and accessibility, and to facilitate a national information exchange on methods and other technical aspects. The proposed National Laboratory Network for Advanced Water Quality Analysis (NLNAWQA) consists of a Regional Laboratory Network (RLN), which has to be developed. Due to the common aims of the RLN and the national (virtual) centre for advanced water quality analysis, it is proposed that for analysis of CECs and other advanced analysis, a similar approach be adopted as that of the RLN for aquatic toxicity testing. The ensuing proposals for the NLNAWQA are thus largely based on the framework for aquatic toxicity testing in South Africa.

#### *2.5.2.1 Aims of the NLNAWQA Regional Laboratory Networks*

It is the intention that the NLNAWQA and water reuse RLNs will:

- Facilitate regional cooperation between the laboratories.
- Propose validated, standard operating procedures.
- Provide competitive analysis costs (different packages) for WSPs.
- Develop regional capacity and expertise that can again be made available nationally through the NLNAWQA.
- Promote the exchange of scientific data and technical knowledge.

#### *2.5.2.2 Strategy for establishment of the NLNAWQA and RLNs*

Laboratories, academic institutions and other research laboratories, in water boards or metros, but also performing research work should be lobbied to join the RLN in their respective provinces. The listed laboratories. The Department should make inputs towards the required institutional arrangements for establishment of the NLNAWQA and the four Regional Laboratory Networks. However, it is suggested that the functioning of the NLNAWQA and the RLNs follows the same structure as that recommended in the Chapman report (Chapman et al., 2011). According to this, the Regional Laboratory Networks report to the NLNAWQA Committee via Regional Committees (RCs) for the four RLNs. The RCs are comprised of representatives from the laboratories in their respective provinces. Water Boards and Municipalities who have potable water reuse systems or who are planning on potable reuse schemes may have representatives in the networks. The RCs may also have representatives for every university and relevant research laboratory in the regions. Lastly, a representative of the regional offices of DWS must also be present on the RC. The NLNAWQA Committee is made up of a representative of every one of the RCs, and this group communicates with the national office of DWS via a nominated member who acts on behalf of the NLNAWQA. The nominated member liaises with national government at a forum (which may be facilitated by the WRC) for national coordination in terms of regulatory matters and requirements from the regional laboratories that have been identified. Nominated representatives from DWS must be present at the forum. Issues that could be included for discussion at such a forum would include: quality assurance, development of new methodologies, validation of standard operating procedures, development and maintenance of a national proficiency testing scheme, organisation and promotion of training needs and opportunities, and technical advice relating to specialized testing methodologies.

## 2.6 SUMMARY

The use of treated wastewater for direct potable applications can play an integral role in meeting future water demands. However, wastewater reuse that has not been adequately treated can be a possible exposure pathway to a high number of emerging contaminants and their metabolites. With regards to national analytical capabilities, a previous investigation found that there are a limited number of laboratories that undertake water quality testing in the country (Balfour et al., 2011). It was further found that many of these laboratories have capacity limitations. The process and cost of ISO 17025 accreditation with SANAS has been highlighted as a stumbling block for many laboratories (Balfour et al., 2011). As a result, DWS was reported to be then (2011) in the planning stages of implementing a laboratory strategy for ensuring the credibility of results from drinking water quality laboratories, based on a scaled down version of ISO 17025, and focusing on technical competency. In this study, establishment of a National Laboratory Network for Advanced Water Quality Analysis (NLNAWQA) consisting of a Regional Laboratory Network (RLN) has been proposed. Due to the common aims of the RLN and the national centre for advanced water quality analysis, it is proposed that for analysis of CECs and other advanced analysis, a similar approach be adopted as that of the RLN for aquatic toxicity testing. The ensuing proposals for the NLNAWQA are thus largely based on the framework for aquatic toxicity testing in South Africa.

## **CHAPTER 3: SELECTION AND PRIORITISATION OF EMERGING CHEMICALS OF CONCERN FOR WATER RECLAMATION SYSTEMS**

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### **3.1 INTRODUCTION**

The classification or inclusion of a substance on the list of priority emerging contaminants is based on a series of factors such as persistency in the environment, extensive industrial applications, possession of EDCs properties, occurrence either naturally or synthetically, and water solubility, among others. In North America, the USEPA listed 112 priority pollutants whereas in the European Union a list of 58 chemical compounds was included as priority. (See Volume II for the tables listing the chemicals). Laws et al. (2011) provides a list of 52 compounds considered to be useful indicators of trace organic chemicals in water based on detection frequency and levels in North American surface waters where compounds that did not occur at a frequency above 80% or were not present in secondary- or tertiary-treated wastewater at concentrations at least five times higher than their respective limits of quantification were eliminated. In 2010, the Californian State Water Resources Control Board convened a panel of experts to address the monitoring strategies for CECs in recycled water providing recommendations for monitoring reclaimed water (Anderson et al., 2010). The panel provided a conceptual framework for assessing potential CEC targets for monitoring and used the framework to identify a list of chemicals that should be monitored (Anderson et al., 2010). The chemicals the panel recommended for monitoring are those found in recycled water at concentrations with human health relevance. In addition to risk-based priority chemicals, the panel recommended monitoring both the performance of treatment processes to remove CECs using selected “performance indicator CECs,” and surrogate/operational parameters to verify that treatment units are working as designed. Surrogates include turbidity, DOC, and conductivity. Health-based CECs selected for monitoring included caffeine, 17 $\beta$ -estradiol, NDMA, and triclosan. Performance-based indicator CECs were selected by the panel, each representing a group of CECs: caffeine, gemfibrozil, n,n-diethyl-meta-toluamide (DEET), iopromide, NDMA, and sucralose. Caffeine and NDMA serve as both health and performance-based indicator CECs.

In 2012 (Ncube et al., 2012) suggested a protocol for the selection and prioritisation of contaminants in drinking water in which Rand Water, RSA, was used as a case example. A priority list of organic contaminants was identified which could then be used by Rand Water to optimise their resources and efficiency without compromising of public health. It was derived from primary lists of organic pollutants of concern which was based on occurrence criterion in both international and national literature. The study carried out by Osunmakinde et al. in 2013 involved compiling a priority list of target analytes relevant to South Africa based on data collected from the health sector (Table 3-1). The prescription volume of drugs was considered, and in some cases the stability of the drugs was also considered. The compounds were often the same as those commonly detected in water systems worldwide. Although not strictly accurate, the prescription volume can be used as a surrogate to represent the level of occurrence in the environment. The South African investigation of contamination of water resources by agricultural chemicals and the impact on environmental health (Dabrowski et al., 2014) identified a list of priority pesticides based on volume of usage, toxicity, mobility into the water environment and persistence.

**Table 3-1: Most prescribed drugs in the public health sector in South Africa grouped according to the class of drug (Source Osunmakinde et al., 2013)**

DRUG	DRUG TYPE
Paracetamol	Analgesic
Lamivudine	Analgesic
Albendazole	Anthelmintic
Chlorphenoxamine hydrochloride	Anti-Allergic
Chloramphenicol; Amoxycillin; Ampicillin; Ceftriaxone; Furosemide	Antibiotics
Hydrocortisone acetate	Corticosteroid
Co-trimoxazole; Lamivudine; Efavirenz; Stavudine; Tenofovir disoproxil fumarate	ARV
Salbutamol	Sulphate Asthma
Simvastatin	Cholesterol
Levonorgestrel and Ethinylloestradiol; Norgestrel; Norethisterone enantate	Contraceptive
Cocillana	Cough syrup
Metformin Hydrochloride; Gliclazide; insulin	Diabetic
Hydrochlorothiazide; Enalapril maleate and Hydrochlorothiazide; Amlodipine; Nifedipine; Perindopril; Medroxyprogesterone	Hypertension
Methyl salicylate	NSAID
Atenolol	β-blocker

### 3.2 DEVELOPING A PRIORITY LIST FOR WATER RECLAMATION SYSTEMS

Developing a first CEC recommended prioritisation list involved filtering the overall list for the following:

- Compounds detected in South African potable waters
- Compounds which are persistent
- Compounds that are not removed by water treatment processes
- Pharmaceuticals prescribed in the largest volumes
- Pesticides identified as high-risk priority pesticides in South Africa
- Chemicals representing each of the groups of CECs
- Indicator compounds known to occur in high concentrations in wastewaters to illustrate process efficiencies compounds that have an established analytical detection method.

For example:

- **Carbamazepine** would be included as it has been detected in South African drinking waters, is prescribed in abundant quantities, and is persistent.
- **Paracetamol** and **Carbamazepine** are both used as indicators of removal efficiency, are risk exemplar contaminants, recommended in the Australian drinking water quality guidelines and detected in treated wastewater and are therefore good candidates to be included on a priority list of chemicals.
- **Lamivudine** and **Stavudine**, the antiretroviral drugs should be included in a South African priority chemical list as they are of the most prescribed drugs and may be persistent in the environment.



- As antimalarial drugs are not normally included in the European, Australian and North American priority lists, and the antimalarial drugs, **Cinchonidine** and **Cinchonine** are both prescribed, and have been detected, they should therefore be included in a recommended South African priority list of chemicals.
- Indicator compounds representing different groups of compounds and present in large amounts in wastewater such as **caffeine**, the hormone, **17 beta estradiol**, the plasticiser, **Bisphenol-A**, the biocide **Triclosan**, the X-ray contrast fluid **Iopromide**, and flame retardants **TDCPP** and **TCEP** are found more frequently in water at detectable levels that may cause harmful effects to the ecosystem or human health and should be included in the priority list.

The recommended priority list representing (1) the different groups of contaminants of emerging concern based on best-available knowledge, (2) South African prevalence, (3) potential for exposure and other criteria such as analytical ability for detection, is shown below (Table 3-2), and forms a framework for discussion for potential monitoring for reclaimed potable water.

**Table 3-2: Recommended priority list of contaminants of emerging concern (CECs) for assessing water quality for direct potable reuse**

GROUP	TYPE	CHEMICALS
Industrial chemicals	Flame retardants	TDCPP and TCEP
	X-ray contrast fluid	Iopromide
	PAH	Benzo(a)pyrene
Pesticides, biocides and herbicides	Herbicide	Atrazine
	Herbicide	Terbutylazine
	Insecticide	Imidacloprid
	Pesticide	Simazine
Natural chemicals	Stimulant	Caffeine
	Hormone	17-beta estradiol
Pharmaceuticals and metabolites	Antiretroviral drugs	Lamivudine Stavudine
	Anti-epileptic drugs	Carbamazepine
	Anti-malarial drugs	Cinchonidine Cinchonine
	Analgesic	Paracetamol
	Antibiotic	Sulfamethoxazole
Personal care products	Anti-microbial	Triclosan
Household chemicals and food additives	Plasticiser	Bisphenol-A
Transformation products	By-product	N-Nitrosodimethylamine (NMDA)

It is important to note that the priority list cannot be seen as an exhaustive list, as each reclaimed potable water reuse project should interrogate the relevance of each of the chemical. This is to consider whether extra chemicals might need to be added to the priority list. For example, total DDT may need to be included in areas where DDT usage is known to occur. DDT was not included in the prevalence screening as the extraction process focusses on polar water-soluble compounds and was not present in the library of compounds selected for.

### 3.3 HEALTH RISKS ASSOCIATED WITH THE PRIORITY CECs

#### 3.3.1 Overview

There are concerns regarding the potential risk from exposure to different doses of pharmaceutically active agents in the environment (Fawell and Ong, 2012). With the rise in utilisation of chemical compounds daily, thousands of regulated and unregulated emerging contaminants have been discharged and detected in the aquatic environment. Depending on their fate and behaviour in the WWTPs and even in the drinking water treatment plants, the probability of human exposure to these compounds is high. To conduct a thorough risk assessment of emerging micro-pollutants for humans, there is a need to assess the exposure rate and the actual dose to predict the associated adverse health effects. Since the concentration of these compounds in water is low, the acute toxicity may be difficult to evaluate. Subsequently, the risk assessment might be technically hard to calculate since long-term exposure data is lacking. Aquatic species are at greater risk for adverse health effects because their exposure to individual or combinations of these compounds is very high. It has been established that feminization of fish in freshwater system is a direct result of exposure to certain endocrine disruptors. Further research is needed to know whether this exposure had a major impact on entire populations.

Strauch (2011) affirmed that the effects of exposure to pharmaceuticals, endocrine disruptors on human toxicity irrespective of their concentration in the water supply is yet to be ascertained but research carried out by Ternes et al. (2004) revealed that estrogenic compounds have a very high bioaccumulation potential with a considerable negative effect on aquatic organisms. This environmental bioaccumulation aggravates the abnormal hormonal control, causes reproductive impairments and persistent antibiotic resistant. This acute and chronic toxicity experienced by aquatic species such as fish upon exposure to these compounds in the freshwater system is like that of health effects caused by exposure to low concentration of metallic elements (Sharpe and Irvine, 2004; Xia et al., 2005; Bisceglia and Roberts, 2006).

Studies conducted by Micheal (2001) also revealed that exposure of aquatic species to endocrine disruptors causes low sperm count and reproductive malfunctions.

Safe (2000) also observed that exposure of aquatic organisms to organochlorines caused feminizations of fish and gulls, and sexual abnormalities in alligators. However, among the aquatic species, fish remain most susceptible to the high dose of these chemical substances. Studies have shown that exposure to diclofenac and 17 $\alpha$ -ethinylestradiol in the aquatic environment induced structural deformities of kidneys and intestines as well as gene alteration thus affected the body's metabolic activities (Kummerer, 2011). In addition to increasing occurrences of reproductive and developmental abnormalities in infants and children, recent reports of temporal downward trends in semen quality and testosterone levels as well as increased rates of testicular and thyroid cancers (Stuart, 2012) among adult male populations has generated concern regarding the potential risk of environmental endocrine disrupting chemicals (EDCs) to men's health. Mackenzie et al. (2005) and Safe, (2000) attributed the declining sex ratios in Canada and the United States to over exposure to EDCs. The potential risk associated with drinking water consumption varies between compounds and often depends on the concentration, exposure time, volume, and metabolism rate.

Currently, it is difficult to link human health effects to exposure to EMs due to the existence of background diseases in humans. Very recently, Standford et al. (2010) conducted a comparative survey on the rate of exposure to oestrogenic activity and other compounds presence in US drinking water, food, beverage, and air. The authors concluded that humans are only exposed to a small fragment of pharmaceutically active compounds via consumption of municipal drinking water and there is no evidence of adverse human health effects due to exposure to US drinking water. Fromme et al. (2009) assessed the rate of exposure to perflourinated octanoic acid and oestrogenic hormone via consumption of Germany and US drinking water and found that the daily exposure rate with respect to population ranged between 0.7 and 2%. Thus, the level

of individual or mixtures of pharmaceutically active substances in drinking water is currently considered to be too low to cause a considerable chronic or acute health effects on human (Bull et al., 2011). However, the extent of exposure still requires further studies. The potential health effects of the CECs that are included in the priority list that was drawn up for monitoring purposes in water reuse (see Table 3-2) are described and discussed in more detail in Volume II.

### 3.3.2 Establishing Safe Levels of CECs

The World Health Organisation first developed drinking water quality guidelines in 1984 that have been revised and updated over the years resulting in the 4<sup>th</sup> edition in 2011. The Guidelines describe reasonable minimum requirements of safe practice to protect the health of consumers and derive numerical “guideline values” for constituents of water or indicators of water quality (WHO, 2011). They specify that the basic and crucial requirements to ensure the safety of drinking-water are a “framework” for safe drinking-water, including health-based targets, adequate infrastructure, proper monitoring and independent surveillance. Important in ensuring a safe drinking water, many aspects need to be assessed, including microbial, chemical, radiological and acceptability aspects. The most important consideration is to ensure the microbial safety of the water. The greatest microbial risks are associated with ingestion of water that is contaminated with faeces from humans or animals (including birds). Faeces can be a source of numerous pathogenic bacteria, viruses, protozoa and helminths. The health concerns associated with chemical parameters of drinking water differ from those associated with microbial contamination in that chemical parameters leading to adverse chronic health effects normally result after long-term exposure to low concentrations (with a few exceptions).

The most common and widespread health risk associated with drinking water is microbial contamination and therefore the control of microbial (microbiology and virus) contamination must always be of primary importance. Although this study does not focus on microbial contaminants, they are included as a group in the contaminants of emerging concern. The quantitative microbial risk assessment, or QMRA, is becoming the norm to estimate the disease burden associated with exposure to pathogens. The risk assessment paradigm involving a 4-step approach is described in detail in the WHO (2011) drinking water quality guidelines. Making use of QMRA, risk-based performance targets may be set to ensure a locally relevant “tolerable risk”. Performance targets are usually applied to treatment performance to calculate the microbial reduction needed to ensure a safe water supply. For example, a performance target of 4 log removal for parasites and a 6-log removal of viruses might be necessary, depending on the quality of the source water. For wastewater reuse, the performance targets must be calculated on a case-by-case basis, depending on the catchment and system where the wastewater is produced.

Most microbial drinking water guidelines only specify the absence of a few specific groups of faecal indicator microorganisms such as *E. coli*, coliphage, and *Clostridium*. Occasionally specific pathogens such as cytopathogenic viruses and protozoan parasites should be tested for and have been included in the latest guidelines and SANS-241 (2015). SANS 241-1:2015 must be applied to regulate water quality in Southern African and is specified in the National Water Act (Act 36 of 1998) as well as the Water Services Act (Act 108 of 1997). This standard is used throughout the African Union especially in sub-Saharan Africa. The current standard makes no mention of any of the persistent organic pollutants listed by the Stockholm Convention but it does require that the WHO Guidelines for Drinking Water Quality (Fourth Edition, 2011) are used as a reference document to guide those who find contaminants of concern in their drinking water.

In addition to those guidelines, a series of guidelines on endocrine disruptors or EDCs are available from the WRC, and include the following volumes:

- Volume I: Introduction (WRC Report No. TT 560/13)
- Volume II: Sampling Guide (WRC Report No. TT 561/13)

- Volume III: Bioassay Toolkit (TBA) – Vol III (namely Bioassays Toolkit Analysis) in the context of this project includes bioassays, organics and inorganics. The bioassay toolkit sets out various biological methods to assess the oestrogenicity of water including drinking water, groundwater and wastewater.
- Volume IV: Monitoring and Assessment (TBA)
- Volume V: EDC Management in Catchments (WRC Report No. TT 563/13)

The Australian NRMMC (2008) recommends the use of the following guideline values for contaminants in reclaimed drinking water during long-term exposure. A reference dose is defined as the dose that is safe for a life time exposure, taking the sensitive subpopulations into consideration. Where reference doses are not available for pharmaceuticals, a surrogate or preliminary reference doses is calculated using the therapeutic dose and dividing it by a safety factor, typically 1000 (NRMMC, 2008). The reference doses and recommended drinking water quality guidelines to protect human health based on a life time exposure are presented in Table 3-3.

**Table 3-3: CEC reference doses and corresponding recommended drinking water quality guideline levels**

Contaminant	Recommended Reference Dose (RfD) (mg/kg/d)	Drinking water guideline (ug/L)	Reference
EE2	0.03335	1.5	NRMMC, 2008
Atrazine	0.04	100	WHO, 2011a
Bisphenol A	0.05	200	EFSA, 2006
Carbamazepine	2.8	100	NRMMC, 2008
Cinchonidine*	0.0016	2	NRMMC, 2008
Imidacloprid	0.06	18	EFSA, 2013
Lamivudine*	0.002	6	NRMMC, 2008
Paracetamol	0.05	175	EMA, 1999
Simazine	0.001	2	WHO, 2011a
Sulfamethoxazole	0.01	35	NRA, 2000
Terbutylazine	0.002	7	WHO, 2011a
Triclosan	0.0015	0.35	NRMMC, 2008

\* Calculated from therapeutic dose and dividing by a safety factor, usually 1000

In some cases, for certain chemical compounds and pharmaceuticals with no reference dose values or acceptable daily intakes, the World Health Organisation recommends the use of a surrogate ADI, which is derived by dividing the lowest daily therapeutic dose by safety factors ranging from 1000 to 10 000 (WHO, 2012). The use of the lowest daily therapeutic dose as a starting point for deriving guideline values or assessing risk has been adopted by others (Webb et al., 2003; Schwab et al., 2005; DWI, 2007; Versteegh, Van der Aa & Dijkman, 2007). For most pharmaceuticals, a safety factor of 1000 is applied to the lowest daily therapeutic dose. The Australian drinking water guidelines make use of a very similar approach based on the structure of a compound called the Threshold of Toxicological Concerns (TTC) approach where chemicals are grouped into three general toxicity classes:

- Class I – Simple chemicals, efficient metabolism, low oral toxicity
- Class II – May contain reactive functional groups, slightly more toxic than Class I
- Class III – Substances that have structural features that permit no strong initial presumption of safety or may even suggest significant toxicity



Human exposure thresholds of 1800, 540, and 90 µg/person/day were proposed for the 3 classes of chemicals which represents dosages of 30, 9, and 1.5 µg/kg body weight/day, respectively assuming a human body weight of 60 kg, and a safety/uncertainty factor of 100 (Munro et al., 1996). Using these TTC human exposure thresholds, an acceptable level of each chemical in reclaimed water was derived as follows:

$$\text{Acceptable Level in recycled water (}\mu\text{g/L)} = \frac{x \mu\text{g per person per day} \times \text{proportion allocated to water}}{2\text{L per person}}$$

Where X = 1800 µg/day for class I compounds, 540 µg/day for class II compounds, and 90 µg/day for class III compounds;

Proportion exposure allocated to water is 0.2 (20% from water intake and rest from food and other exposures) and drinking water intake = 2 L/day.

Therefore, the TTC approach assigns acceptable levels for these three classes of chemicals in reclaimed water as follows:

- 180 µg/L for Class I compounds,
- 54 µg/L for Class II compounds, and
- 9 µg/L for Class III compounds.

It is important to note that the TTC approach was meant solely as a method to derive relatively rapid conservative estimation of risk for compounds without detailed risk assessment or with limited datasets.

### 3.4 SUMMARY

One of the aims of the study was to compile a list of contaminants of emerging concern which may occur and pose a health risk via potable water, either through intentional or unintentional reuse of wastewater. An important consideration is that the management of drinking water is complex with many factors involved which cannot be prescribed on a generic level. Points that should be taken into account are that drinking water quality must be managed on a catchment level. With compounds often grouped by use or source which can be useful in selecting compounds for consideration for monitoring. For example, less than 30 compounds are associated with products used in the metallurgical industry. Therefore, when considering a catchment with metallurgical activities, these compounds would then need to be investigated or included in a routine monitoring programme. From here, a method to develop a priority list of contaminants is recommended which can be used to monitor the quality of reclaimed water and the treatment efficiency of wastewater treatment processes. The CECs found internationally, (in the European Union (EU), Australia and United States (US)) listed as priority pollutants in treated waste water earmarked for reuse were first identified.

To determine a priority CEC list for monitoring reclaimed water in South Africa, the local context needed to be established. Using the priority pollutants identified in previous studies, and monitored pollutants in drinking and wastewaters, along list was compiled. Chemicals that were persistent and able to pass through water treatment processes were identified. Volumes of prescription drugs and pesticide use volumes (South Africa) were considered to represent likelihood of being present in the environment. Making use of the many studies carried out internationally including those chemicals included in the USEPA (112 compounds), the EU (58 compounds), the NRC (National Research Council) potential organic indicator compounds (52 compounds), the Australian drinking water quality guideline compounds (129 compounds) and relevant South African chemical compounds found in water supplies, an initial list was created. From there, the health and environmental risk for individual contaminants of emerging concern must be assessed to prioritise chemicals which should be included in monitoring programs. A risk-based screening framework was used, which includes a few principal steps:

- Establishing which contaminants of emerging concern have been detected in either environmental and/or drinking waters from international literature
- Establishing which chemicals have been detected in South Africa in either environmental and/or drinking waters (representing prevalence).
- Ascertaining the most frequently prescribed pharmaceuticals in South Africa – to represent exposure potential.
- Identifying those chemicals known to be persistent and not easily removed in treatment processes.
- Identifying those chemicals with an established analytical detection method as well as relevant detection limit.



## CHAPTER 4: ASSESSING THE INDICATIVE REMOVAL OF CECs, PLANT PERFORMANCE AND RELIABILITY

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### 4.1 INTRODUCTION

In this chapter, the results obtained from an assessment of indicative removal potential of CECs in water reclamation and wastewater treatment processes are presented. In addition, there is a section that report on plant performance and reliability studies.

### 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 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 water reclamation plants (WRPs) and three wastewater treatment plants (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) which treats water from a river considered to be increasingly polluted with treated wastewater, industrial effluent and agricultural run-off.

#### 4.2.1 Water reclamation plant A (WRP A)

This reclamation plant makes use of the modern dual-membrane treatment process. The system receives secondary treated wastewater from a conventional activated sludge WWTP 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.

#### 4.2.2 Water reclamation plant B (WRP 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<sub>2</sub>O<sub>2</sub> (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.

#### **4.2.3 Wastewater treatment plants C, D and E (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.

#### **4.2.4 Water treatment plant abstracting water from a major river (WTP F)**

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.

### **4.3 ASSESSING THE INDICATIVE REMOVAL OF CECS**

#### **4.3.1 Sampling programmes**

In total the two WRPs, three WWTPs and one WTP were sampled during the three sampling programmes. It should be noted that the sampling programmes were in no way designed to determine the general performance and operation of the plants and no conclusions regarding these subjects can be made based on the results of the sampling programmes. The purpose and design of the sampling programmes were to simply determine the indicative removal capabilities under certain conditions of certain treatment processes for the priority parameters that were identified and listed in Chapter 3 of this report. Three WWTPs were also included in the sampling programmes because the treatment processes of these WWTPs often forms part of DPR systems. Again, it should be noted that these plants were not designed for or are responsible for removing any of the compounds identified and listed in Chapter 3, and therefore the results of the analyses shown at a later stage in this section cannot not be used to evaluate the performance and operation of the WWTPs. It was also decided to include a WTP during the third sampling programme as a means of comparing the treatment processes but also to provide some perspective as to the levels of the priority compounds that can be found in a river in comparison to that found in treated wastewater (de facto reuse).

Not all the plants were sampled during all three of the sampling programmes. Instead, only WRP A and the three WWTPs were sampled during all three of the sampling programmes, WRP B was sampled during the second and third sampling programmes and the WTP was only sampled during the third sampling programme. The exact sampling procedure that was followed for each of the sampling programmes and at each of the plants being sampled can be seen in Volume III. For this chapter, however, it will only be noted that the samples were taken after each of the treatment processes within the WRPs (as well as the WWTPs feeding the WRPs), the WWTPs and the WTP. The only exception is WWTP E where the project was only interested in sampling the raw wastewater and the MBR permeate.

#### 4.3.2 Sampling procedure

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.

#### 4.3.3 Sample analysis

The analyses performed on the samples included one or more of the following:

- Ammonia, nitrate plus nitrite, DOC, TOC, EC, pH, COD, turbidity and UV<sub>254</sub> 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, 17 $\alpha$  ethinyl estradiol (EE2), acetaminophen, atrazine, imidacloprid, carbamazepine, lamivudine, simazine, sulfamethoxazole, terbuthylazine and cinchonidine.

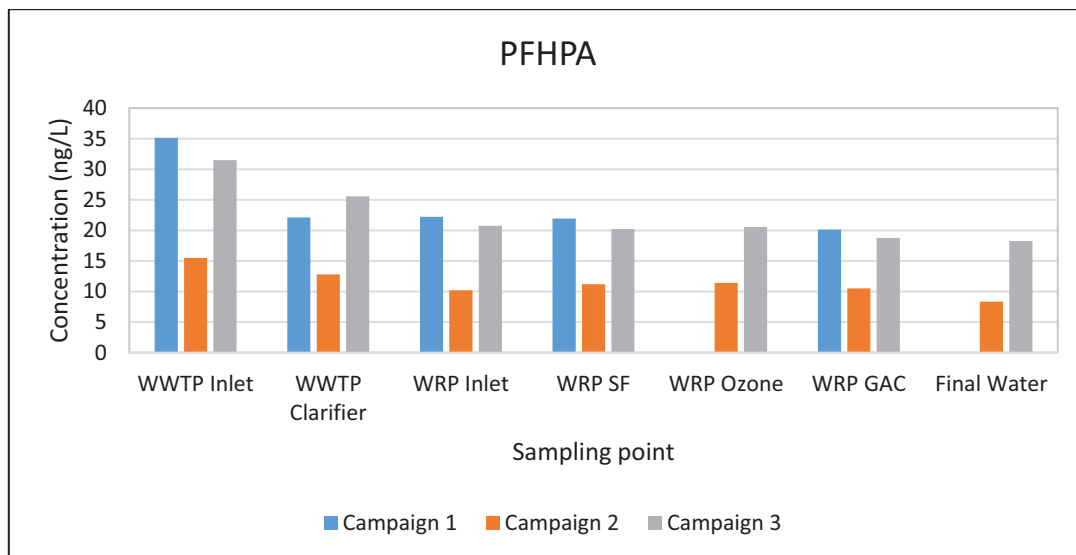
#### 4.3.4 Concentrations of CECs in samples – Water reclamation plant A (WRP A)

Figures 4-1 to 4-18 show a summary of the results obtained for the indicative removal of the selected priority contaminants over the three sampling campaigns.

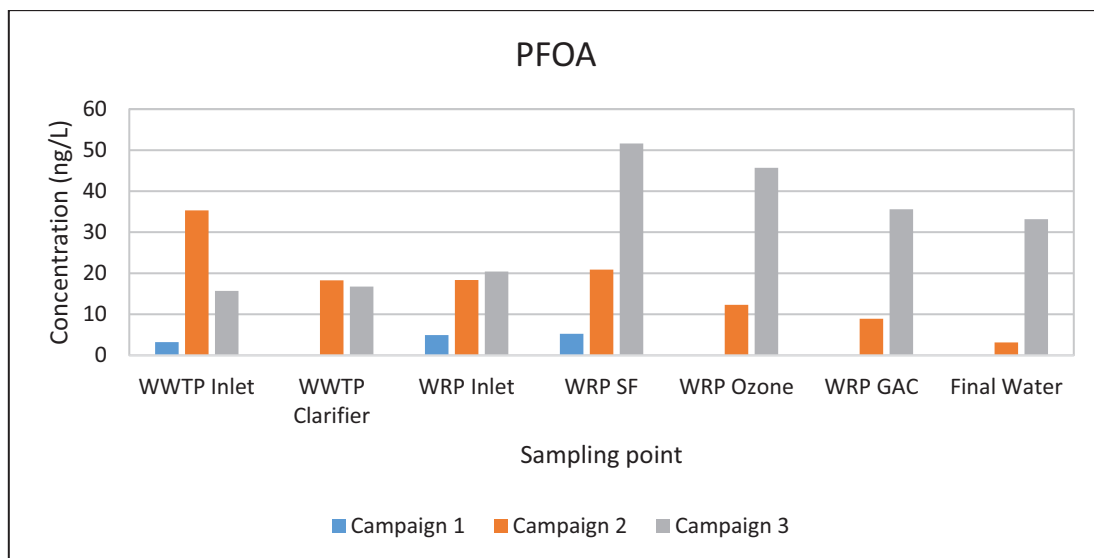
During sampling programme 1, the highest concentrations of PFCs were found in the raw wastewater entering the WWTP. The concentrations decreased through the WWTP and the WRP, and the chemicals were either not detected (i.e. below the detection limit) in the final water from the WRP (PFHPA, PFOA, PFOS and PFDA), or were reduced to very low concentrations (1.12 ng/L PFNA and 1.23 ng/L PFUnDA). The PFCs that had the highest concentrations in the WWTP and WRP inlet streams were the PFHPA and PFNA. PFHPA was reduced from 35.14 ng/L to below detection in the total water reclamation system. PFHPA was, however, high after the RO process, and PFNA after the UF process, but it should be kept in mind that all the samples were taken consecutively at the same time, and not on a time-lag approach. The priority CECs were all reduced to less than 15 ng/L, except for (EE2) (130 ng/L) and carbamazepine (720 ng/L). The highest percentage removal was obtained in the RO process, with further removal taking place downstream in the advanced oxidation (UV-H<sub>2</sub>O<sub>2</sub>) process as well.

During sampling program 2, the organic loading on the WWTP was very high (COD 5637 mg/L, ammonia 107 mg/L as N). The PFCs in the incoming raw wastewater to the WWTP was in the same order of magnitude as during sampling program 1, and were again reduced to low levels in the reclamation system (5.57 ng/L PFHPA, 1.2 ng/L PFOA, and the other PFCs not detected in the final water). The priority CECs were again reduced to low levels in the final water, with five of the CEC concentrations below detection limit. Those that were somewhat elevated were still lower than during sampling program 1 (BPA 86 ng/L, EE2 104 ng/L, carbamazepine 24 ng/L). RO again effectively reduced the concentrations of most of the CECs, and advanced oxidation achieving further reduction in the residual concentrations.

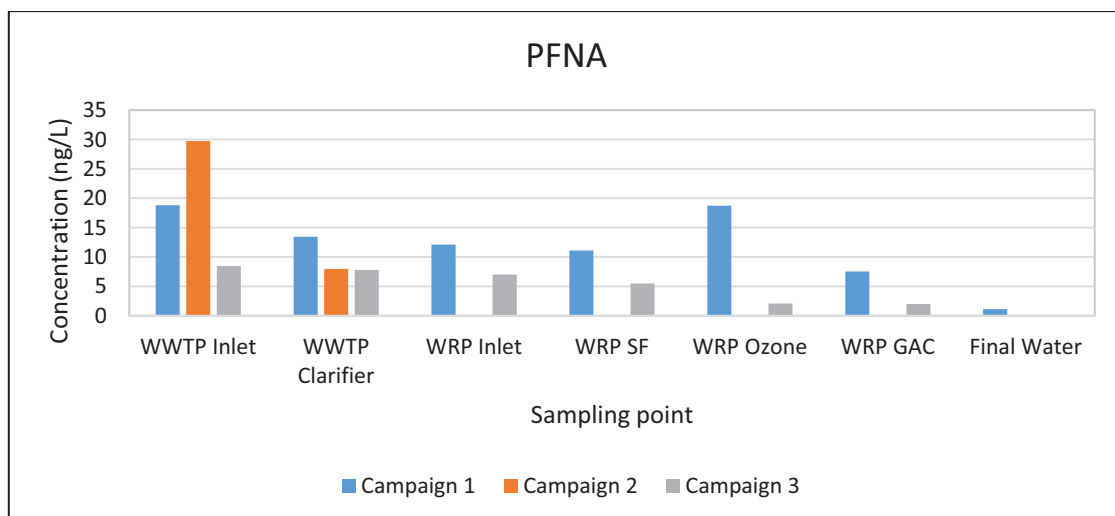
During sampling programme 3, PFHPA and PFOA were present in higher concentrations than the other PFCs that were analysed for, and were also reduced less effectively. PFOS and PFUnDA were not detected in any of the samples. EE2 (432 ng/L) and carbamazepine (102 ng/L) were again higher than the other CECs in the raw wastewater. The only CECs detected in the final water were BPA, triclosan and carbamazepine.



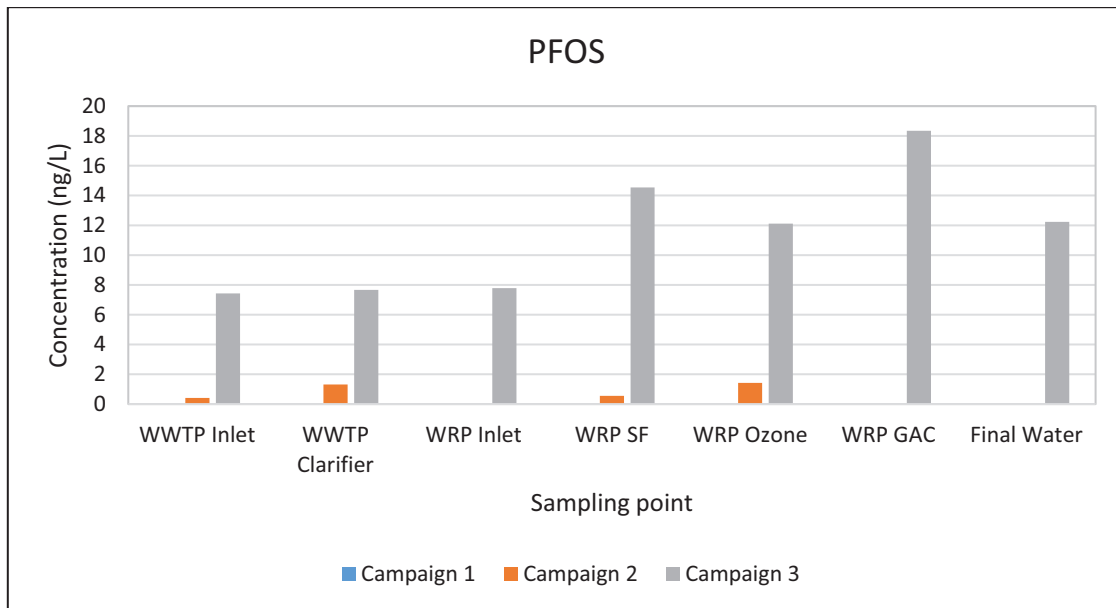
**Figure 4-1: PFHPA for all the sampling campaigns for WRP A**



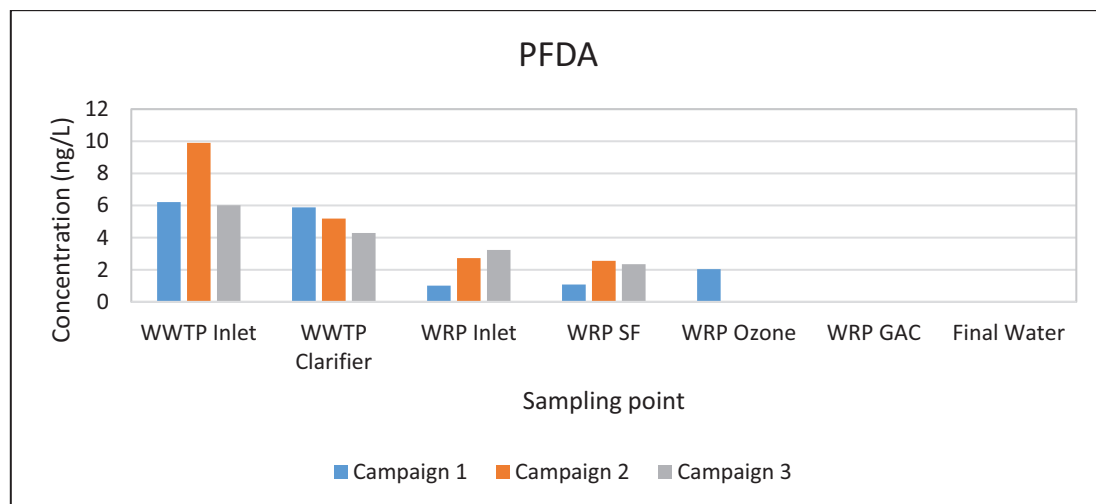
**Figure 4-2: PFOA for all the sampling campaigns for WRP A**



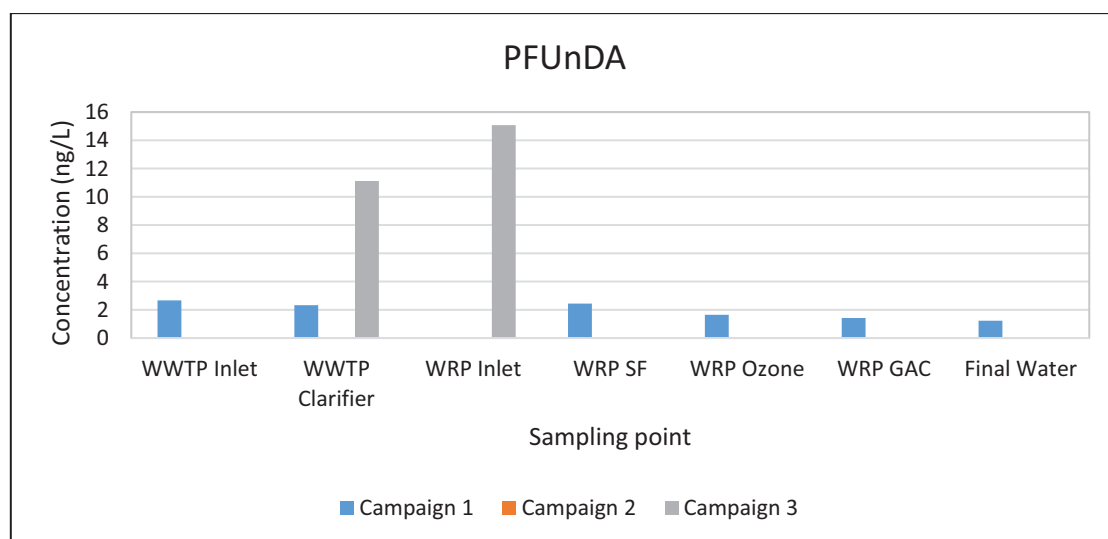
**Figure 4-3: PFNA for all the sampling campaigns for WRP A**



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



**Figure 4-5: PFDA for all the sampling campaigns for WRP A**



**Figure 4-6: PFUnDA for all the sampling campaigns for WRP A**

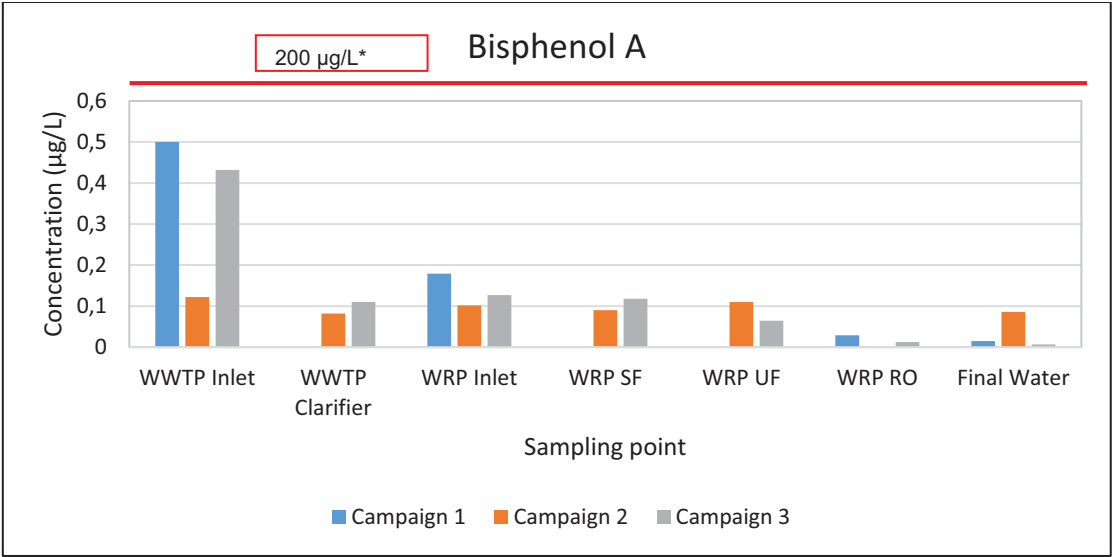


Figure 4-7: Bisphenol A for all the sampling campaigns for WRP A. \* Limit proposed for potable water (NRMMC, 2008 Guideline value)

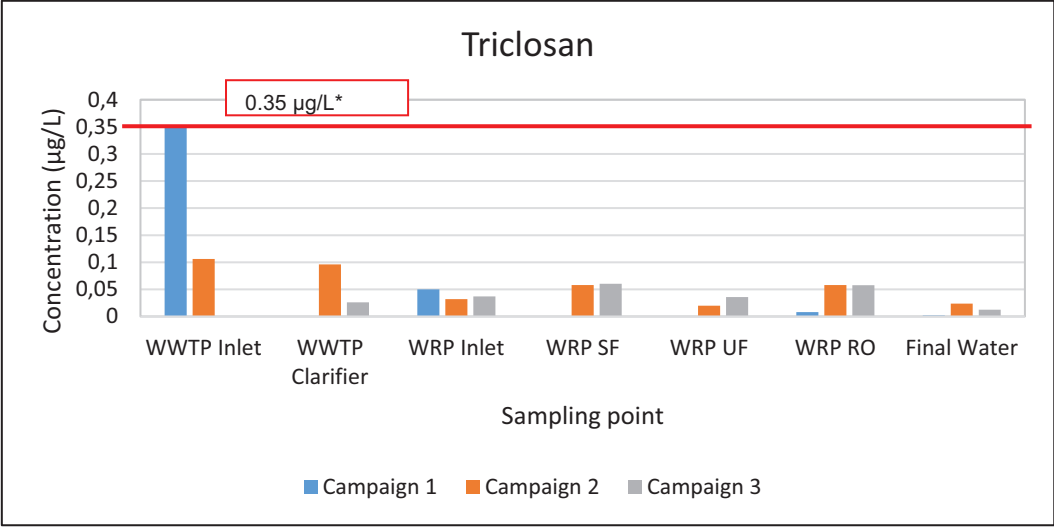


Figure 4-8: Triclosan for all the sampling campaigns for WRP A. \* Limit proposed for potable water (NRMMC, 2008 Guideline value)

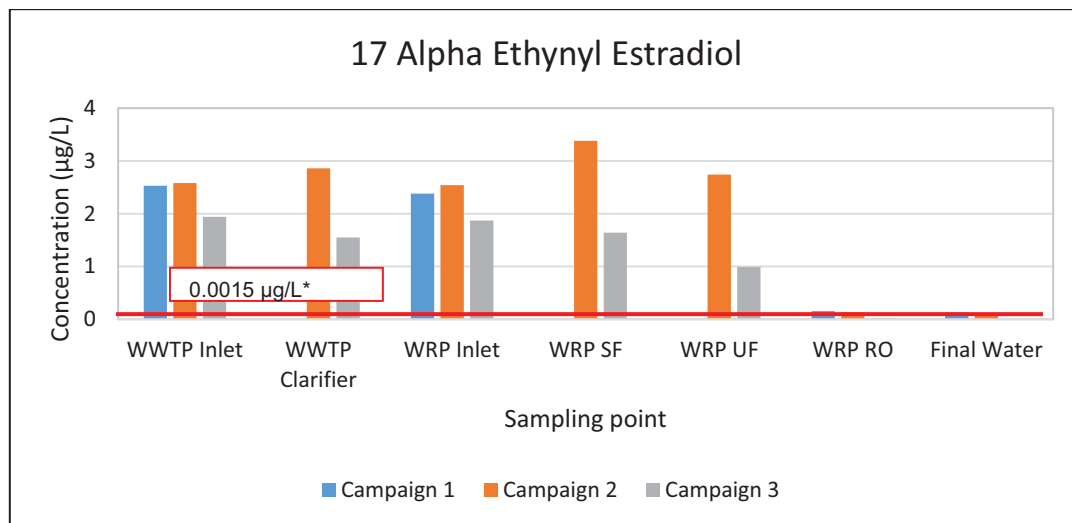


Figure 4-9: 17 Alpha Ethynyl Estradiol for all the sampling campaigns for WRP A. \* Limit proposed for potable water (NRMMC, 2008 Guideline value)

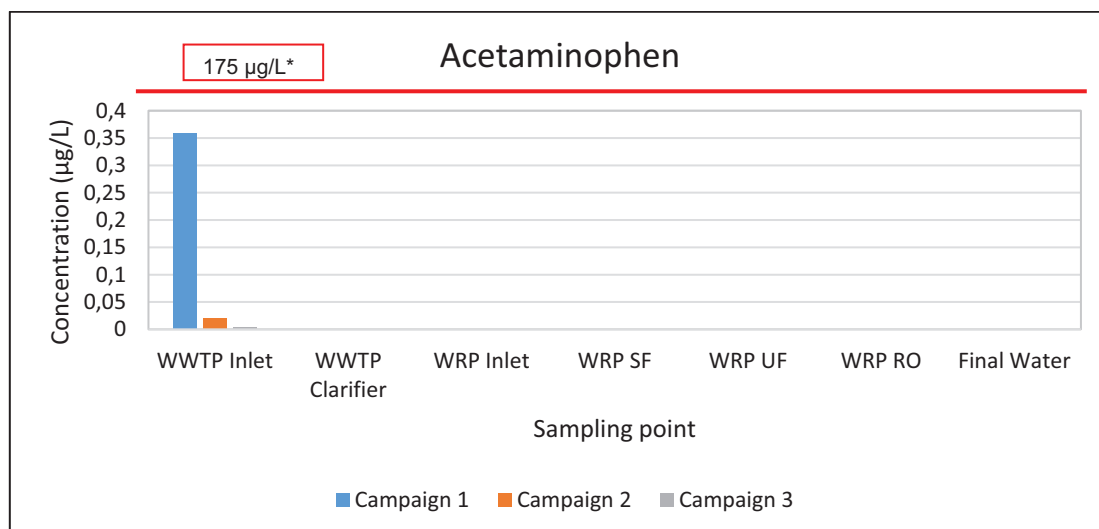


Figure 4-10: Acetaminophen for all the sampling campaigns for WRP A. \* Limit proposed for potable water (NRMMC, 2008 Guideline value)

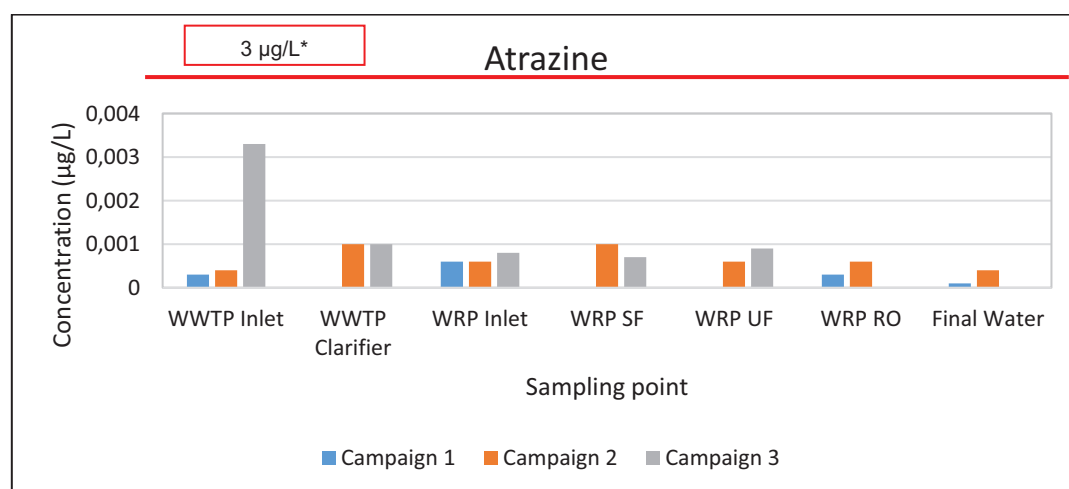
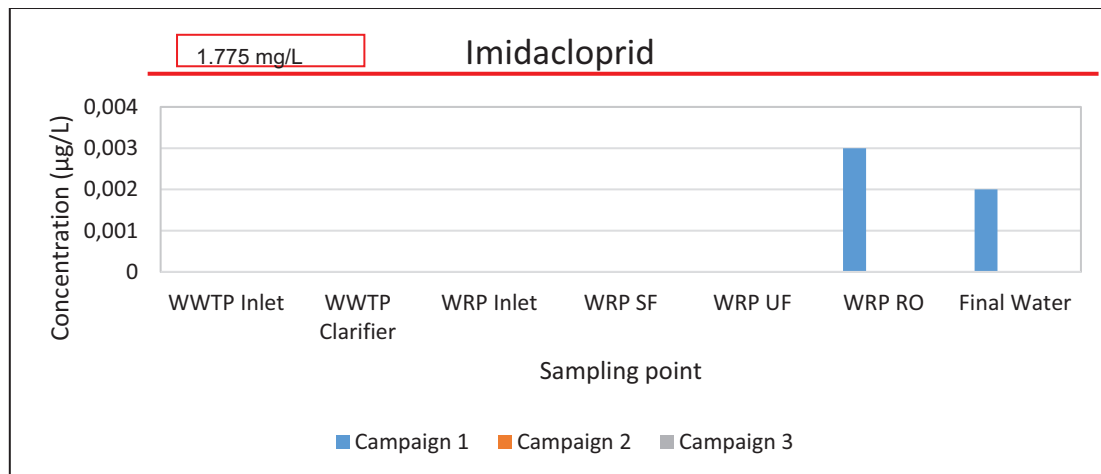
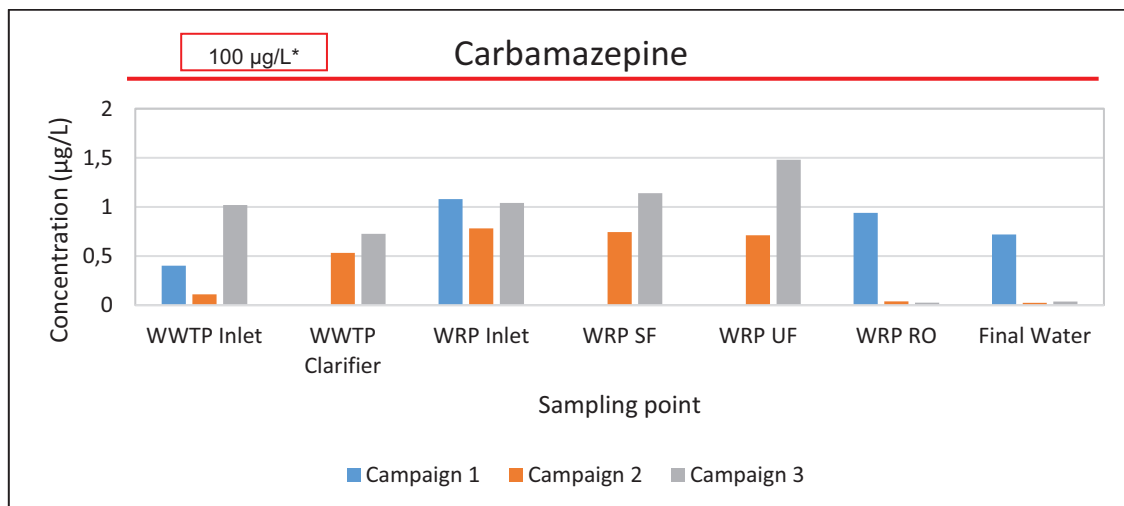


Figure 4-11: Atrazine for all the sampling campaigns for WRP A. \* Limit proposed for potable water (EPA, 2012 California drinking water limits)

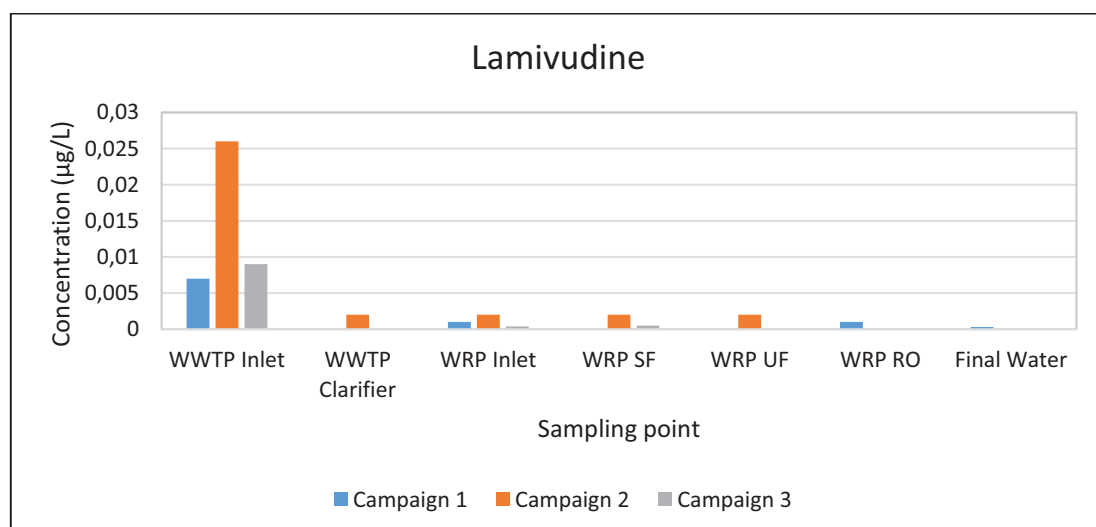




**Figure 4-12: Imidacloprid for all the sampling campaigns for WRP A. \* Limit proposed for potable water (EPA, 2005 California drinking water limits)**



**Figure 4-13: Carbamazepine for all the sampling campaigns for WRP A. \* Limit proposed for potable water (NRMMC, 2008 Guideline value)**



**Figure 4-14: Lamivudine for all the sampling campaigns for WRP A**

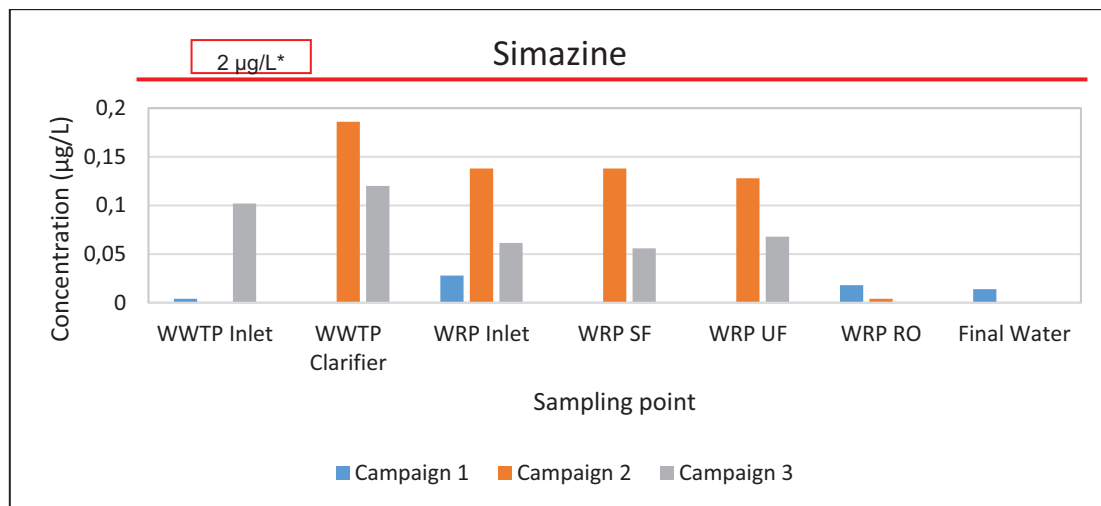


Figure 4-15: Simazine for all the sampling campaigns for WRP A. \* Limit proposed for potable water (WHO, 2011c Guideline value)

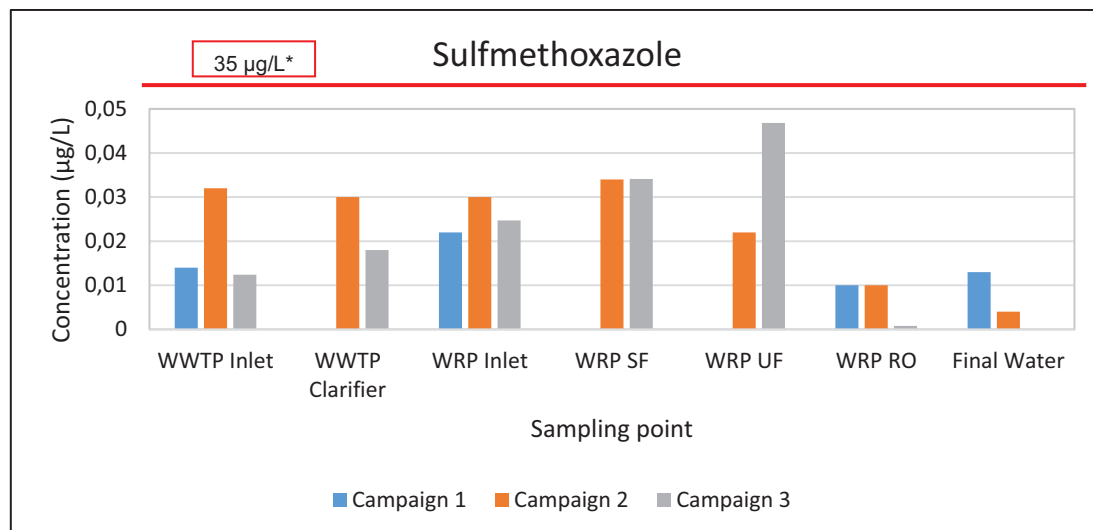


Figure 4-16: Sulfamethoxazole for all the sampling campaigns for WRP A. \* Limit proposed for potable water (NRMMC, 2008 Guideline value)

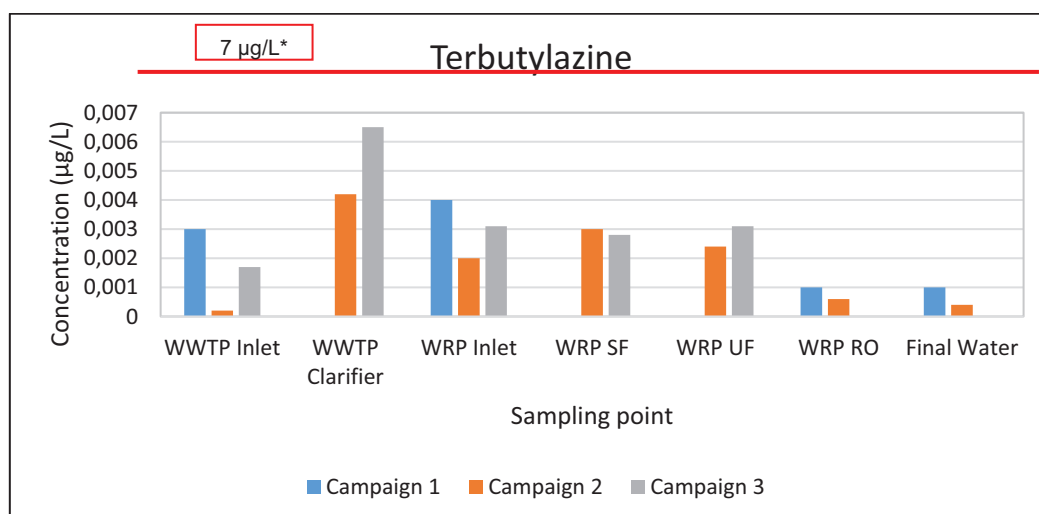
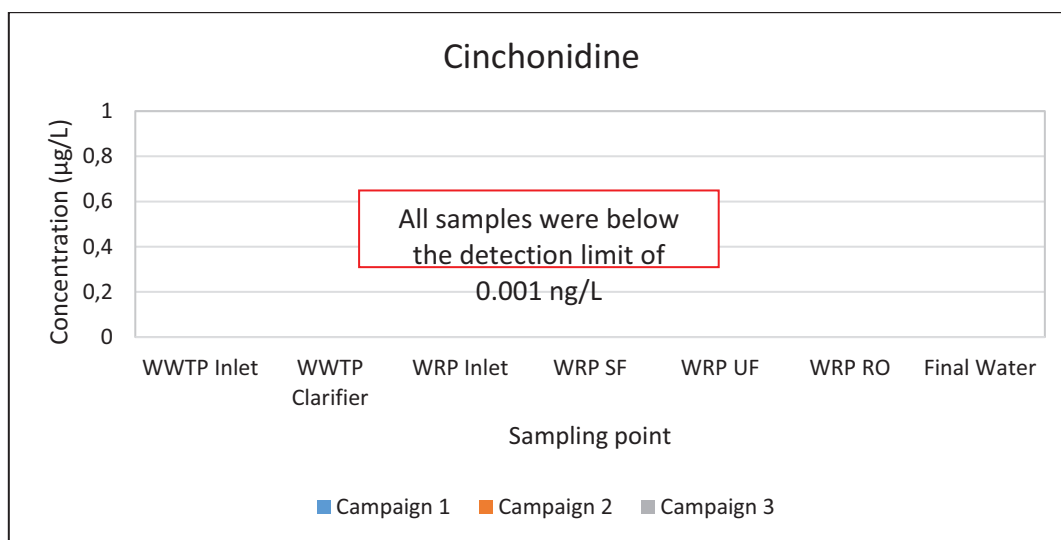


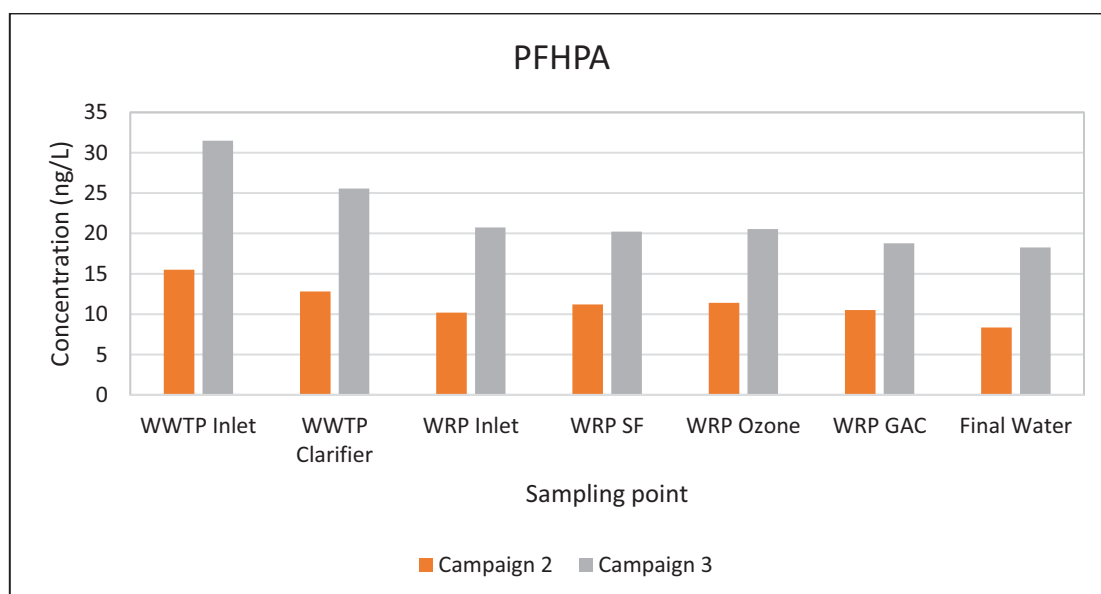
Figure 4-17: Terbutylazine for all the sampling campaigns for WRP A. \* Limit proposed for potable water (WHO, 2011c Guideline value)



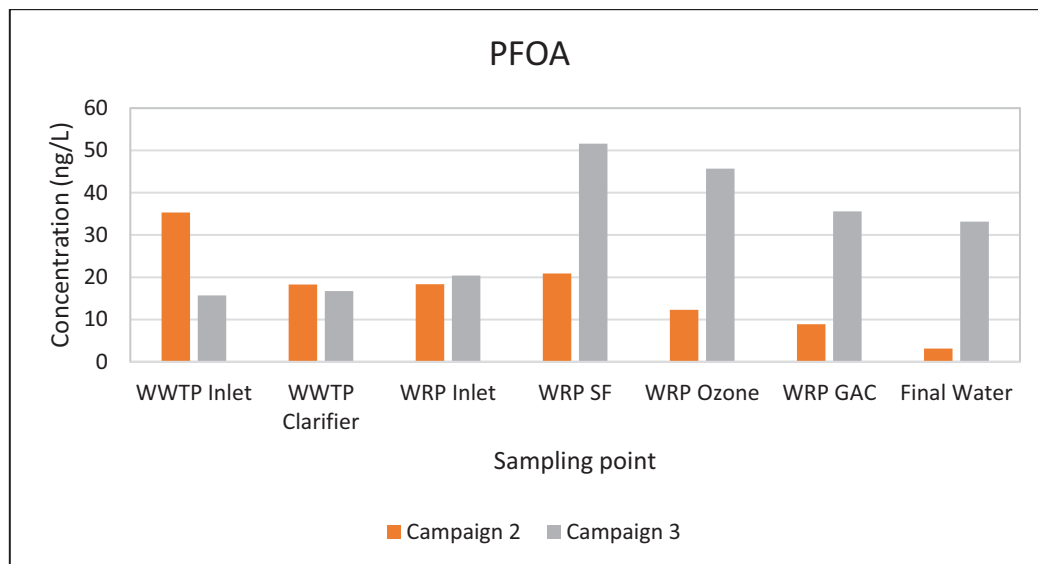
**Figure 4-18: Cinchonidine for all the sampling campaigns for WRP A**

#### 4.3.5 Concentrations of CECs in samples – Water reclamation plant B (WRP B)

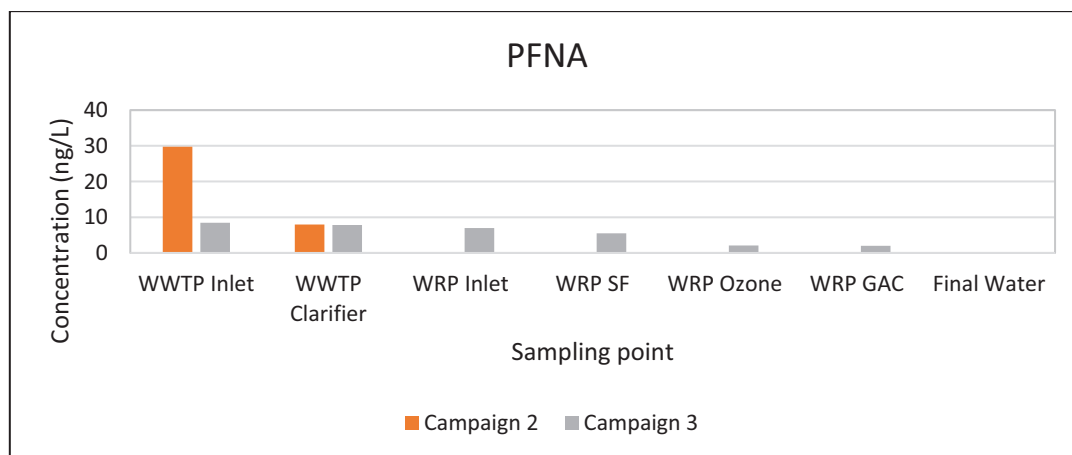
Results of analysis of samples taken during sampling programs 2 and 3 of the WWTP inlet, WWTP clarifier outflow, inlet to the WRP, after the sand filters, after UF, after ozone, after GAC and of the final treated water, are shown in Figures 4-9 to 4-36. During sampling program 2, PFHPA and PFOA were detected in the final water at concentrations of only 8.35 ng/L and 3.14 ng/L, respectively. None of the other PFCs were detected in the final water. The CEC levels in the incoming raw wastewater to the WWTP was lower than that were measured in the inflow to the WWTP of WRP A. The only CECs detected in the final water were EE2 (6 ng/L), atrazine (0.4 ng/L) and terbuthylazine (0.4 ng/L). The results of the bio-assay tests are discussed in section 5.4 below. During sampling program 3, PFHPA, PFOA and PFOS (18.26 ng/L, 33.17 ng/L and 12.23 ng/L, respectively) were detected in the final water. Concentrations were higher than in sampling program 1. PFOA and PFOS in the sand filters outflow were more than 100% higher than in the filter inflow.



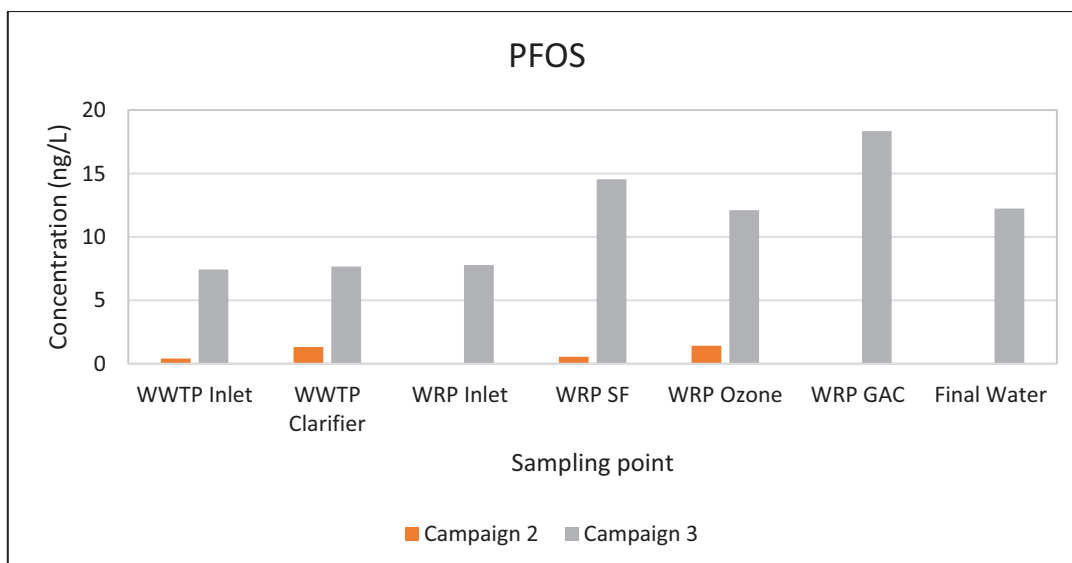
**Figure 4-19: PFHPA for all the sampling campaigns for WRP B**



**Figure 4-20: PFOA for all the sampling campaigns for WRP B**



**Figure 4-21: PFNA for all the sampling campaigns for WRP B**



**Figure 4-22: PFOS for all the sampling campaigns for WRP B**

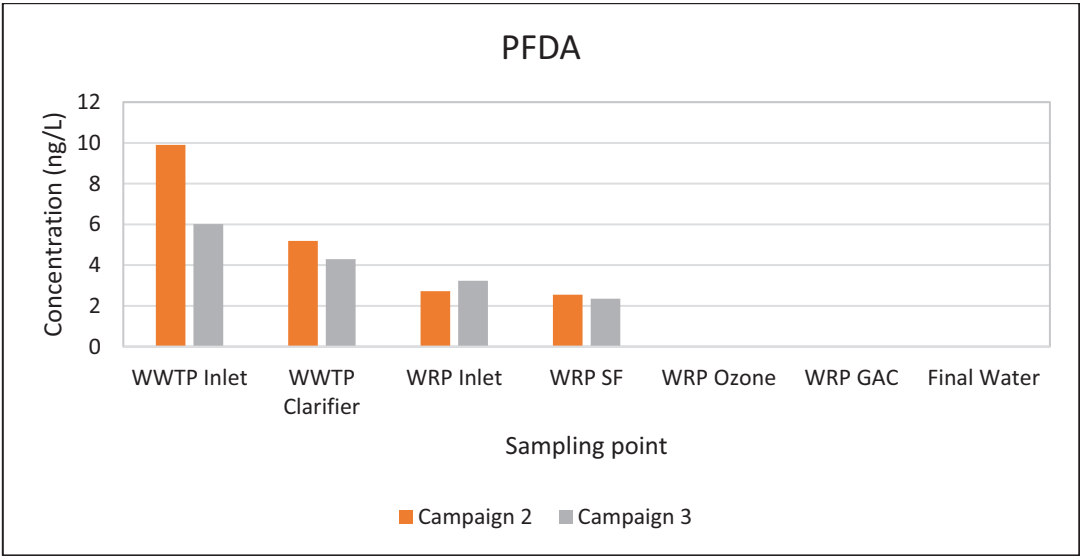


Figure 4-23: PFDA for all the sampling campaigns for WRP B

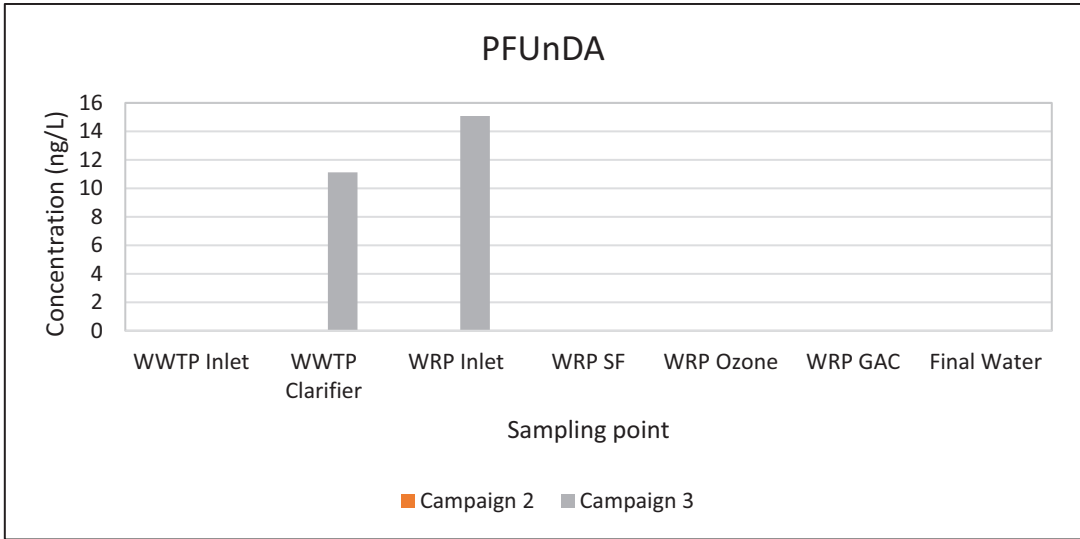


Figure 4-24: PFUnDA for all the sampling campaigns for WRP B

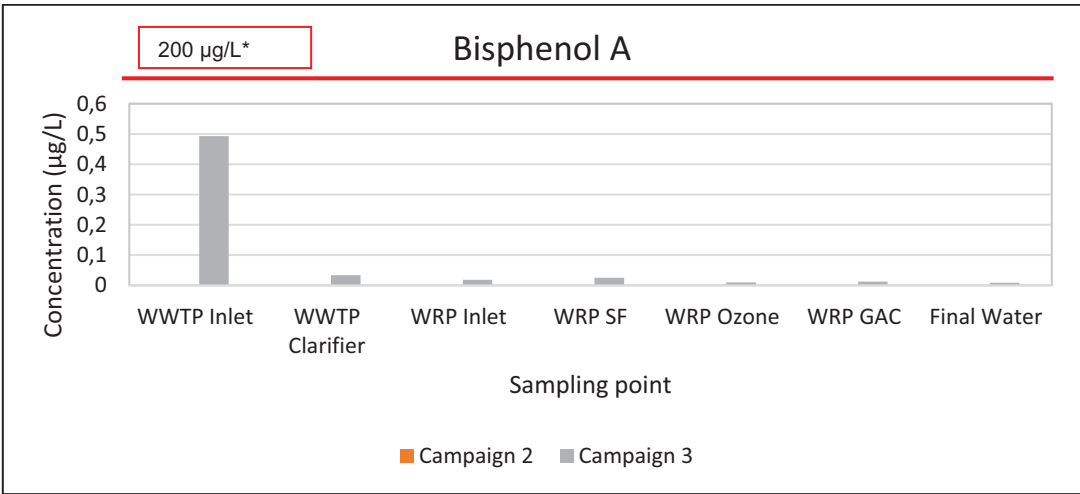


Figure 4-25: Bisphenol A for all the sampling campaigns for WRP B. \* Limit proposed for potable water (NRMCC, 2008Guideline value)

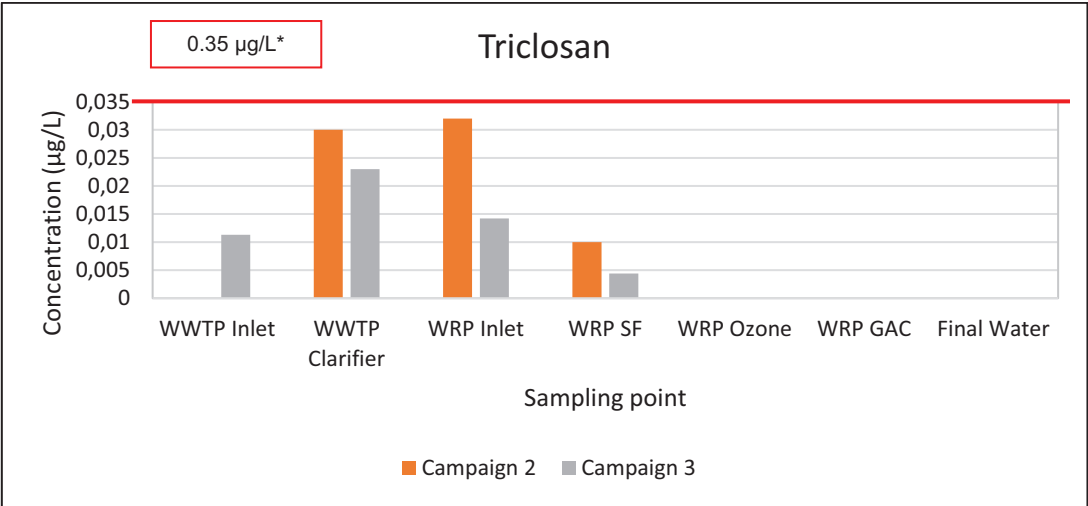


Figure 4-26: Triclosan for all the sampling campaigns for WRP B. \* Limit proposed for potable water (NRMMC, 2008 Guideline value)

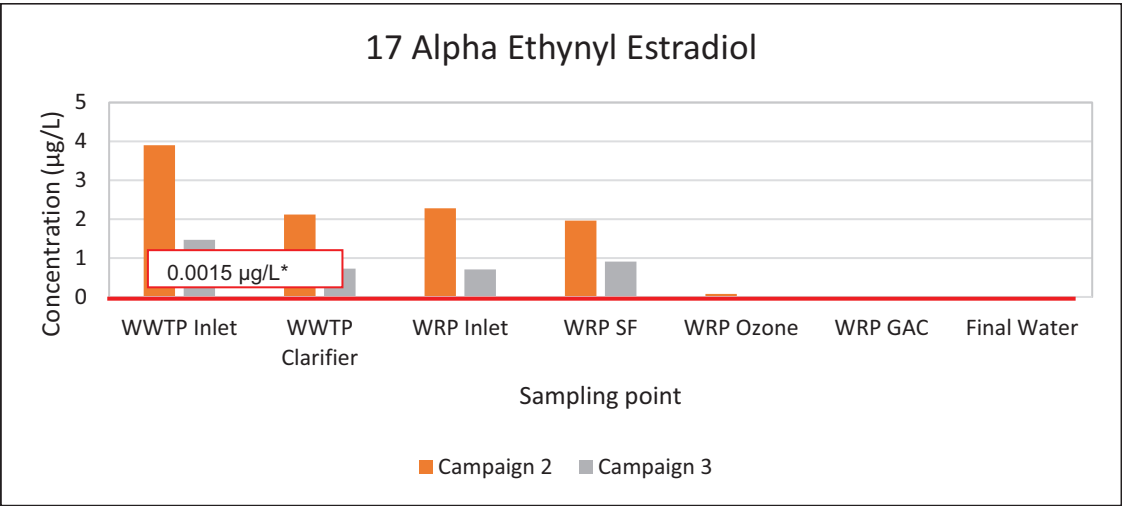


Figure 4-27: 17 Alpha Ethynyl Estradiol for all the sampling campaigns for WRP B. \* Limit proposed for potable water (NRMMC, 2008 Guideline value)

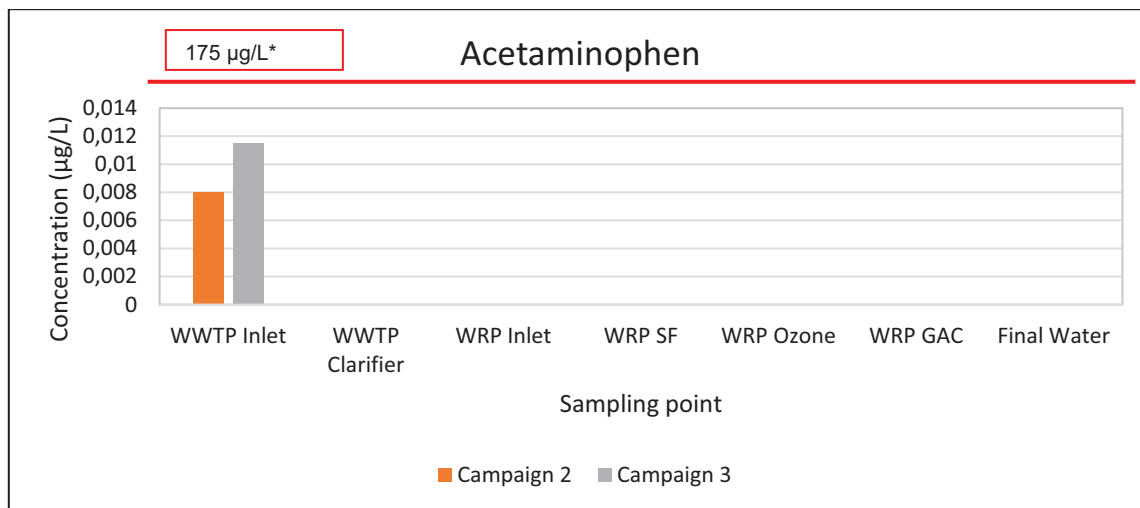


Figure 4-28: Acetaminophen for all the sampling campaigns for WRP B. \* Limit proposed for potable water (NRMCC, 2008 Guideline value)

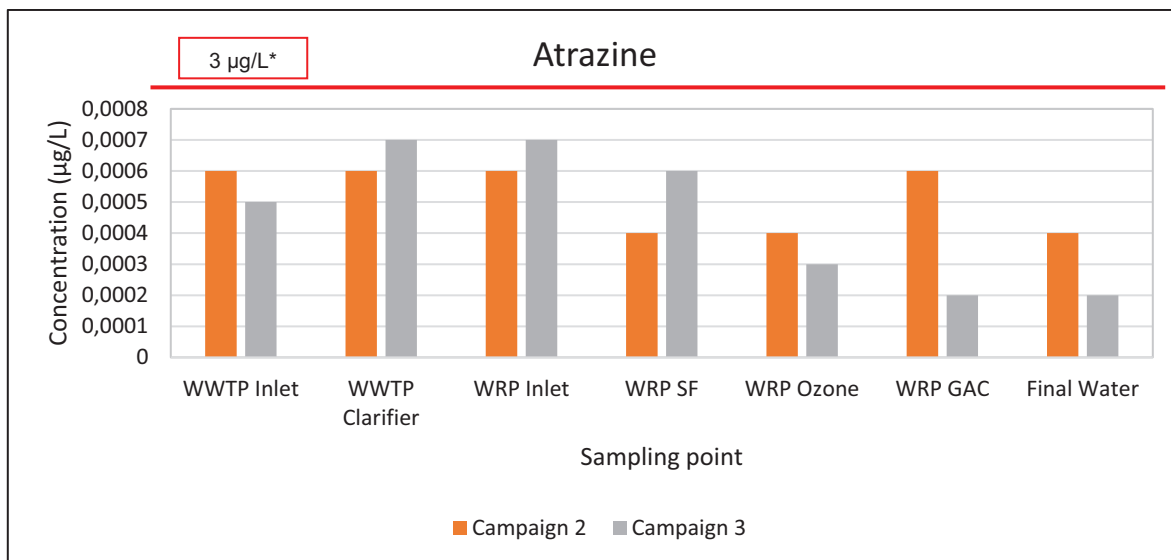


Figure 4-29: Atrazine for all the sampling campaigns for WRP B. \* Limit proposed for potable water (EPA, 2012 California drinking water limits)

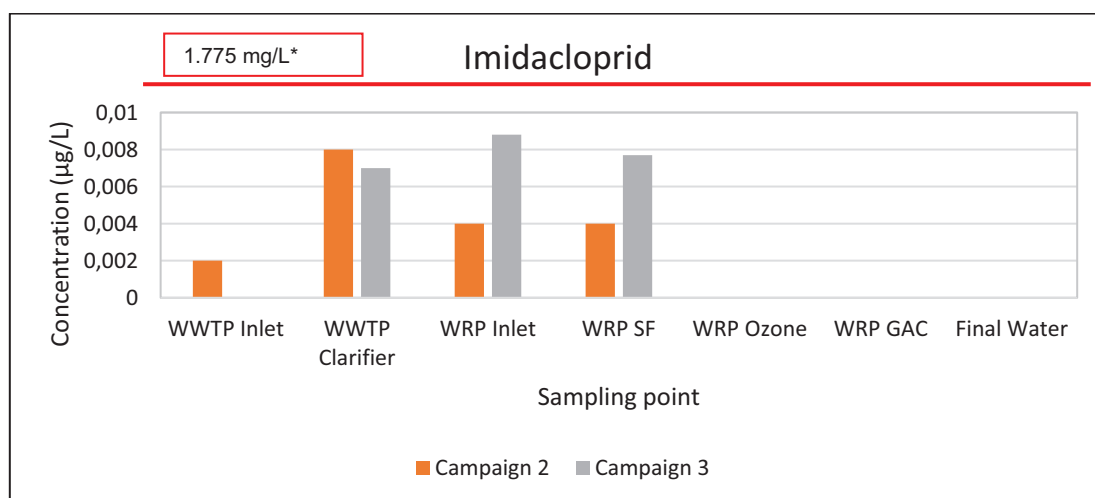


Figure 4-30: Imidacloprid for all the sampling campaigns for WRP B. \* Limit proposed for potable water (EPA, 2005 California drinking water limits)



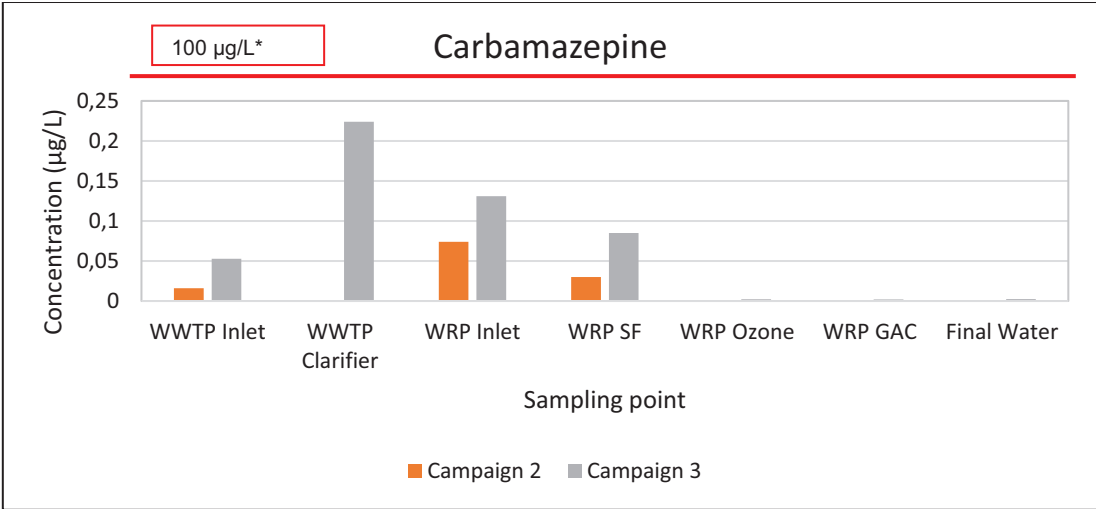


Figure 4-31: Carbamazepine for all the sampling campaigns for WRP B. \* Limit proposed for potable water (NRMMC, 2008 Guideline value)

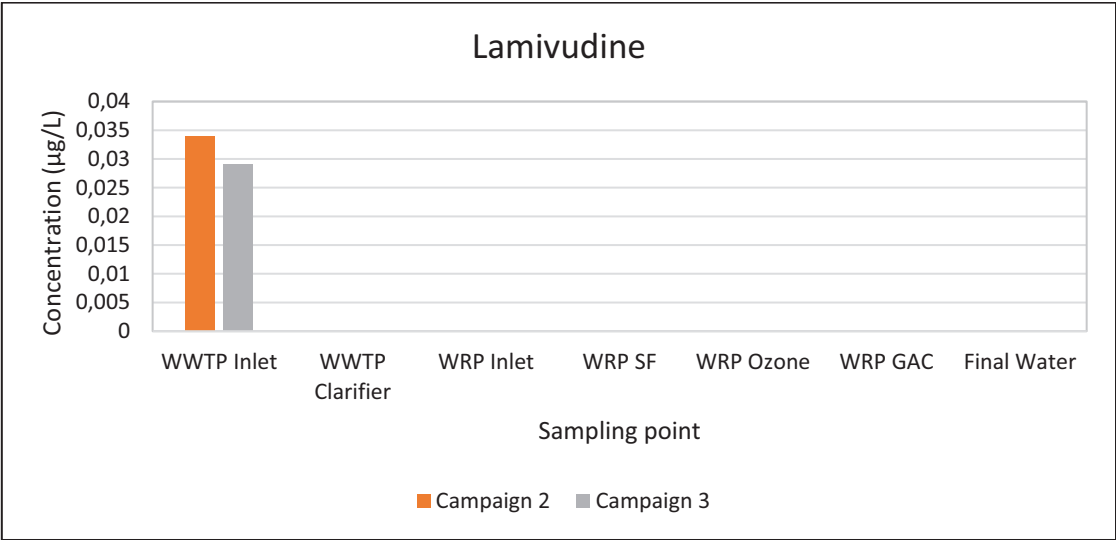


Figure 4-32: Lamivudine for all the sampling campaigns for WRP B

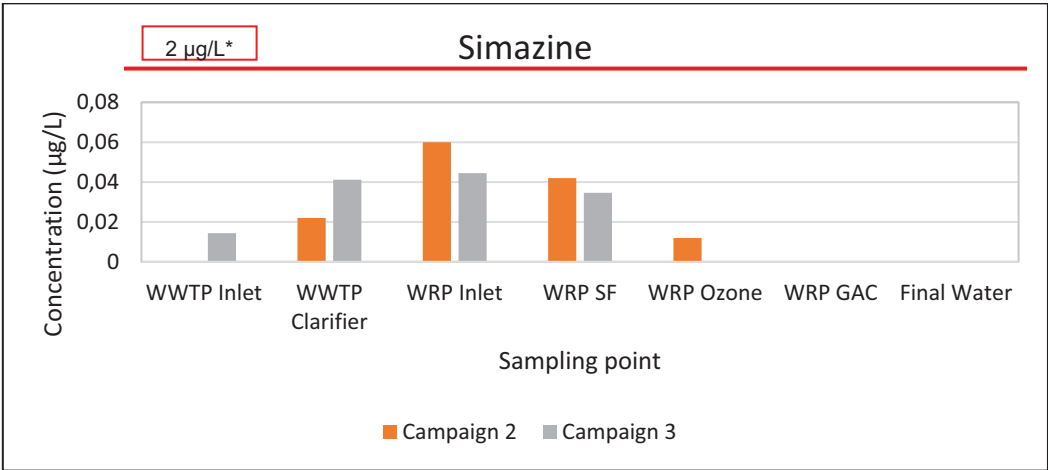


Figure 4-33: Simazine for all the sampling campaigns for WRP B. \* Limit proposed for potable water (WHO, 2011c Guideline value)

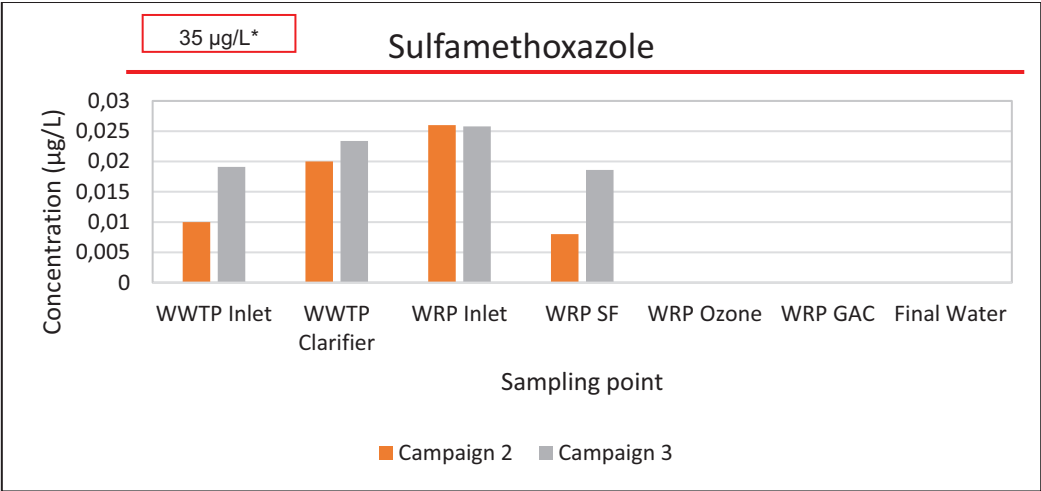


Figure 4-34: Sulphamethoxazole for all the sampling campaigns for WRP B. \* Limit proposed for potable water (NRMCC, 2008 Guideline value)

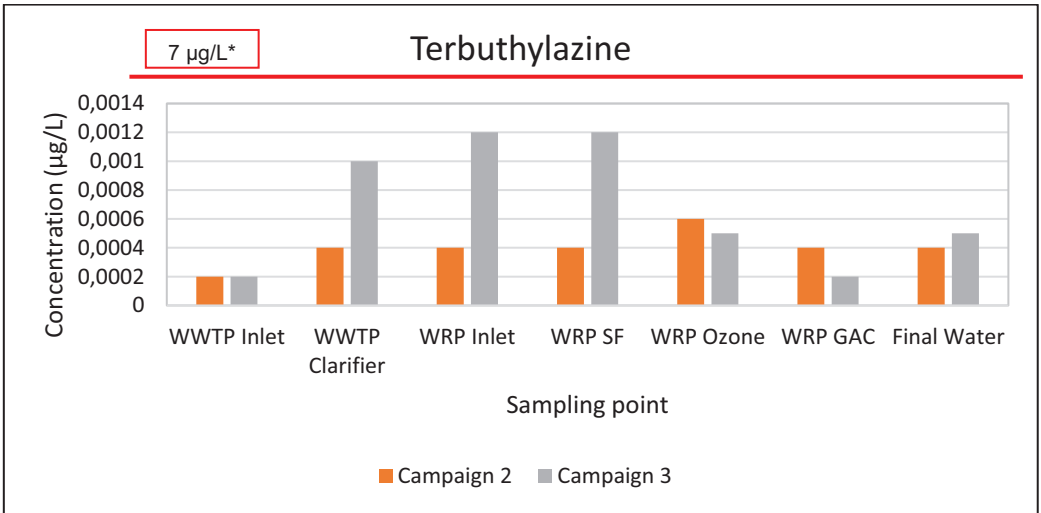


Figure 4-35: Terbutylazine for all the sampling campaigns for WRP B. \* Limit proposed for potable water (WHO, 2011c Guideline value)

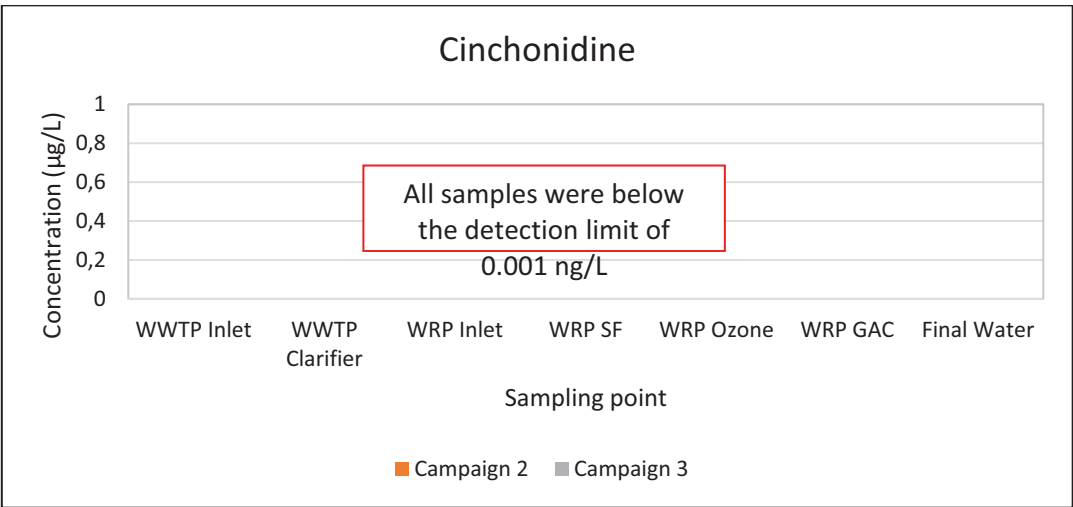


Figure 4-36: Cinchonidine for all the sampling campaigns for WRP B

#### 4.3.6 Concentrations of CECs in samples – Wastewater treatment plants C, D and E (WWTP C, D and E)

Figures 4-37 to 4-54 show the results of analysis of samples taken during sampling programs 1, 2 and 3 of the raw, after activated sludge, after MBR and of the final effluent.

An increase in concentrations of PFOA, PFNA and PFOS was observed in the WWTPs effluents during sampling 1. Chularueangakorn 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. The samples taken at the wastewater treatment plants were not analysed for the CECs on the priority list during sampling program 1, but it was done for the samples taken during sampling programs 2 and 3.

During sampling program 2, both WWTP C and WWTP D the PFOA levels increased, but in WWTP E the PFOA concentration was reduced from the raw wastewater to the final effluent. PFOS and PFUnDA were not detected in the final effluents of WWTP D, WWTP E and WWTP C (MBR final). PFOS was not detected in any of the samples. EE2 was again present in the raw wastewater in elevated concentrations (WWTP C 4240 ng/L, WWTP D 2820 ng/L and WWTP E 6000 ng/L). Simazine was also present at elevated levels. The simazine concentration in the activated sludge train raw inflow of WWTP C was very high (11660 ng/L) compared to WWTPs A, B, D and E. Overall, the wastewater treatment plants on their own (i.e. without a downstream advanced water treatment plant) were not able to remove the CECs effectively (which is to be expected, as the WWTPs were not designed with the aim of removing trace amounts of organics).

Results of sampling program 3 confirmed that the WWTPs are not able to remove the CECs effectively (nor were they expected to). PFHPA, PFOA, PFNA and PFDA were again found in relatively high concentrations. PFOS and PFUnDA again not detected in the samples of all three plants, except PFUnDA which was high in the WWTP E final effluent from the MBR train (10122 ng/L). Removal of CECs were also not effective in the WWTPs during sampling program 3. Levels of EE2, imidacloprid and Simazine remained high throughout (EE2 up to 2630 ng/L, imidacloprid up to 5660 ng/L, and simazine up to 21900 ng/L).

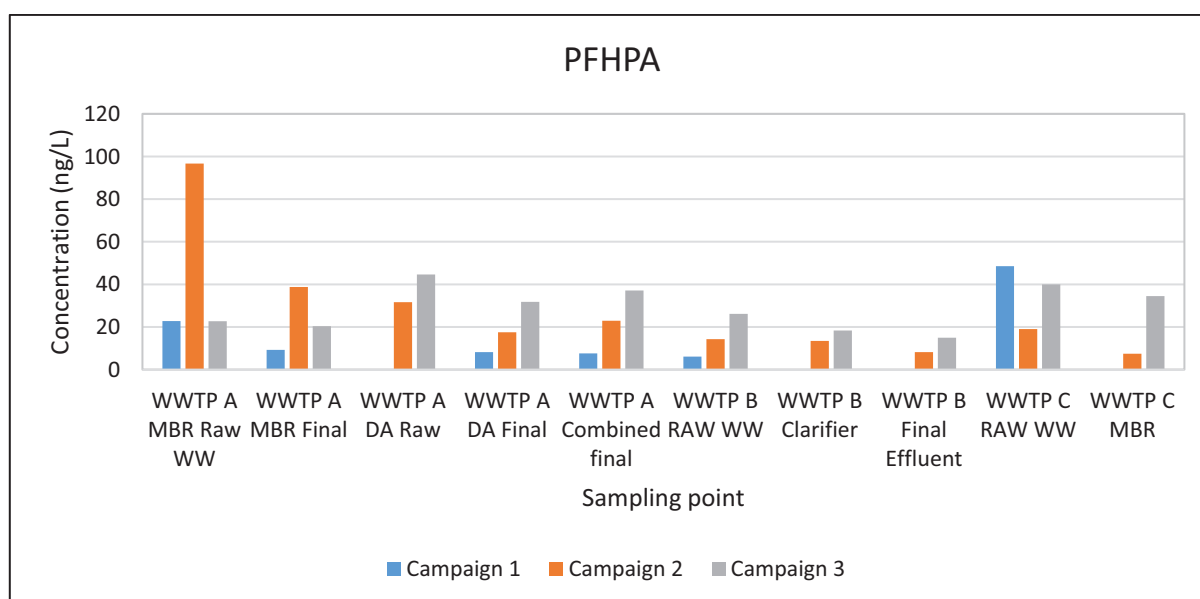


Figure 4-37: PFHPA for all the sampling campaigns for all WWTP samples

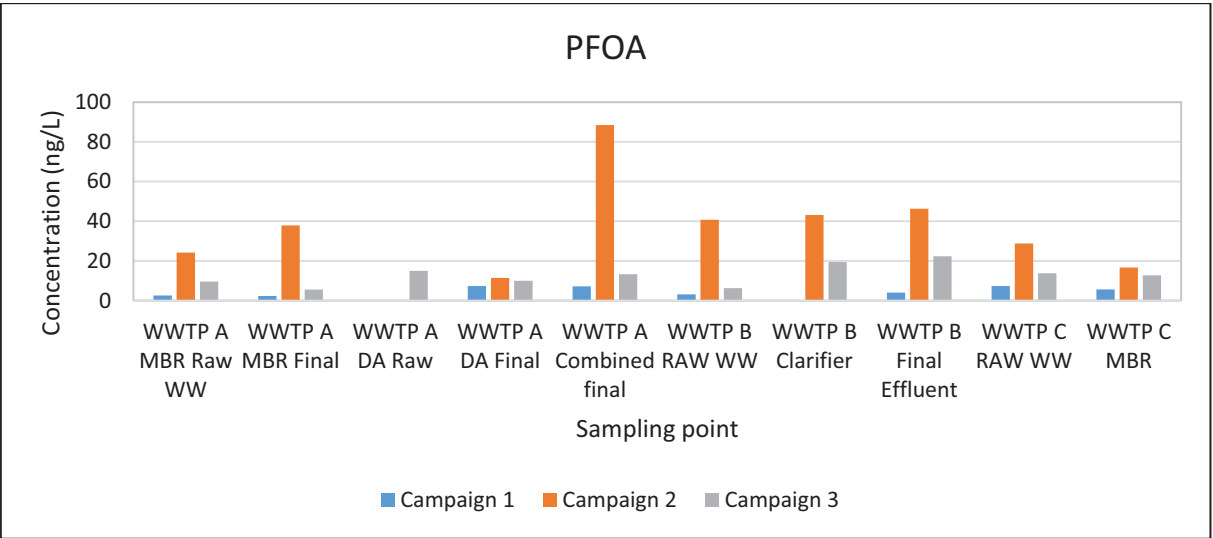


Figure 4-38: PFOA for all the sampling campaigns for all WWTP samples

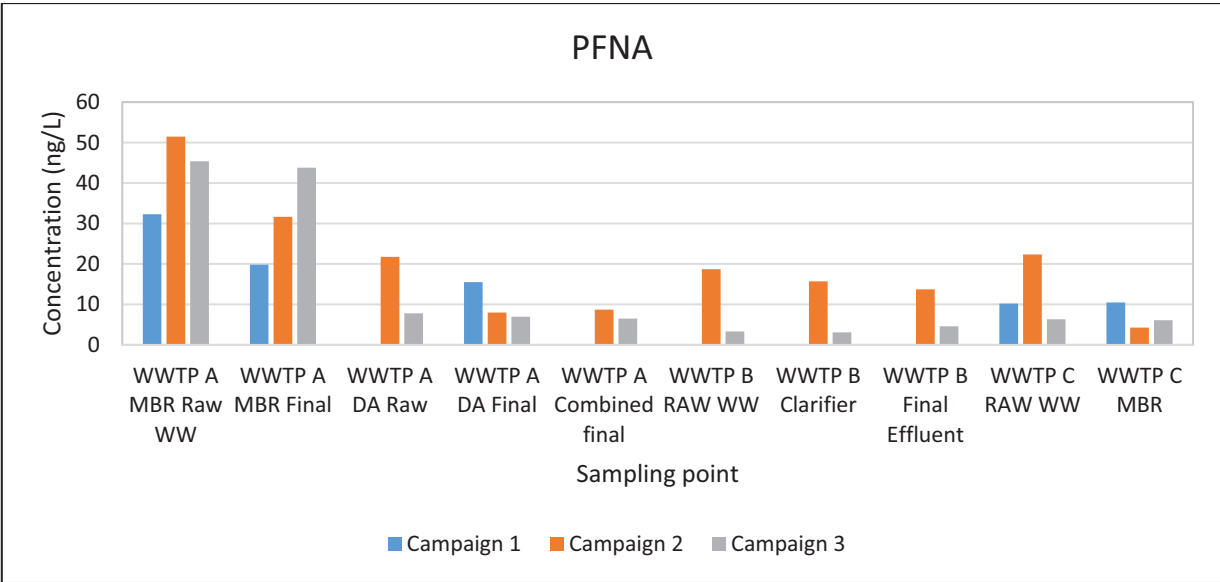


Figure 4-39: PFNA for all the sampling campaigns for all WWTP samples

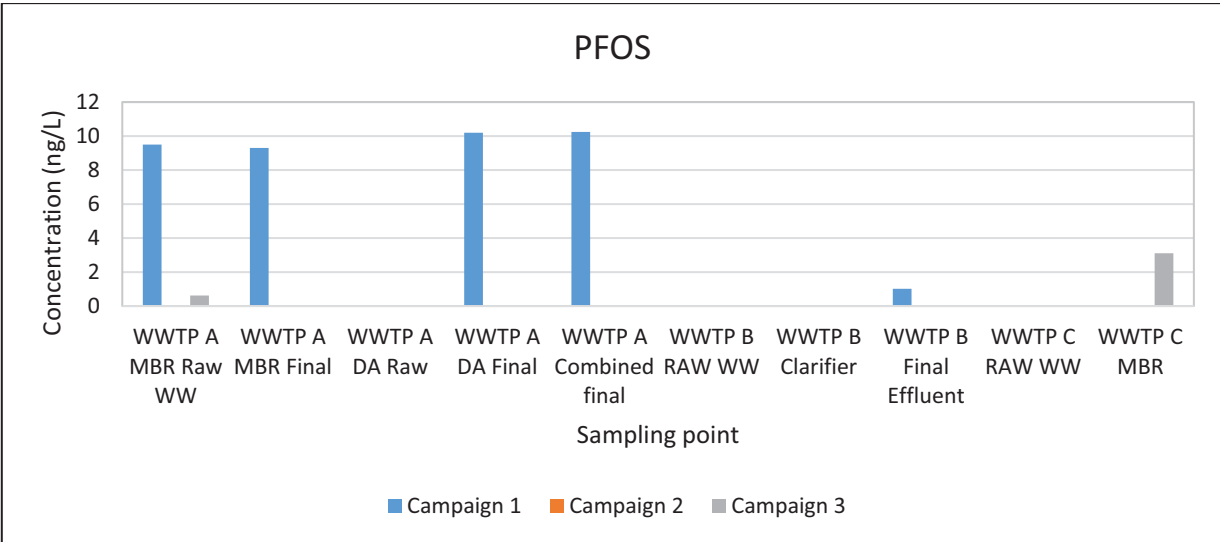


Figure 4-40: PFOS for all the sampling campaigns for all WWTP samples

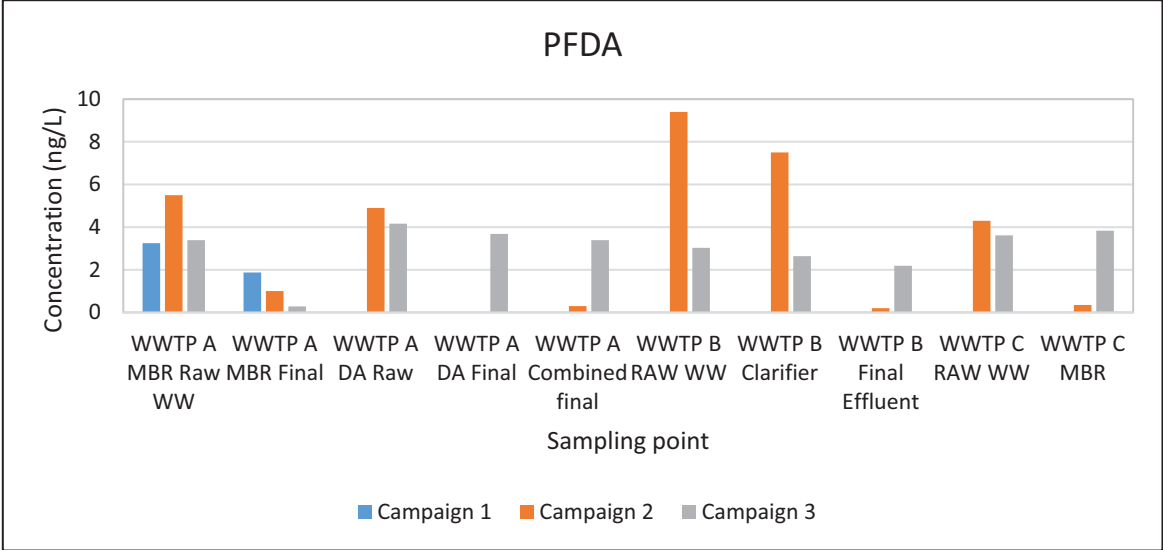


Figure 4-41: PFDA for all the sampling campaigns for all WWTP samples

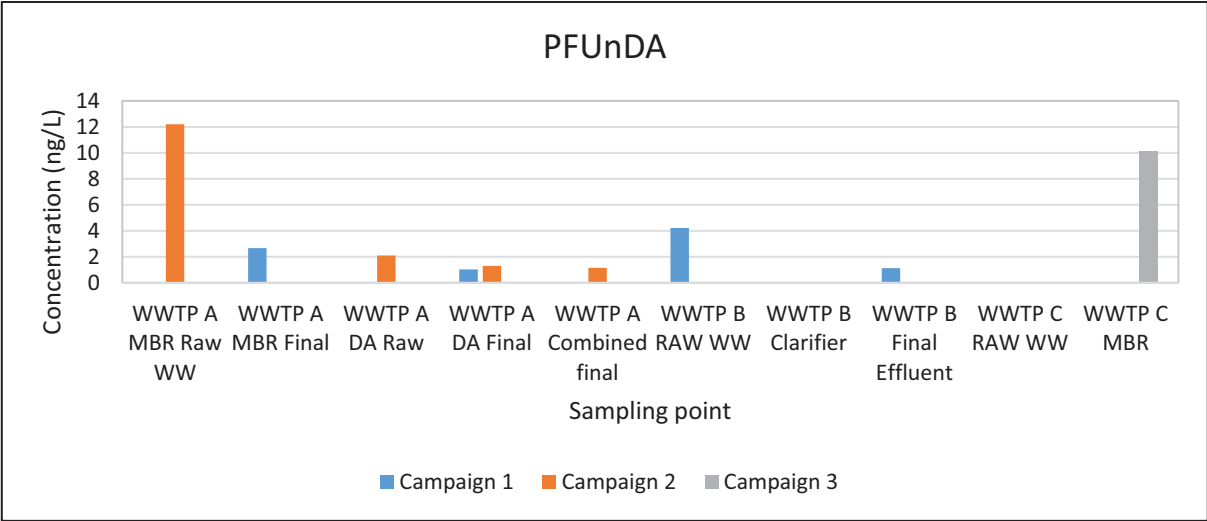


Figure 4-42: PFUnDA for all the sampling campaigns for all WWTP samples

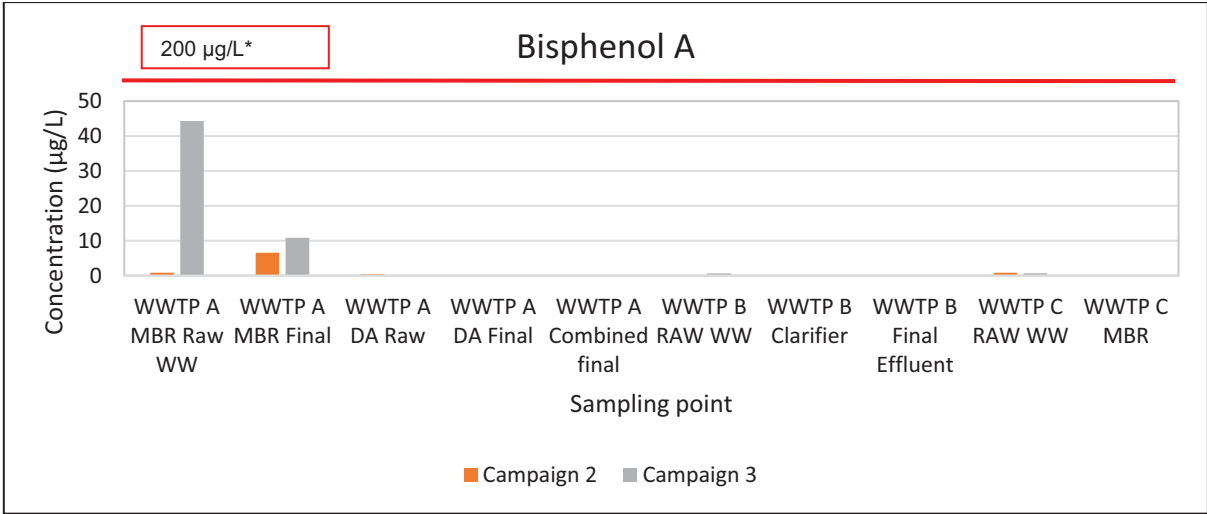


Figure 4-43: Bisphenol A for all the sampling campaigns for all WWTP samples. \* Limit proposed for potable water (NRMMC, 2008 Guideline value)

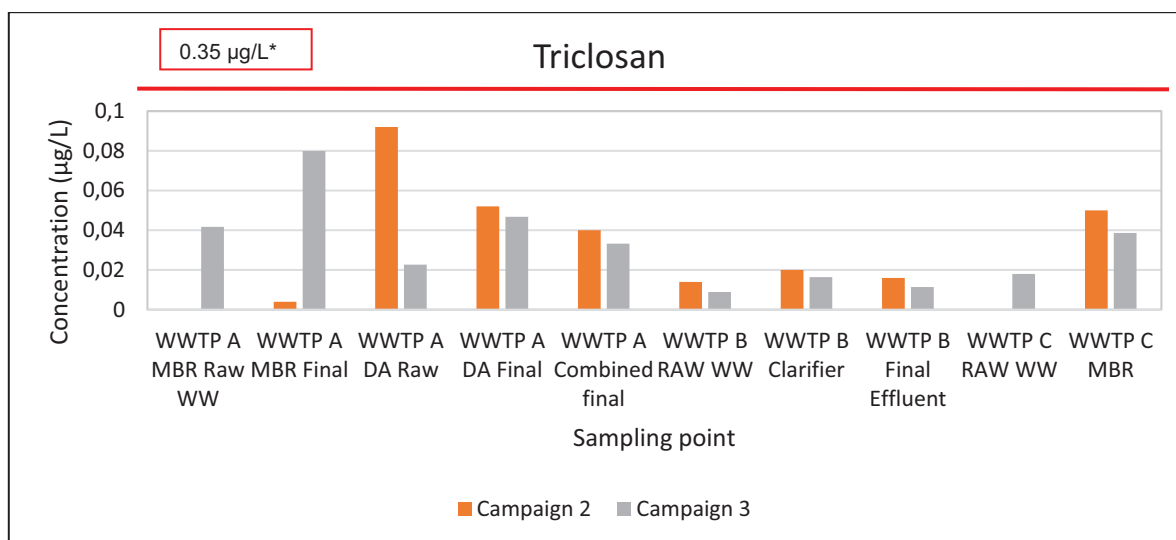


Figure 4-44: Triclosan for all the sampling campaigns for all WWTP samples. \* Limit proposed for potable water (NRMMC, 2008 Guideline value)

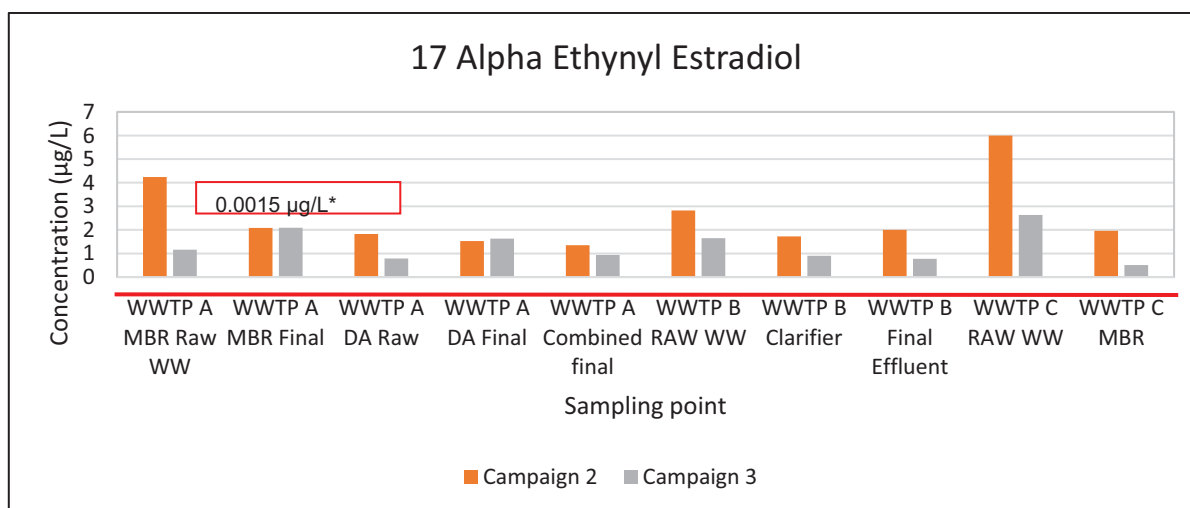


Figure 4-45: 17 Alpha Ethynyl Estradiol for all the sampling campaigns for all WWTP samples. \* Limit proposed for potable water (NRMMC, 2008 Guideline value)

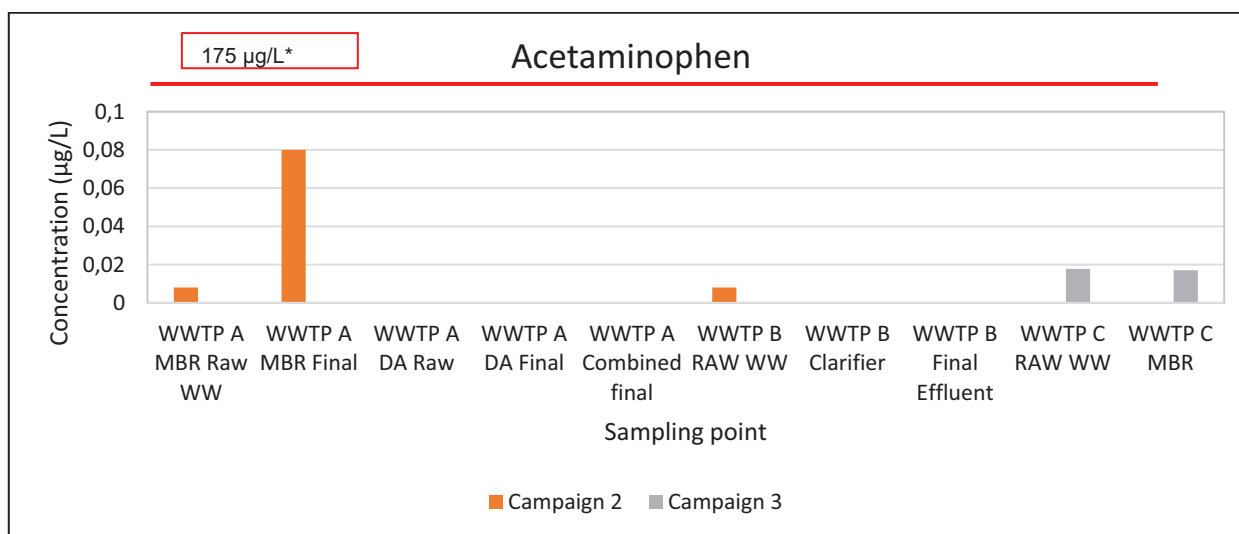


Figure 4-46: Acetaminophen for all the sampling campaigns for all WWTP samples. \* Limit proposed for potable water (NRMMC, 2008 Guideline value)

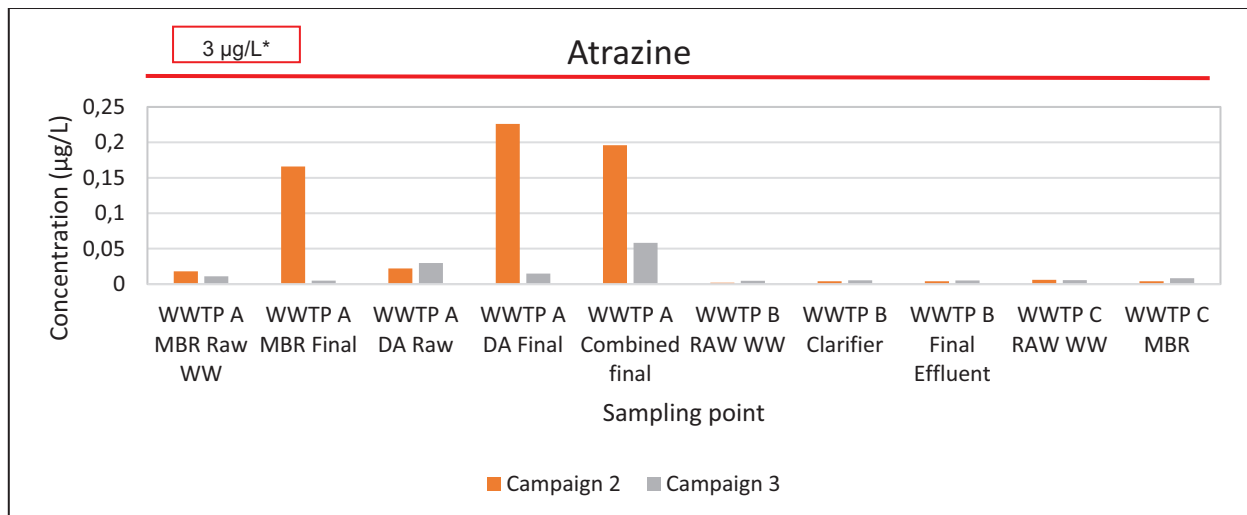


Figure 4-47: Atrazine for all the sampling campaigns for all WWTP samples. \* Limit proposed for potable water (EPA, 2012 – California drinking water limits)

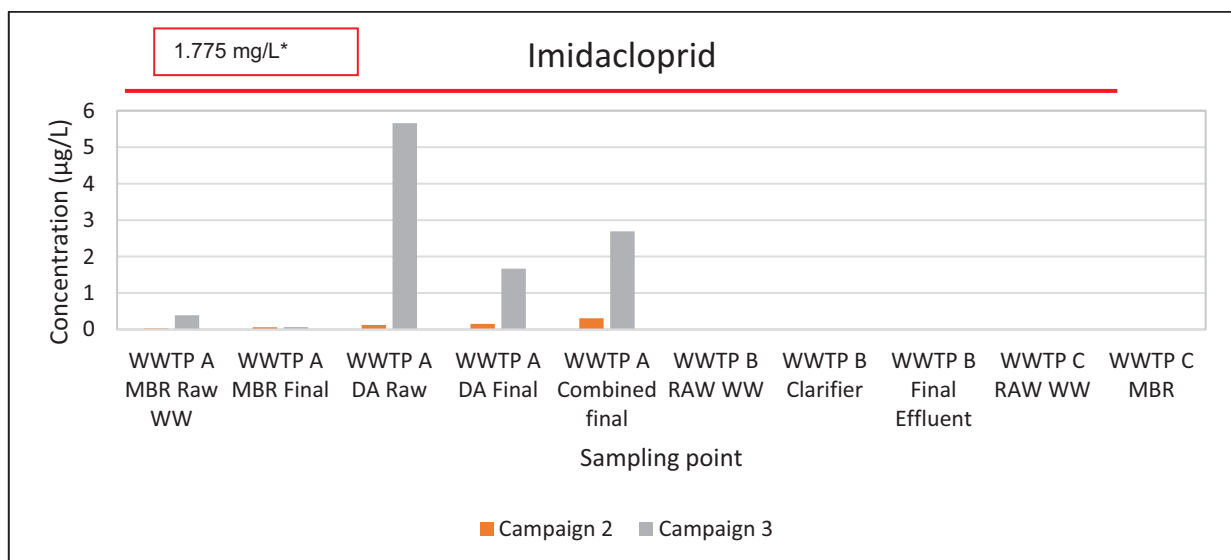


Figure 4-48: Imidacloprid for all the sampling campaigns for all WWTP samples. \* Limit proposed for potable water (EPA, 2005 California drinking water limits)

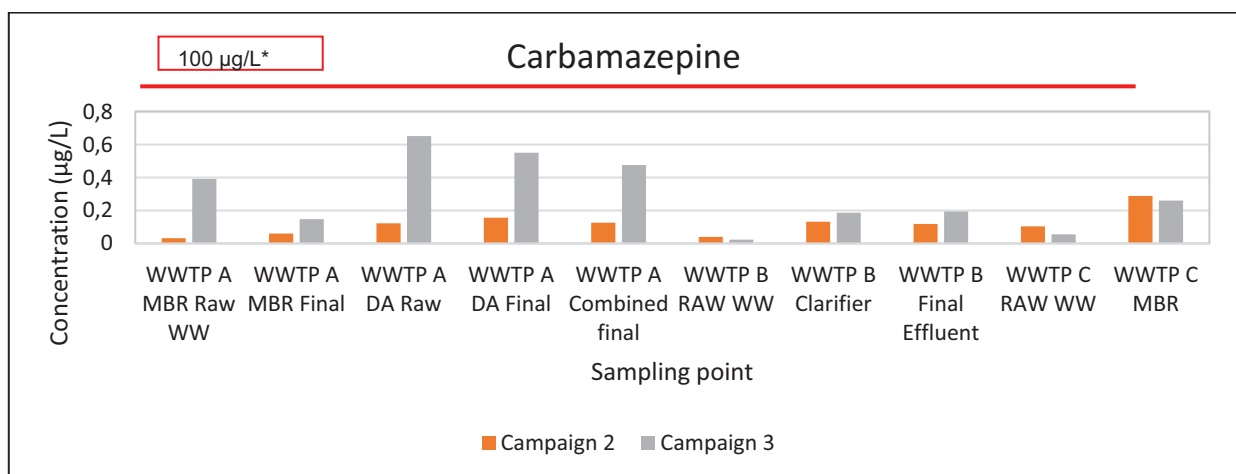
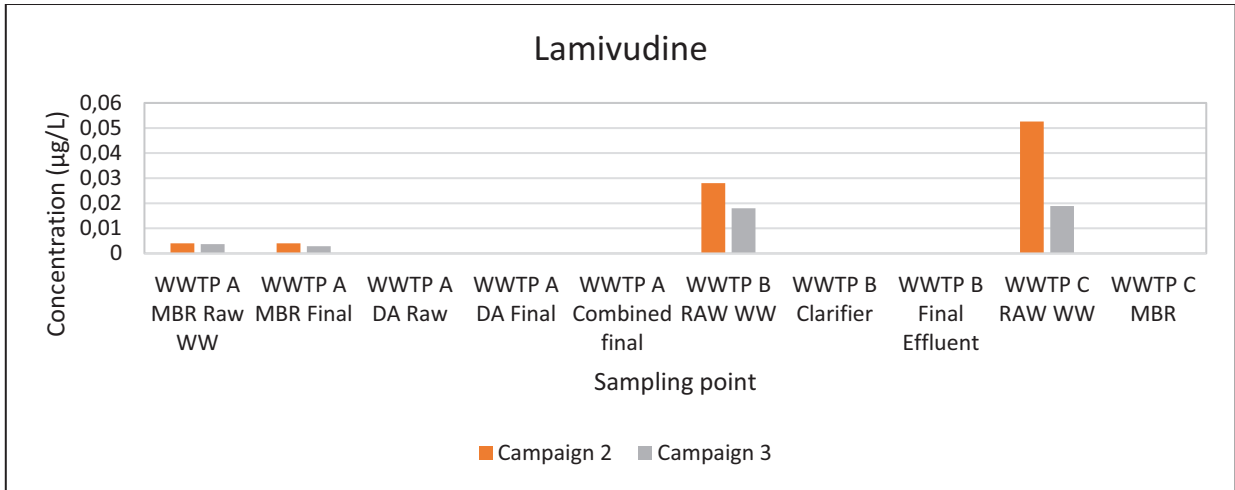
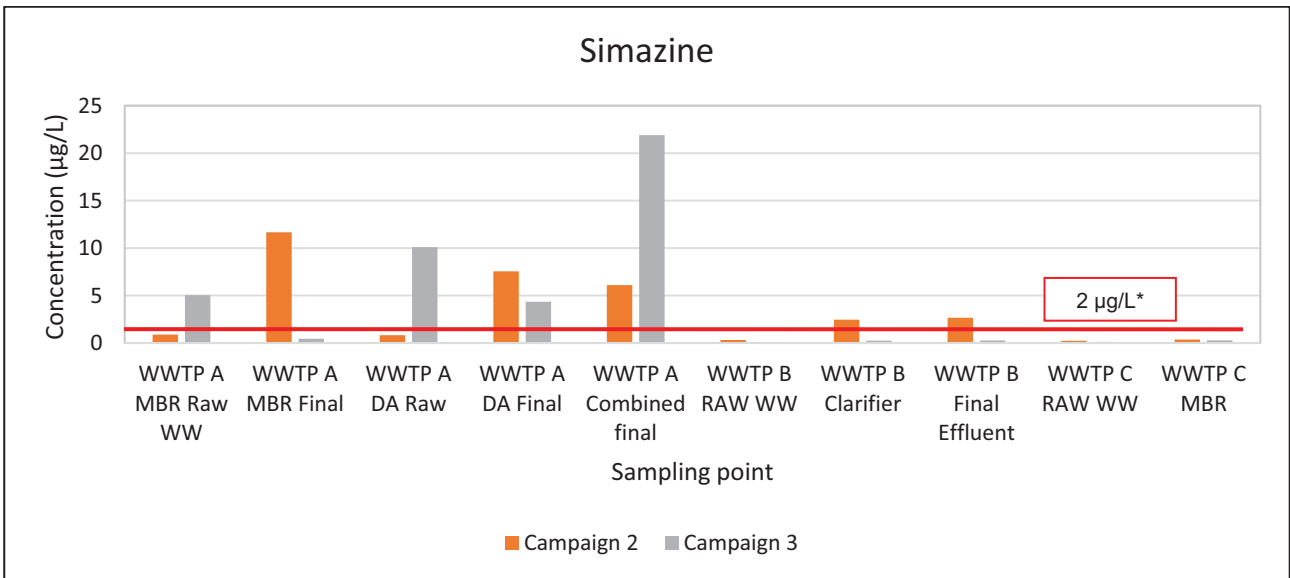


Figure 4-49: Carbamazepine for all the sampling campaigns for all WWTP samples. \* Limit proposed for potable water (NRMCC, 2008 Guideline value)

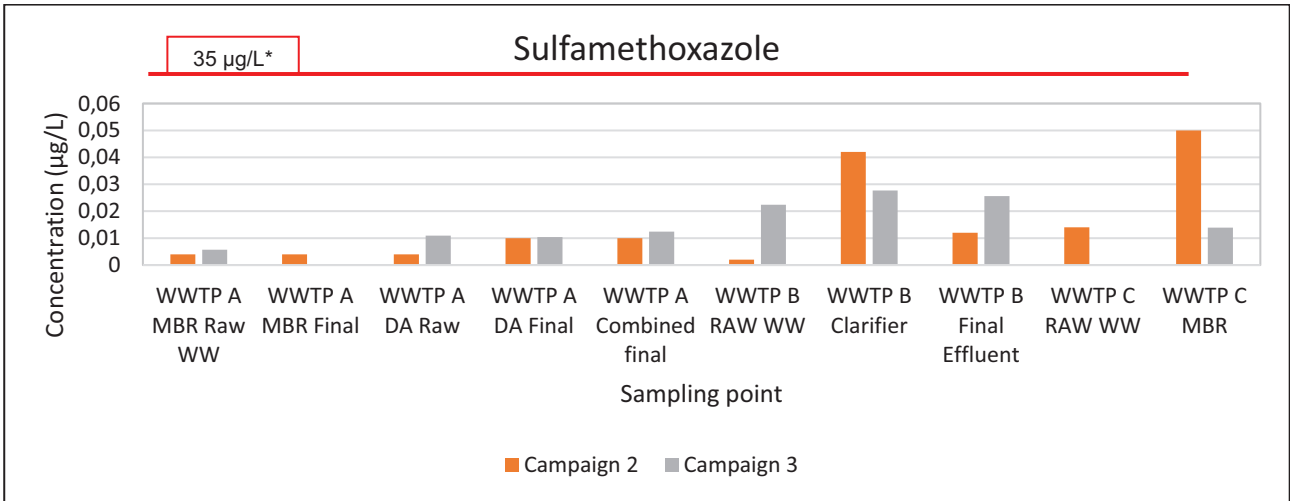




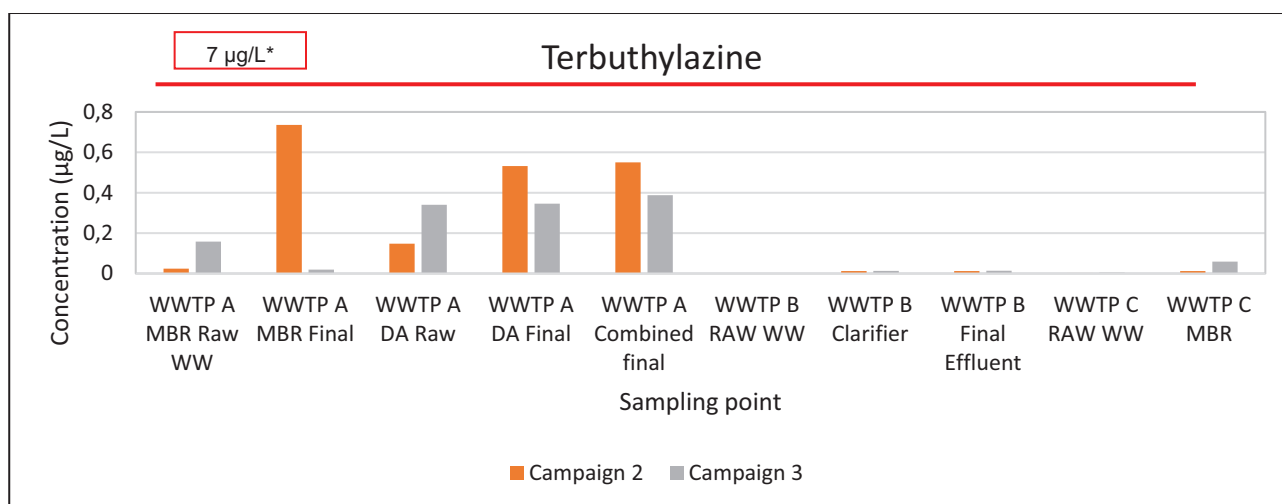
**Figure 4-50: Lamivudine for all the sampling campaigns for all WWTP samples. \* Limit proposed for potable water (NRMMC, 2008 Guideline value)**



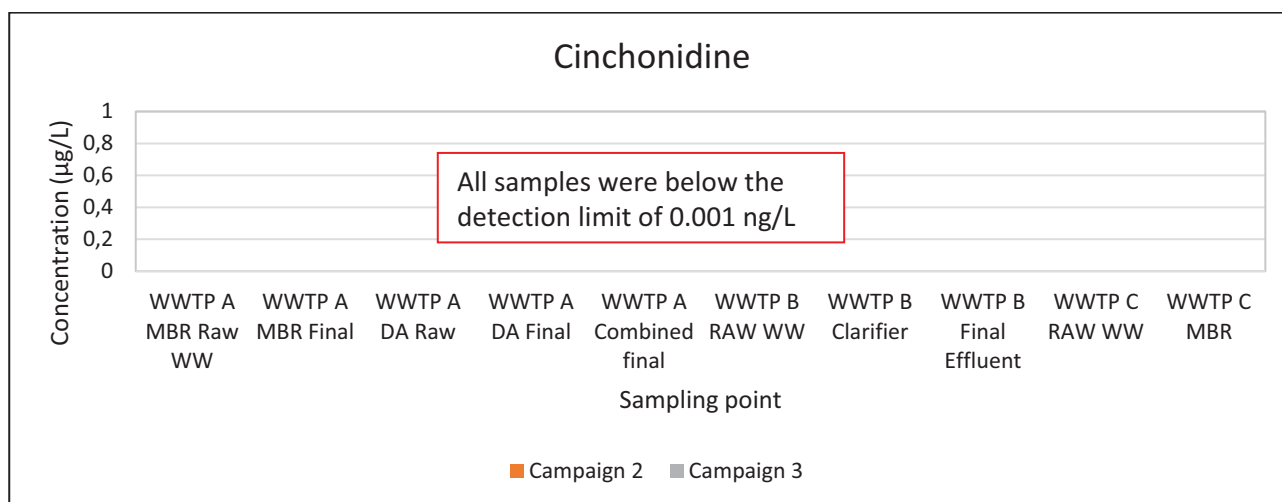
**Figure 4-51: Simazine for all the sampling campaigns for all WWTP samples. \* Limit proposed for potable water (WHO, 2011c Guideline value)**



**Figure 4-52: Sulfamethoxazole for all the sampling campaigns for all WWTP samples. \* Limit proposed for potable water (NRMMC, 2008 Guideline value)**



**Figure 4-53: Terbuthylazine for all the sampling campaigns for all WWTP samples**  
\* Limit proposed for potable water (WHO, 2011c Guideline value)



**Figure 4-54: Cinchonidine for all the sampling campaigns for all WWTP samples**

#### 4.3.7 Concentrations of CECs in samples – Water treatment plant abstracting water from a polluted river

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 **Error! Reference source not found.** (macro-determinants chemical and physical parameters), Table 4-2 (PFCs) and Table 4-3 (Priority CECs). Samples were only taken during sampling programme 3 only. All the PFCs tested for were detected in the water samples (except for PFOS and PFUnDA). The concentrations of PFCs found in the final water of the WTP was higher than that for the water reclamation plants, indicating that advanced treatment processes are indeed required for effective removal of the PFCs. Five of the 12 CECs tested for were found to be present in all the water samples (EE2, atrazine, carbamezapine, simazine and terbuthylazine). The concentrations of the other seven chemicals were below the detection limits.

**Table 4-1: 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 4-2: Perfluorinated compounds (PFCs): Sampling campaign 3 (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 4-3: 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	Terbutylazine	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

## 4.4 EVALUATING TREATMENT SYSTEM PERFORMANCE AND RELIABILITY ANALYSIS

### 4.4.1 Approach

In addition to the actual on-site evaluation of treatment plant capability for removal of CECs on the priority list through three sampling programmes, statistical analysis of historic plant performance and operational data was used as a potential tool to determine the treatment system performance as well as plant reliability. To perform analyses for this reclamation plant, dependable plant data should be used. This data should include water quality data for each of the treatment units, operational data for each of the treatment units and any additional information pertaining to the performance, operation and control of the plant during the period being analysed for. This data also includes error and critical event logs, replacement dates of treatment unit consumables (sand, activated carbon, membranes, etc.) and maintenance schedules for the work done on the treatment units.

#### 4.4.2 WRP data

WRP B was selected to perform the statistical analysis on because it had the rawest water, operational and compliance data available. The data included five years (2009-2014) of water quality results performed on-site by process controllers, as well as results from composite and grab samples analysed by independent laboratories. Operational data was also supplied for a period from 2011-2014. The operational data comes from logs completed by process controllers daily. Other information that is critical to performing the reliability analysis include the water quality and operational parameter boundaries, or limits, which can be used to evaluate the performance of the treatment units. A list of operational parameter limits was obtained from the report by Swartz et al. (2016). In addition, operational guides that have been set at the plant were used (see Table 4-4:).

**Table 4-4: WRP B operational parameter limits**

Unit No	Description	Limit
1.	Raw Water Mixture turbidity	above 10 NTU
2.	Flocculation pH	6-7
3.	DAF Outlet turbidity	1.5 NTU (Alarm 1); 5.0 NTU (Alarm 2) 8.0 NTU maximum
4.	Sand Filter Outlet turbidity	0.2 NTU (Alarm 1); 0.35 NTU (Alarm 2) 0.5 NTU maximum
	Sand Filter Outlet iron and manganese	0.05 mg/L maximum Fe and 0.03 mg/L maximum Mn
5	Ozone Residual in Outlet to BAC	0.15 mg/L maximum
	Oxygen Purity	90% minimum
	Oxygen Feed Pressure	150 kPa minimum
6	Ultrafiltration permeate turbidity	0.1 NTU maximum
7	Final Water turbidity	0.2 NTU maximum
	Final Water pH	7.6-8.0
	Final Water free chlorine	0.9-1.2 mg/L

#### 4.4.3 Process performance analysis

Before the performance analysis could be completed, it was advised to determine what the basic data requirements were to successfully apply the performance analysis techniques. The following aspects of the data had to be tested to determine whether the plant data was sufficient for conducting the plant performance analysis:

- Missing data characterisation
- Dirty data characterisation
- Data reconciliation
- Minimum data set sizes
- Sufficient representation

Each of these aspects could be tested using various statistical techniques. For a detailed explanation of how these tests work and why they are important, the reader is referred to Volume III. Unfortunately, the tests concluded that the available data was not sufficient for conducting proper statistical plant performance analysis. Volume III needs to be consulted should similar plant performance related analyses be considered.

#### 4.4.4 Plant reliability analysis

From the previous section it is known that the data obtained from WRP B was not ideal for performing data analyses. However, the data requirements for conducting plant reliability analyses are much less stringent. Basic reliability analyses could therefore be performed, but due to the quality of the data, the results cannot be considered a true representation of the actual plant reliability. 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).

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

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. Several different standards and guidelines were used to provide target values that can be used for the effluent requirements. The next step in the process consisted of determining the probability distribution for each of the effluent variables being tested. Most of the distributions were determined to be empirical, with a few variables showing a log-normal distribution. With the distributions available, it was possible to determine the probability of failure for each of the variables being tested. Several of the variables have an expected percentage of compliance less than 80%. This is alarming considering that a standard rate of failure is considered one failure per year, which results in an expected percentage of compliance of 99.7%. Further work has been done to indicate how the current set point or designed set points of the treatment units must be changed to result in a satisfactory probability of compliance.

#### 4.5 SUMMARY

Findings from this study indicated that the available treatment process in WRP A could 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 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 D 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. 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 D 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 C), and 95.8% (WWTP D).

With regards to process performance analysis, the current historical process data was not suited for this analysis. 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). 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 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.

## CHAPTER 5: HUMAN HEALTH RISK ASSESSMENT

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### 5.1 INTRODUCTION

Human health risk assessment followed by a case study of risk assessment at a water reclamation plant to illustrate the practical application of this approach. 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 to reduce the unacceptable risks. The specific aims were to:

- Determine which processes in the WRP A system can 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.

### 5.2 BIO-ASSAYS FOR TESTING EFFICIENCY OF WATER TREATMENT

Three bioassays recommended by the OECD and GWRC, the Ames mutagenicity test, the Daphnia toxicity test and the oestrogenicity activity test representing different trophic levels to provide an overall assessment of water quality were done in this study, and a brief description of each is presented in the sections below.

#### 5.2.1 Bioassay toxicity testing

##### 5.2.1.1 *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 mutagenic. An additional bacterial strain that mimics human metabolic activation (TA 98 p450) for those chemicals that may become mutagenic after metabolic activity was also tested. Diluted samples (1 in 10) were included to reduce potential toxic effects. (This could not be included in each round of testing of 6 treatment plants due to the restrictions in funds).



#### 5.2.1.3 *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.

#### 5.2.1.4 YES Oestrogenicity Activity Test

*In vitro* screening of wastewater samples collected from selected water treatment works were tested for oestrogen receptor agonistic activity (Figure 5-3). 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 17 $\beta$ -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 wastewater treatment works were calculated with a limit of detection (LOD) of 1,7 ng/L.

#### 5.2.1.5 Sampling and sample analysis

In total the two WRPs, three WWTPs and one WTP (refer to Section 4.2) 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<sub>254</sub> 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, 17 $\alpha$  ethinyl estradiol (EE2), acetaminophen, atrazine, imidacloprid, carbamazepine, lamivudine, simazine, sulfamethoxazole, terbuthylazine and cinchonidine.
- Ames mutagenicity test (only raw and final samples)
- Oestrogen mimicking test (only raw and final samples)

### 5.2.2 Results – Bioassay tests

#### 5.2.2.1 Ames Mutagenicity test

Toxicity was observed in raw wastewater with reductions observed in the majority of wastewaters, the exception being the wastewater treatment plant treating two different wastewater streams (Figure 5.1). Where no mutagenic activity was observed it is likely that it was masked by the toxicity.



Figure 5-1: Ames Mutagenicity test results from each plant

### 5.2.2.3 *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 (Figure 5-2). All wastewaters showed 100% toxicity (results are not included in the figure) with improvements in effluents shown in Figure 5-2. 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.

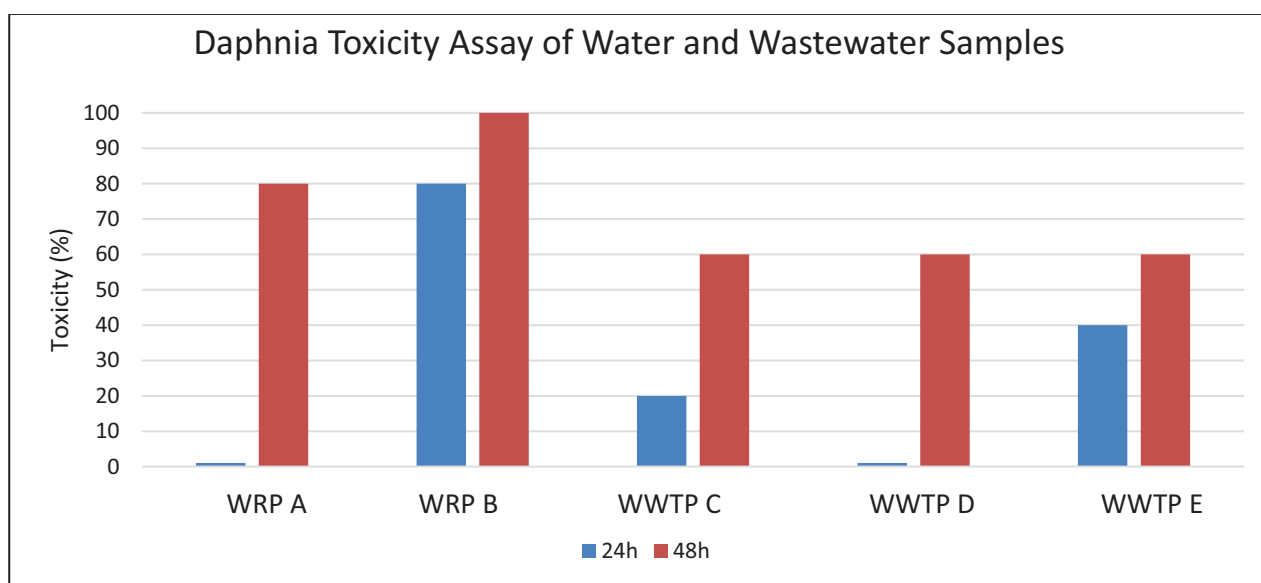


Figure 5-2: *Daphnia* toxicity results

### 5.2.2.4 *YES Oestrogenicity Activity Test*

*In vitro* screening of wastewater samples collected from selected water treatment works were tested for oestrogen receptor agonistic activity (Figure 5-3). 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 17 $\beta$ -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 wastewater 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. These 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.

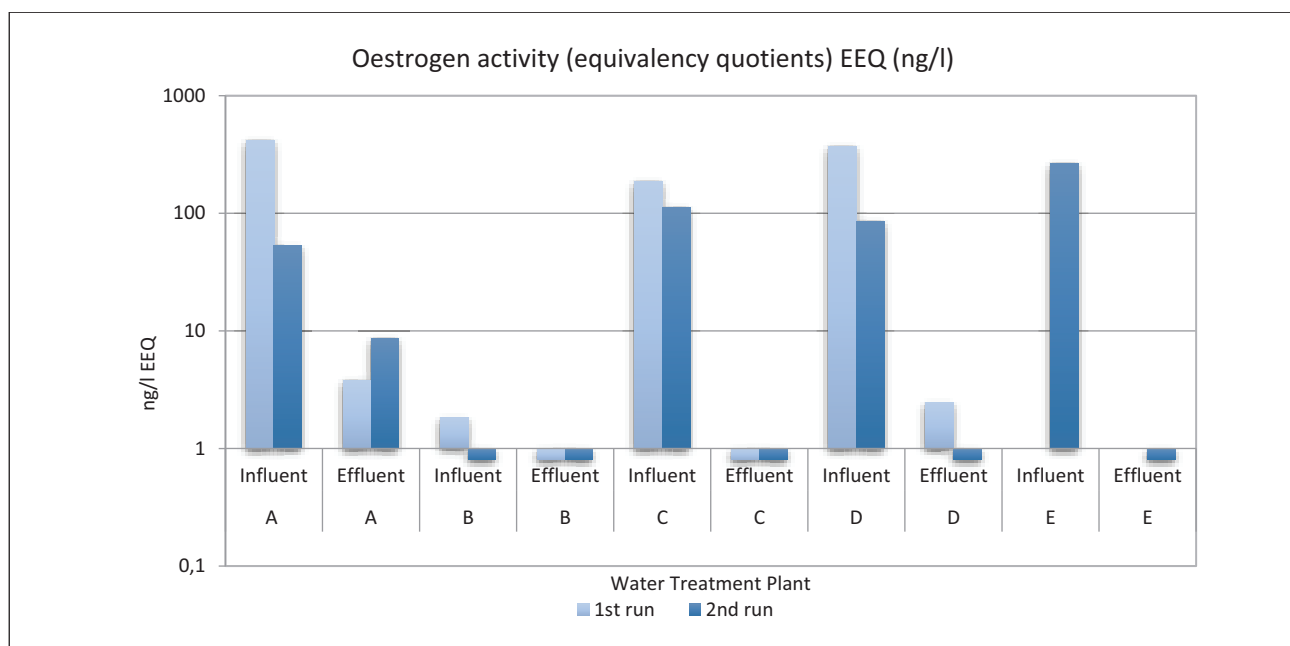


Figure 5-3: Oestrogen activity (EEQs in ng/l) removal at water treatment plants

## 5.3 CHEMICALS RISK ASSESSMENT

### 5.3.1 Approach

#### 5.3.1.1 The risk matrix approach

The risk matrix approach was used. This method provides a relatively simple way of analysing the likelihood of many potential hazards or events to take place, and what the consequence would be should it take place. It presents the results of the analysis in a matrix which the different risks can be seen in a visual format with the different severities of risks shown in different shaded areas (where high risks are shown in red [unacceptable risks], medium risks in amber [ALARP risks, meaning 'As Low As Reasonably Practical'], and low risks in green [acceptable risks]). To evaluate risks, the "As Low as Reasonable Practicable" (ALARP) principle can be used (Lindhe, 2010). The risks are then considered to be unacceptable, acceptable or in the ALARP region, which means that they are acceptable if it is unreasonable due to technical or economic reasons to reduce them, see Figure 5-4.

Likelihood of occurrence	5	<i>Almost certain</i>	5	10	15	20	25	<div>Unacceptable</div> <div>ALARP region</div> <div>Acceptable</div>
	4	<i>Likely</i>	4	8	12	16	20	
	3	<i>Moderate</i>	3	6	9	12	15	
	2	<i>Unlikely</i>	2	4	6	8	10	
	1	<i>Rare</i>	1	2	3	4	5	
			<i>Insignificant</i>	<i>Minor</i>	<i>Moderate</i>	<i>Major</i>	<i>Catastrophic</i>	
			1	2	3	4	5	
			Consequence					

Figure 5-4: Schematic picture of a risk matrix

More information on the method that was used for calculating the consequences and probabilities can be found in the Appendix to Volume III of this report series.

Table 5-1 shows the levels of probabilities (likelihood) and consequences which were used in this study, as recommended by the World Health Organisation (WHO) and by the Natural Resource Management Ministerial Council (NRMMC) in Australia.

**Table 5-1: Likelihood and consequence levels and descriptions used in the risk assessment**

Level	Likelihood		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 5 years or has never occurred	Insignificant	Insignificant or not detectable

#### 5.3.1.2 Multi-criteria decision analysis

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 control measure are usually used (Lindhe, Rosén, and Røstum, 2013). The objectives, which in drinking water applications are the suggested control measures, are given scores based on how they are expected to perform for each criterium (DCLG, 2009). 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 control measure.

#### 5.3.1.3 Sampling and analysis of chemicals on the priority list

In total the two WRPs, three WWTPs and one WTP were sampled for the risk assessment studies. During the first sampling programme (April 2015), samples were analysed qualitatively to determine the presence of the CECs that were on the priority list. Samples were taken at the following points: raw wastewater inflow; after activated sludge treatment; before chlorination; after chlorination; after ultrafiltration; after reverse osmosis and after UV/H<sub>2</sub>O<sub>2</sub> (final water). New samples were taken in May 2015 at the same locations, and quantitative analyses performed to obtain concentrations of the contaminants to be used as input in the risk matrix. During the second and third sampling programmes, samples were again taken at the same sampling points, and analysed for the same chemicals from the priority list of CECs. The samples were analysed for the contaminants of emerging concern in the priority list of CECs that were identified in the project (Table 3.2). The analyses were done by LiquidTech at the University of the Free State in Bloemfontein on those contaminants that was possible to analyse for with standardised methods. Caffeine was a prioritised contaminant in the list drawn up in this project due to its use as an indicator of wastewater in unknown water sources. It has a low toxicity, though, and the presence of wastewater was obviously already known. Caffeine was therefore excluded in the quantitative analysis. Iopromide, Stavudine and Cinchonine were excluded due to their absence in the qualitative analysis performed in Sampling Programme 1.

### 5.3.2 Results

The results display that two risks have high risk priority numbers. Risk D1 that corresponds to the constant presence of 17 $\alpha$ -ethinylestradiol (EE2) in the effluent gets the risk priority number 216 and is located in the ALARP region of the risk matrix. Furthermore, risk E1, 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. In order to decrease the overall risks of the system the focus was laid on decreasing these two risks and the following countermeasures are based on these. EE2 is an oestrogenic hormone commonly used as the main ingredient in female contraceptives (Johnson and Sumpter, 2001) and most of the hormone is assumed to end up in the sewage water (Adolfsson-Erici, Pettersson, Wahlberg, and Asplund, 2005). The absence of effective removal of EE2 from wastewater has been shown for WWTPs all around the world (Koh, 2008). Exposure of effluents from WWTPs was discovered to cause feminisation of aquatic organisms including male fishes and the fate of oestrogens and other endocrine-disrupting compounds has therefore been largely investigated (Purdom, 1994).

## 5.4 SUMMARY

The use of membrane technologies has shown to reduce the concentration of oestrogenic hormones in wastewater (NRMCC, 2008) but is according to Pauwels et al. (2006) not a satisfying solution for treatment due to the production of a brine stream with elevated concentrations of hormones without degradation. The use of chlorination has shown to successfully degrade EE2 (Racz and Goel, 2009). It is a cheap technology, but has the disadvantage of increased reaction products with persistent characteristics (Lee et al., 2004; Moriyama et al., 2004). Partial degradation of EE2 has also been shown by UV treatment but not efficiently enough to be an economically reasonable option (Racz and Goel, 2009). When the unstable gas ozone is reacting with water, free radicals with oxidation powers are formed (Asano et al., 2007). The process of using ozone is called ozonation and is commonly used as a disinfection process. The ozonation process has successfully shown to degrade EE2 with removal efficiencies of higher than 90 per cent (Huber, Canonica, Park, and von Gunten, 2003), but it is important to take into consideration that these technologies in the meantime could increase the formation of other oestrogens (Huber, Ternes, and von Gunten, 2004). The reaction products from ozonation have been assigned lower oestrogenic activities than EE2 itself and ozonation has therefore been proposed as an effective technology for EE2 removal (Pauwels, Deconinck, and Verstraete, 2006). The high cost for large-scale ozonation is the largest disadvantage.

Electrodialysis is a process where a semipermeable membrane is separating ions moved by electrical potential (Asano et al., 2007). Electrolytic removal has not yet been a widespread technology for water treatment (USEPA, 2011) but a high treatment efficiency of 85-98 per cent EE2 removal has been shown in laboratory tests (Pauwels, Deconinck, and Verstraete, 2006). This kind of electrochemical treatment has many advantages due to low maintenance cost, low need for labour, short reaction time and relatively simple equipment (Chopra, Kumar Sharma, and Kumar, 2011). Granulated Activated Carbon (GAC) is used in pressure or gravity filtration and consists of an organic base material with a diameter greater than 0.1 mm (Asano et al., 2007). The removal of EE2 by using GAC varies in the literature, including an EE2 treatment reaching over 99.8 per cent according to De Rudder et al. (2004) and Bodzek and Dudziak (2006). This variation could appear due to dissimilar concentrations of dissolved organic compound or humic acids that could block pores in the activated carbon structure, even though GAC is generally a very efficient treatment technology for EE2 (Racz and Goel, 2009). It should be noted that the potential concentration of EE2 in the final water will be diluted four-fold before the water is used for drinking purposes. Based on this, further research will indicate whether the use of GAC may be required or not for removal of EE2.

## CHAPTER 6: CONCLUSIONS AND RECOMMENDATIONS

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### 6.1 CONCLUSIONS

Many lists of contaminants of emerging concern have been compiled internationally and locally. In this project, a priority list for CECs in direct potable reuse was developed. Developing the CEC recommended prioritisation list involved using compounds detected in South African potable waters which also represents those compounds which are persistent and are not removed by water treatment processes, pharmaceuticals prescribed in the largest volumes, pesticides identified as high-risk priority pesticides in South Africa, and chemicals representing each of the groups of CECs. Other chemicals were included as indicator compounds known to occur in high concentrations in wastewaters to illustrate process efficiencies. Chemicals representing the different groups of contaminants of emerging concern based on best available knowledge, South African prevalence, potential for exposure and other criteria such as analytical ability to detect are included in the recommended list. It is recommended that each reclaimed potable water reuse project interrogate the relevance of these chemicals according to the specific area, to consider whether additional chemicals might need to be added to the priority list. For example, total DDT where DDT use is known to occur, or metals, if a metallurgic industry occurs in the catchment. Screening tests looking at the quality of the wastewaters should initially be carried out on a frequent and regular basis, to establish which compounds are found or are consistently absent, before the more expensive quantitative tests be used on a routine basis to monitor removal of CECs. A number of CECs were present in the final water from the direct potable reuse reclamation plants (i.e. for drinking water purposes), although at levels considerably lower than that considered to be safe.

In the last couple of years, there has been tremendous progress in analytical techniques for analysing emerging micro-pollutants. However, the identification and perhaps quantification of CECs in the environment depends solely on the availability and accessibility of advanced analytical facilities. There is a lack of sufficient number of laboratories undertaking these analyses, and the laboratories also do not perform all of the analyses, making it particularly difficult for owners of water treatment facilities and researchers alike to submit samples and interpret results. During wide discussions within the water sector, including, and in particular also the DWS, the conclusion was reached that it is imperative that a national (virtual) centre for water reclamation analysis (but for that matter all specialised chemical and microbiological analyses) be established, consisting of a network of laboratories. More specifically, the following is proposed:

- That a national facility for water reuse analysis be established, and that it will have the framework of a virtual centralised facility, but consisting of regional laboratory networks in four of the provinces, namely Western Cape, Gauteng, KwaZulu-Natal and Free State.
- Due to the common aims of the RLN and the national (virtual) centre for water reclamation and reuse water quality measurements, it is proposed that from this water reuse project, a similar approach be adopted as that of the RLN for aquatic toxicity testing.
- It is the intention that the NCWRA and water reuse RLNs will:
  - Facilitate regional cooperation between the laboratories.
  - Propose validated, standard operating procedures.
  - Provide competitive analysis costs (different packages) for WSPs.
  - Develop regional capacity and expertise that can again be made available nationally through the NCWRA.
  - Promote the exchange of scientific data and technical knowledge.

With regards to plant performance, the available treatment process in the different water treatment plants could effectively remove almost all the contaminants to very low levels. An assessment of water quality and toxicity using bio-assays showed the improvements in wastewater quality following treatment through the various



treatment works, and the results showed how these bio-assays can 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 if various activities are tested. For example, different oestrogen mimicking assays and anti-androgenic activity may be included. Findings from risk assessment studies highlighted two increased chemical health risks for drinking water production. Both risks were related to elevated concentrations of the hormone 17 $\alpha$ -Ethinylestradiol (EE2), commonly used as a contraceptive. Recommendations to install Granulated Activated Carbon (GAC) filter to reduce these risks have been communicated to the respective plants. No increased risks were found connected to technical failures resulting in short-term exposure of EE2, neither was any risk connected to any other of the identified contaminants of emerging concern at WRP A. The risk assessment has shown that the clear majority of the contaminants are reduced to an insignificant level during the treatment process. The use of direct potable water reclamation is therefore a technology that should be considered as a good option when options for drinking water augmentation or supplementation. More research about hormones, their degradation products and possible treatment technologies are needed to better understand the risks in reclaimed water. It is suggested that further risk assessments are conducted including more contaminants as well as microbial risks.

## 6.2 RECOMMENDATIONS

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 if various activities are tested. For example, different oestrogen mimicking assays and anti-androgenic activity may be included. During wide discussions within the water sector during carrying out this project, including, and in particular also the DWS, the conclusion was reached that it is imperative that a national (virtual) centre for analysis of contaminants of concern (including all specialised chemical and microbiological analyses) be established, consisting of a network of laboratories. More specifically, the following is proposed:

- That a national laboratory network for advanced water quality analysis be established, and that it will have the framework of a virtual centralised facility, but consisting of regional laboratory networks in four of the provinces, namely Western Cape, Gauteng, KwaZulu-Natal and Free State.
- It is the intention that the national laboratory network for advanced water quality analysis will:
  - Facilitate regional cooperation between the laboratories.
  - Propose validated, standard operating procedures.
  - Provide competitive analysis costs (different packages) for WSPs.
  - Develop regional capacity and expertise that can again be made available nationally through the NCWRA.
  - Promote the exchange of scientific data and technical knowledge.
- Support (financial and institutional) by the Department of Water and Sanitation (DWS) will be crucial in ensuring the success and sustainability of the water reuse RLNs. DWS is the sector leader and as such needs to set the tone regarding the importance of credibility in water quality testing results. Private-public partnerships (PPP) could also be a viable option for this purpose, either as part of the Strategic Water Partners Network (SWPN) or similar thereto.
- A further important factor, and one that needs to be addressed from the outset, is the need for well-trained and experienced personnel and managers for the regional laboratory networks (RLNs). Follow-up projects by the WRC, WISA, Universities, Water Boards and EWSETA will be required to create and enabling climate for planning the staffing and career development in the RLNs. Capacity building initiatives in current WRC projects are already driving this strongly.



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